

NANOCHEMICAL, NANOSTRUCTURAL AND BIOCOLLOIDAL ASPECTS OF TRANSFORMATIONS IN DISPERSIONS OF IRON- ALUMINOSILICATE MINERALS



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НАЦІОНАЛЬНА АКАДЕМІЯ НАУК УКРАЇНИ
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ОДЕСЬКИЙ ДЕРЖАВНИЙ ЕКОЛОГІЧНИЙ УНІВЕРСИТЕТ МОН УКРАЇНИ

**НАНОХІМІЧНІ,
НАНОСТРУКТУРНІ
І БІОКОЛОЇДНІ
АСПЕКТИ
ТРАНСФОРМАЦІЙ
ДИСПЕРСІЙ
ЗАЛІЗОАЛЮМО-
СИЛІКАТНИХ
МІНЕРАЛІВ**

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ІНОЗЕМНОЮ МОВОЮ»*

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It was considered the modern ideas of colloidal and biocolloidal nanoscience concerning complex transformational processes in widespread dispersions of iron-aluminosilicates. It was shown for the first time that they influence on catastrophic phenomena in marine turbiditic-pelitic sediments and soils consisting of iron-aluminosilicates. The fundamental study results of nano- and microstructure transformations of disperse iron-aluminosilicate compositions are presented. And it was established the possibilities of their application in: constructing of protective structures; balneology and medicine; metallurgy; development of the problem of saving the ecological balance in the sea hydrosphere; developing the new branch of science — biocolloidal marine geoecology.

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LIST OF SPECIAL ABBREVIATIONS AND TERMS

IASSMs — polydisperse, generally macro- and microstructured, iron-aluminosilicate systems and materials, which include ferri- and ferro-aluminosilicates, and iron-containing and iron-bearing systems and materials. Their general formula $(\text{FeO})_x(\text{Fe}_2\text{O}_3)_y(\text{Al}_2\text{O}_3)_z(\text{SiO}_2)_n \cdot m\text{H}_2\text{O}$

NIASSMs — nanostructured IASSMs

PS — pelagic (pelitic) sediments — polymineral and polydisperse iron-aluminosilicate bottom sediments of seas and oceans

PELOIDS (therapeutic muds) — a form of pelagic sediments, geologically young fine-disperse natural formations consisting of water, mineral and organic substances of homogenous and pasty consistency

TURBIDITES — deposits of ooze flows with high content of coarse-disperse formations on slopes and bottom of seas and oceans, usually in a mix with fine-disperse pelagic sediments

PCGM — physicochemical geomechanics (and nanogeomechanics)

PCM — physicochemical mechanics

ULTRAANOMALY OF VISCOSITY (UOV) OF SUSPENSIONS AND DISPERSIONS — an anomalous viscous phenomenon revealed in superconcentrated dispersions, in contrast to Urjev hyperanomalous viscous phenomenon (HV) revealed in concentrated dispersions. UoV (in contrast to HV) is characterized by an absence of coincidence of direct and reverse rheological curves at low shear rates. UoV is described by anomalous plastic flow of elastoplastic structures transforming from plastic to elastic state at low shear rates

ELASTICITY — phenomenon conditioned by reversible small deformations of interatomic (intermolecular) bonds, their change is described by Hooke's law

VISCOSITY OF DISPERSIONS — phenomenon characterized by proportionality between shear stresses and shear rates; it is described by Newton's law

PLASTICITY — in contrast to elasticity and viscosity, it is non-linear behavior of disperse or all-solid bodies, with no proportionality between the mechanical stress and deformation

COAGULATION CONTACTS — contacts between particles or particle nanoaggregates in disperse systems, conditioned by physical interactions through equilibrium layers of disperse medium

PHASE CONTACTS — contacts, where particle bonds in dispersions are conditioned by short-range cohesion forces realized on surfaces of substantially bigger sizes than the unit cell, i.e. bonding is realized by at least 10^2 - 10^3 interatomic bonds

CATASTROPHIC (STRESS) PHENOMENA — extremal natural transitions of huge masses of the Earth's crust materials, for example, catastrophic turbiditic currents involving large-scale transformations of the Earth's crust surface or abyssal underwater plains, sometimes with big social and economic negative consequences

*In memory of Mykola Pertsov,
scientist and friend*

GENERAL COMMENTS

Polymineral nano- and microdisperse iron-aluminosilicate systems and materials (NIASSMs and IASSMs) are widespread in the Earth's crust. They occupy an important place among natural dense and disperse rocks and their products. Colloid-chemical researches of such systems and materials on the basis of iron ores, sediments (sludges, oozes), and sands of different original ways attracted great attention [1, 2]. Over the last decade, they have been actively studied not only from the view point of the influence on their properties of colloid chemical, nanochemical and physicochemical geomechanics laws [3-7], but also with the aim to find out the mechanisms of complex biocolloidal interactions, which can be considered as interphase colloid-chemical and nanochemical transformations of NIASSMs and IASSMs and of similar disperse systems developed under the action of microorganisms metabolism products [8]. However, the interpretation of such influences on polymineral NIASSMs and IASSMs in many specific cases stays insufficient and not yet completed because of complexity of multifaceted physicochemical, geomechanochemical, colloid-chemical, and biocolloidal methods of their researching and of ambiguity of relevant conclusions.

It is roughly known that physicochemical, colloid-chemical, nanochemical transformations and contact interphase interactions in IASSMs, NIASSMs and clay-containing pelitic sediments (PS) aided with microbiological processes in biogeocenosis lead to formation of new disperse polymineral nanostructural materials having new disperse and other properties. Such materials as IASSM, NIASSM, and PS mainly consist of iron, aluminum and silicon oxides, and also, but in smaller quantities, of many other inorganic and organic components, which role in similar processes is, generally, not clear yet. Disperse systems and materials widely used in practice include sedimentary ironoxide-silicate ores, iron-containing clays, pelitic marine and lake sediments, coastal and shelf sands, other sedimentary and solid ore deposits, and also soils of different origin. Many of them in the course of their geological history were transformed under the influence of primary physicochemical, microbiological and mechanochemical processes of dense rock dispersion, and of secondary colloid-chemical, nanochemical and tectonic processes of further dispersion or compacting of disperse materials. It has been established recently, for example, that solid microcrystalline iron quartzites (jaspilites), the basis of general iron ore deposits, started their for-

mation 2 billion years ago with the formation of finely dispersed polymineral compositions at first, then their enrichment due to activity of microorganisms, and, finally, the subsequent compacting of enriched iron-aluminosilicate dispersed formations.

Practical importance of both IASSMs and nanostructural materials extracted from them in an empirical way is constantly growing. That is why the attention to them of technologists and researchers studying fundamental transformation mechanisms of IASSMs and relevant materials is growing as well. Therefore, such investigations of problem questions are actual. And here, the major tasks, necessary for solving the problem are set as follows:

1. First, there have been no developed ideas about the role of physicochemical mechanics and geomechanics in dispersion, transformation and following secondary interphase transformations of sedimentary deposits of iron-aluminosilicate and iron oxide-hydroxide materials.

2. The mechanisms of NIASSMs particles secondary contact transformation under the action of coagulation-crystallization processes have not been studied enough.

3. The influence of microbiological processes on mechanisms of transformation of IASSMs, NIASSMs is known in general terms only.

4. Nanochemical, mechanochemical and nanostructural transformations of IASSMs and NIASSMs, firstly, of iron oxides and hydroxides, and also silicate minerals and quartz have been studied quite superficially. These transformations of IASSMs and NIASSMs, both in some inorganic iron-oxide-hydroxide-silicate systems and in compositions with bio-originated materials have not yet found their generalized solution both from the theoretical consideration of corresponding processes and their experimental confirmation.

5. Development of ideas concerning complex mechanisms of IASSMs and NIASSMs transformation also needs to create new colloid-chemical and geomechanical views on stress (catastrophic) phenomena in Earth crust and on its surface.

6. Recommendations for creating science-based effective ecogeotechnological solutions concerning practical use of IASSMs and NIASSMs and prevention of catastrophic (stress) phenomena, which can occur on seafloors and in technogenic buildings (like dams) with the participation of polydispersed iron-aluminosilicate nanostructured materials need further generalizations.

As follows, mentioned considerations show significant actuality of the problem questions and the necessity of their solution by conducting relevant systematic experimental and theoretical researches of iron-aluminosilicate systems and materials with the aim of their generalization and formation of persistent views on colloid-chemical, mechanical and geomechanical transformations in IASSMs, NIASSMs and PSs with the participation of nano-, ultra- and microdispersed particles.

CHAPTER

1

**CURRENT STATE
OF COLLOID-CHEMICAL,
NANOCHEMICAL
AND BIOCOLLOIDAL RESEARCHES
OF IRON-ALUMINOSILICATE
SYSTEMS
AND IRON-CONTAINING
PELITIC (PELAGIC)
MATERIALS, SEDIMENTS
AND PELOIDS
(IASSMS AND NIASSMS)**

1.1. General characteristics of IASSMs and NIASSMs (dispersity, mineralogical and chemical composition, surface and structural properties)

Studying laws of colloid-chemical, nanochemical, physicochemical, mechanical and biocolloidal processes in polydisperse, generally macro- and micro-structured, iron-aluminosilicate systems and materials, which include ferri- and ferro-aluminosilicates, and iron-containing and iron-bearing systems and materials (IASSMs) and nanostructured IASSMs (NIASSMs) is the main source of information about mechanisms of transformation of such systems and materials in natural and technological conditions. Substantiated ideas concerning this subject also allow reliable prediction of the behavior of natural dense, micro- and nanostructural rocks [1, 8-23] as the main compounds of relevant systems and materials in natural, technological, biomedical and other processes. Thus, researches of IASSMs and NIASSMs are actual to create modern technological processes and further development of fundamental ideas concerning their natural geomechanical transformations under the action of external factors, including stress (catastrophic) phenomena.

Widespread in the Earth's crust iron-aluminosilicate materials and aqueous disperse and ultradisperse systems on their basis take an important place among natural dense nanostructural rocks and technogenic products of their technological processing. Their physicochemical, physicommechanical and chemical transformations in the Earth's crust and reservoirs, generally in seas and lakes, lead to the occurrence of disperse nano- and microstructured sedimentary materials of polymineral composition (Table 1.1). Iron, silicon and aluminum oxides, and also many other compounds are their components (Table 1.2). In addition, such compositions may also consist of nanoamorphous and fine-crystalline carbonates and silicates formed as a result of biocolloidal and mechanical transformations aided by metabolism products of microorganisms according to the laws of physicochemical geomechanics. Deep sea and shallow (shelf) deposits of pelitic sediments, peloids (therapeutic muds), iron-containing clays, sedimentary disperse iron silicate carbonate ores, and soils are the main types of such materials. Nano-

and microdisperse crystalline iron quartzites (jaspilites), the products of secondary biocolloidal transformation of sediments under the action of diagenesis processes in the Earth's crust [22], and other products [4-15, 20] should be attributed to ore materials on the basis of NIASSMs. The mineralogical composition of similar sedimentary materials, which is partly given in Table 1.1, shows, that they consist of feldspars (found in 73-90% of tested samples), magnetite (in 80-100% of the samples), illite-montmorillonite clays (in 6-40% of the samples), quartz (in 30-80% of the samples), glauconite (in 6-20% of the samples), manganese nodules (in 31-70 % of the samples), volcanic glass (in 31-79% of the samples) *etc.* Magnetite and other oxide-hydroxide iron-containing minerals are the most common and present in most important sediments [9-15, 18, 19, 22, 23].

Table 1.1. Probability of finding minerals in samples of some IASSMs and NIASSMs [10, 12]

Main inorganic components	Probability, %			
	Red clay	Radiolarian ooze	Diatom ooze	Globigerina ooze
Fieldspars (sum)	76	90	60	73
Magnetite	89	—	100	80
Illite, montmorillonite	27	10	100	26
Quartz	30	—	80	42
Glauconite	9	—	20	11
Manganese nodules	79	70	—	31
Number of analyzed samples	70	9	5	118

Table 1.2. Chemical composition of main pelagic sediment types [10, 12]

Component	Red clay, %	Limestone ooze, %	Silica ooze, %	Component	Red clay, %	Limestone ooze, %	Silica ooze, %
SiO ₂	53.93	24.23	67.36	K ₂ O	3.65	1.40	2.15
TiO ₂	0.96	0.25	0.59	P ₂ O ₅	0.09	0.10	0.10
Al ₂ O ₃	17.46	6.60	11.33	H ₂ O	6.30	3.31	6.33
Fe ₂ O ₃	8.53	2.43	3.40	CaCO ₃	0.39	56.73	1.52
FeO	0.45	0.64	1.42	MgCO ₃	0.44	1.78	1.21
MnO	0.78	0.31	0.19	C _{org}	0.13	0.30	0.26
CaO	1.34	0.20	0.89	N _{org}	0.016	0.017	—
MgO	4.35	1.07	1.71	Total	100.20	100.17	100.10
Na ₂ O	1.27	0.75	1.64	Total Fe ₂ O ₃	9.02	3.14	4.98

So, it is possible, that such minerals of sediments have a universal effect on properties of IASSMs and NIASSMs, both in fine-disperse and in dense fine- and nanocrystalline states. The data in Table 1.2 show that SiO_2 amount in samples of sediments are the highest and reach 53.93% in red clays, 24.23 and 67.36% in limestone and silica oozes, respectively. A significant amount of Al_2O_3 (17.46, 6.60, and 11.33% in the appropriate oozes) also shows that the three mentioned oxides (Fe_2O_3 , SiO_2 , Al_2O_3) play a general role in structural transformations of sediments. Limestone ooze, which contains up to 57% of CaCO_3 , has also a significant biocolloidal and colloid-chemical effect of calcium minerals on its properties, and their ascertainment has just started [16, 17, 23].

Distribution of different sediments is presented in Table 1.3; some properties and structure of marine sediments are given in Table 1.4. The data in Table 1.4 evidence that marine sediments have a developed enough surface, and sizes of some particles in the composition of red clays are 27.0-86.7 nm. That is why, red

Table 1.3. The area (in 10^6 km^2) of dissemination of pelitic sediments [10, 12]

Type of sediment	Atlantic Ocean		Pacific Ocean		Indian ocean		Total	
	Surface	%	Surface	%	Surface	%	Surface	%
Limestone oozes:								
globigerina	40.1	—	51.9	—	34.4	—	—	—
pteropodium	1.5	—	—	—	—	—	—	—
Total	41.6	67.5	51.9	36.2	34.4	54.3	127.9	47.7
Silica oozes:								
diatom	4.1	—	14.4	—	12.6	—	—	—
radiolarium	—	—	6.6	—	0.3	—	—	—
Total	4.1	6.7	21.0	14.7	12.9	20.4	38.0	14.2
Red clay	15.9	25.3	70.3	49.1	16.0	25.3	102.2	38.1
Total	61.6	100.0	143.2	100.0	63.3	100.0	268.1	100.0

Table 1.4. Surface properties and porous structure of sea sediments [10, 12]

Type of sediment	Carbonate content, mass%	Total density, g/cm^3	Actual specific surface, m^2/g	Average particle size, nm
Red clay		0.92	28.2	83.0
» »	27.2	0.66	86.7	27.0
» »			54.7	86.7
Diatom ooze		0.41	17.9	170.0
Shelf (terrigenous) sediment		0.91	12.4 (110, 150 °C)	190.0

clays can be attributed to nanostructural materials. However, since the day this fact was established (about the 1970s and up to our days), the specific role of nanoparticles in the composition of deep-sea oozes practically has not been studied [16, 17]. Shallow-water oozes (diatomic and shelf ones) have a highly disperse microstructure and the size of ultradisperse particles about 170-190 nm. It is interesting, that red clays containing about 9% of iron oxides (Table 1.2), are the most widespread in oceans (Table 1.3). Their area reaches $340 \cdot 10^6$ km².

To sum up, the important role of NIASSMs in natural, technogenic and anthropogenic processes is indisputable, but it has been investigated incompletely and irregularly. Thus, the role of NIASSMs in natural and technological processes has been studied from the ancient times, but without consideration of the influence of their nanostructural composition and nanostructuring processes on the properties of rocks, and marine, shelf, lake and river sediments formed from them [9-15, 18, 19, 24-33]. This partly refers to anthropogenic processes as well. Thus, the use of clays and peloids via empiric procedures in balneology and medicine has been known for a long time [27, 34] and it continues today with traditional and new clay minerals [35-50], for example, glauconite [35-40] and ion-exchange materials [51]. Recently, the researches of nanoparticle influence on the medical properties and stress phenomena in the Earth's crust are expanding [37, 44, 52, 53]. However, they still do not have a generalized character, which is marked in [16, 17]. Therefore they need new systematic researches, first of all, using methods of nanochemistry, physicochemical mechanics and geomechanics, and also biocolloidal approaches related to them.

1.2. Formation of IASSMs and NIASSMs, their types and transformations due to their nano- and microstructuration

The most interesting among IASSMs and NIASSMs, for example, in metallurgy are sedimentary fine-disperse ironsilicate ores of biocolloidal origin; in medicine and balneology — pelagic deposits, which include shallow- and deep-water bottom sediments of seas and oceans [10-12]. They are formed by gradual accumulation in basins due to river transport (carry-over) of disperse materials into sea water areas and due to processes of sedimentation and biocolloidal heterocoagulation with subsequent chemogenic separation and biocolloidal enrichment of separated disperse and highly dispersed particles suspended in water [8]. Among the carry-over materials important for the formation of NIASSMs, the planktonic residues of microorganisms responsible for biocolloidal accumulation of C_{org} in sediments [18, 21, 42, 53], as well as FeO and Fe₂O₃ formed owing to the iron bacteria life activity [22], should be mentioned. Clay and other silicate mate-

rials, volcanic ash and cosmic dust also occupy an important place. Sediments formed at the depth of the shelf zone (above 200 m), are usually attributed to the deep-water sediments. Fine-grained products of the pelitic or aleuric type, terrigenous deposits (clay or pebble), biogenic (carbonate and silicic), volcanic oozes, and also red deep-water clay oozes are the most common among sediments. Deep sea sands (foraminiferal sands of submarine ridges, terrigenous sands, volcanic terrigenous sands) are well known as well [8-15]. However, not all mentioned sediments have industrial importance or remedial properties, which can be determined only by tests. The composition of sediments with the rapeutic properties (peloids, therapeutic muds) includes skeletal formations of microorganisms, such as radiolarians, diatoms, foraminifera etc., fine-grained terrigenous and volcanic formations, or autogenous mineral new formations (ironsilicate, iron-manganese nodules, montmorillonite (nontronite), glauconite, kaolinite). Such sediments constitute most of the World Ocean area. They also include diatomic oozes and polygenic deep-sea oozes, which are part of red clays, and are characterized by low rate of sedimentary accumulation and oxidation, the presence only of the most fine-dispersed terrigenous material, low content of organic matter and impoverishment of bottom fauna [10, 18].

In addition to deep sea sediments, there are more coarsely-disperse terrigenous deposits of so-called phaseolinic oozes [18] in a shallow shelf zone of seas and oceans at depth under 200 m. There are also biogenic, chemogenic and volcanic deposits [11-15].

There are also other sea sediments and deposits, which find their application not only in medicine or balneology, but also in agriculture, building of protective structures, and as a raw material for extraction of mineral resources. The origin of marine sediments and deposits in most detailed way is considered in works [12-15]. According them, sea deposits and sediments exceed three times the continental deposits (75% of total volume of continental part of the Earth's crust). Their formation began 3.5-4 billion years ago and continues now, and gradual metamorphic transformations during the processes of diagenesis led to formation of sedimentary externally dense, but internally nanostructured rocks, which mostly include dolomites, marls, siliceous rocks, limestones, clays, argillites, siltstones, sandstones and such minerals as sedimentary iron and manganese ores, phosphorites, combustible shales, gneisses and marbles [1, 9, 11, 13-15, 19, 24-27, 30, 32, 33]. All of these fossils are mostly of biocolloidal origin.

The conditions of sea deposits formation were not similar during the whole geological history. For example, in Proterozoic and Paleozoic, chemogenic deposits were accumulated, where as in Mesozoic and Cenozoic — biogenic (biocolloidal) deposits, which were aided by microorganisms. In Precambrian and early Paleozoic sea dolomites were formed, and in the following epochs — mainly

limestones. In Proterozoic, about 2 billion years ago, iron quartzites (jaspilites) were formed. As established in [22], microorganisms which took part in biocolloidal processes played a great role in their formation. Biocolloidal processes and consecutive metamorphic transformations in diagenesis process led to formation of jaspilites, which are a basis of most modern nano- and microcrystalline ore deposits of iron and iron-manganese ores and of many other macrostructured dense, but at the same time nano- and microstructured materials [16, 17, 53]. Part of them formed in more recent times stayed in the form of sedimentary oolitic iron ores or polymetallic ores (about 25%).

As above noted, depending on the formation conditions of NIASSMs and pelitic sediments, such as the depth of deposition, distance to shore, currents, relief of bottom, conditions of existence and type of sediment-forming organisms, etc., different processes of sediment formation occurred in the same sea reservoir, which led to different forms of marine sediments. Thus, in the shallow coastal zone, terrigenous sands, pebbles, and shell rock were accumulated in the conditions of storms, while clays and aleurites were formed in quiet conditions near mouth of rivers. Biogenic limestone sediments and sands were formed on underwater rises, while clays and aleurites rich in organic substances — in ditches, and reef formations of limestones and dolomites — in shallow waters [10]. Shallow-water sediments include sedimentary iron (oolitic) and manganese ores, and also ferrous bauxites and phosphates. It comes out from mentioned, that sediments may have very different properties and different spheres of their practical use depending on the conditions of their formation and metamorphism. This question is waiting for its comprehensive solution as well. For example, it has been shown [10, 18] that fossil sea sediments often contain remains of marine organisms, whose biocolloidal activity led to sedimentation with previous separation and enrichment with definite minerals (Fe_2O_3 , Al_2O_3 , etc.). They are characterized by the presence of authigenic minerals of the glauconite type, along with texture features, where nanostructurization of sediments and deposits is marked recently as important one among the other features [16, 17, 25, 53]. In addition, their formation depends on the climate conditions. Terrigenous sands, aleurites and clays are formed in humid zones in seas in the conditions of carry-over from rivers, while diatomic oozes are formed in cold water reservoirs. There is also known biocolloidal carbonate accumulation, and the appearance of foraminifera, coccolith and pteropod sediments. Coral formations and chemogenic oolitic limestone accumulations appeared in warm seas. Both biocolloidal and geochemical transformations participate in most of these processes and affect the IASSMs and NIASSMs structure formed in the following metamorphic processes. In most cases, nano- and microstructuring of different ore-bearing deposits take place during the sedimentation process in such conditions, and also there are

formed nano- and colloid particles [10, 12, 22] followed by their re-cementation in secondary dense rocks. However, these data are preliminary. Thus, mechanisms of metamorphic nano- and microstructuring of the solid phase in the composition of IASSMs and NIASSMs and pelitic sediments need further theoretical and experimental justification, most likely with the use of physicochemical and geo-mechanics methods [20, 54] and with modern biocolloidal, mechanical and rheological methods and methodology [55-88].

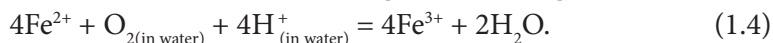
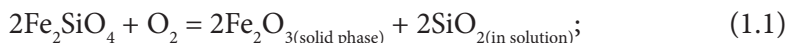
1.3. Nanochemical and colloid-chemical mechanisms of iron oxide-hydroxide transformation in IASSMs and NIASSMs in the presence of microorganisms

The processes of chemical (nanochemical) transformations of mineral substances, first of all in salt and sea waters of seas and oceans [10, 11], are preceded by the processes of their metamorphism in the Earth's crust in rock-water-air-microorganisms systems [12]. Many other processes of chemical transformations without microorganism participation can also be seen on the Earth surface [11, 12, 13]. Some of them are processes of disperse mineral substance transportation into ocean with the help of solar (weathering) and gravitation energy. As for the initial stage of releasing individual grains of minerals from rock in these processes, conceptions of chemical and microbiological influence of the surrounding solution around individual grains become wholly recognized as well, as the processes that only just began to be studied [20, 23, 52, 53] with the help of physicochemical methods [20, 54]. These not much before investigated ideas [9-15, 24-30], have become studied in detail nowadays [18, 22, 23, 40-43, 53]. For example, it has been established that the chemical reaction ability of solutions can be reinforced by microorganisms living on the surface of rocks [8, 16, 17]. Such ideas also relate to dispersion influence and are based on the laws of physicochemical geo-mechanics have not yet enough developed, and their fundamental dependencies are still unclear. Therefore, this does not allow us to formulate and generalize the laws of nanostructural and biocolloidal interactions in NIASSMs now. It is however known that almost all volcanic and metamorphic rocks on the Earth surface have iron in the form of magnetite and different silicates, mainly with divalent iron in their compositions [1, 9, 11, 12-17, 19, 25, 30, 33, 89]. Such data lead us to the most probable opinion that the minerals were formed not only by the chemical way in the conditions of poor oxygen in depth of the Earth's crust. Thus, a large number of minerals on the Earth surface and at small depth were formed in the form of nanostructured sediments of polymineral ores; microorganisms also took part in their formation [42] aiding with surface and chemically active products of

their metabolism. However, most of these minerals are unstable over time on the Earth's surface at a sufficiently high partial oxygen pressure. In such conditions magnetite transforms to hematite [9, 26, 30, 36], the main mineral of crystalline iron ores (jaspilites) [22]. In sedimentary iron silicate ores, especially in coastal regions, iron stays in divalent state, mainly in the form of iron oxide-hydroxides and nontronite-saponite, due to the activity of microorganisms [16, 17, 89].

Besides iron oxide-hydroxides, silicon compounds exert a significant influence on formation of NIASSMs and their ore deposits. However, sea water is not saturated with silicon. In order to achieve the balance of sea water and silica (SiO_2), the concentration of silicon in water has to be five times greater than it is [10, 12]. Despite this, sea microorganisms (radiolarians and diatomea) have the ability to extract amorphous types of silicon compounds from sea water into sediment under the certain conditions, which easily dissolve and participate in the following formation of different iron silicates by relevant chemical reactions with amorphous iron oxide-hydroxides, which appear due to the microbiological processes as well.

Such processes are accompanied by chemical reactions between water and particles of earth rock, for example, in the following way:



These reactions create possibilities for further nanostructuring processes.

These examples and reviewing information on microorganisms role in IASSMs and NIASSMs formation make it clear that the influence of microorganisms on such reactions needs wider fundamental decryption. At the same time, the conceptions of chemical redox processes relevant to formation of iron-aluminosilicates and iron oxide-hydroxides have been developed at the level of micro- and macroparticles, but are not enough developed at the level of nanotransformations [9-15], and therefore need more detailed researches.

1.4. Redox processes in formation of iron compounds in IASSMs and NIASSMs

Despite the fact, that all the questions related to redox reactions in dispersions of NIASSMs can be solved, as it is shown in general form in the previous section, but another way of solving such problems is used more often. It is

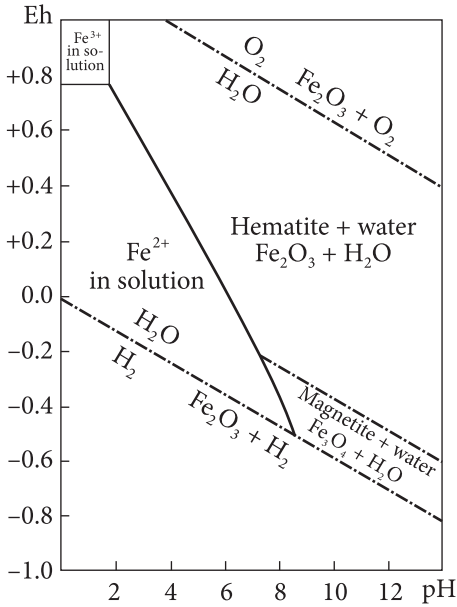


Fig. 1.1. Diagram of the Eh and pH correlation which shows the fields of stability of the main iron compounds [10-12]

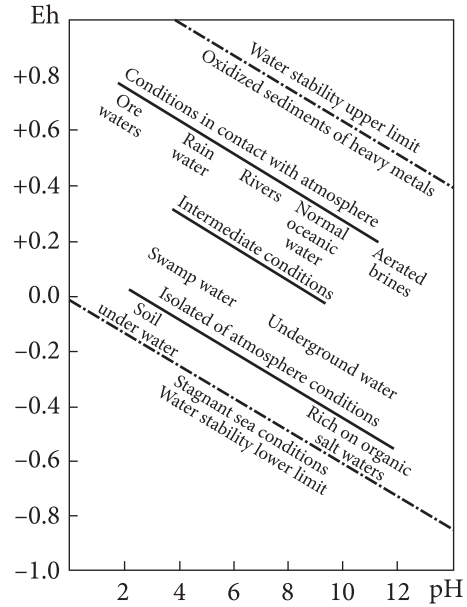


Fig. 1.2. Eh—pH dependence for different natural conditions [10-12]

based on standard methods for electrochemical measurements in ionic systems, according to the reaction of electrode potential:

$$E = E^0 + \frac{RT}{nF} \ln a_{\text{Fe}^{2+}}, \quad (1.5)$$

where F is the Faraday constant and n is the number of electrons that take part in the reaction.

The standard electrode potential relates to change in the standard free energy:

$$\Delta G^0 = -nFE^0. \quad (1.6)$$

If a platinum electrode is placed, for example, in a solution containing ions Fe^{2+} or Fe^{3+} , then the potential is formed:

$$E_h = E^0 + \frac{RT}{nF} \ln \left[\frac{\text{Fe}^{2+}}{\text{Fe}^{3+}} \right]. \quad (1.7)$$

It is easy to calculate the redox potential E_h from this equation for different chemical reactions, including reactions with mineral iron compounds participation. Fig. 1.1 illustrates the diagram for main iron compounds in the Eh—pH coordinates. Their change limits are generalized in Fig. 1.2 according changes

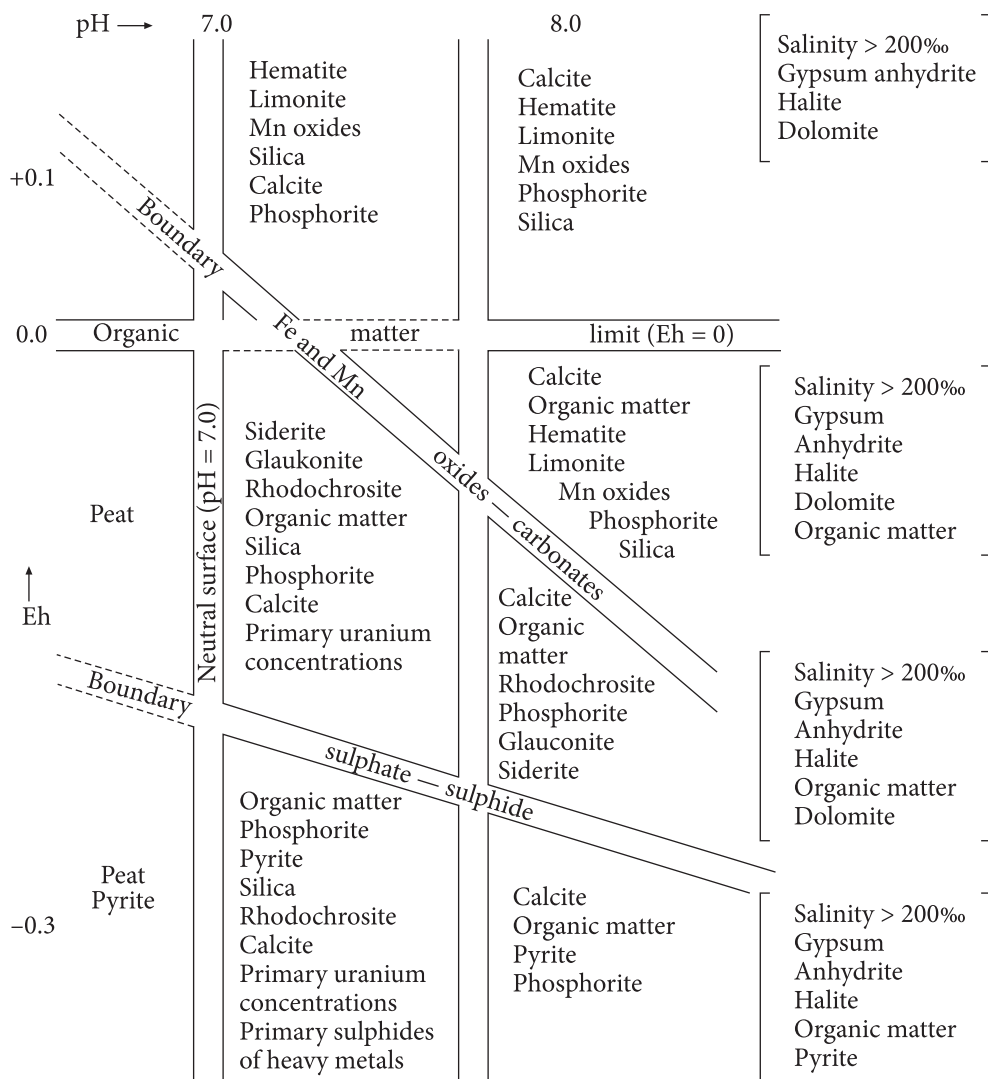


Fig. 1.3. Correlation of Eh i pH in the areas of common sedimentary minerals formation [10–12]

of parameters in Eh—pH coordinates for different nature conditions on Earth’s surface. Here with, not very acidic or slightly alkaline pH values and reducing conditions (low Eh) usually are associated with the activity of organic life. At that, bacteria can recover sulfates and release hydrogen in free state [12, 48-50, 89], or create compounds of unstable double layered Fe(II)—Fe(III)—hydroxides of the Green Rust type, which have high reducing and catalytic properties [90-104].

Fig. 1.3 generalizes conditions of the Eh—pH correlation for formation of ordinary sedimentary minerals and preservation of organic substances. As seen, organic substance is preserved at $Eh < 0$, salinity of water 200‰, in the interval of pH 7-8. It is interesting, that in the pH interval 7-7.8, $Eh < 0$ and salinity of 200‰ the conditions for precipitation and separation of iron-containing minerals containing uranium appear, and at $Eh < 2$ sulfides of heavy metals are added to them.

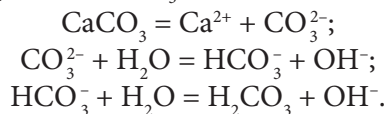
1.5. Chemical transformation processes of calcium, silica, and aluminosilicate compounds in formation of IASSMs, NIASSMs, and related iron-containing ore minerals

All minerals are characterized by solubility in water, which is an additional factor of their transformations in the course of weathering, transport of small fractions by rivers, gravitational separation and sedimentation in sea areas and in industrial conditions [1, 8, 9-17, 105-108]. Here with the solubility is accompanied by formation of ions or sedimentation of relatively insoluble minerals. The balance between solid phase and solution, or solubility, is characterized by the constant of chemical equilibrium K , called the solubility factor. Thus, for example, if calcite dissolves in water ($CaCO_3 = Ca^{2+} + CO_3^{2-}$), then equilibrium is fulfilled under the condition:

$$\mu_{CaCO_3}^0 = \mu_{Ca^{2+}} + \mu_{CO_3^{2-}} = \mu_{Ca^{2+}}^0 + RT \ln a_{Ca^{2+}} + \mu_{CO_3^{2-}}^0 + RT \ln a_{CO_3^{2-}};$$

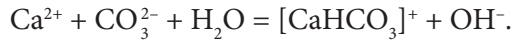
So, if $\Delta\mu^0 = \mu_{Ca^{2+}}^0 + \mu_{CO_3^{2-}}^0 - \mu_{CaCO_3}^0$, then $-\Delta\mu^0 = RT \ln(a_{Ca^{2+}})(a_{CO_3^{2-}})$ and the solubility factor equals: $K = MP = [Ca^{2+}][CO_3^{2-}]$; then $-\Delta\mu^0 = RT \ln K$.

From this equation it comes out, that at constant T and P , the value of $\Delta\mu^0$ is also constant, and so is the solubility factor K . However, there are controlling factors which influence solubility. Thus, $CaCO_3$ dissolves in water according to the scheme:



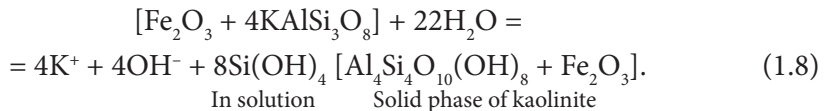
Sulfides dissolve in the same way. Since, solubility depends on pH and P_{CO_2} (P_{H_2S} for sulfides), the constant of solubility factor ($a_{Ca^{2+}})(a_{CO_3^{2-}}$) or $(m_{Ca^{2+}})(m_{CO_3^{2-}})$ ($\gamma_{Ca^{2+}})(\gamma_{CO_3^{2-}}$) shows that any substance increases the mole concentration in solution, or solubility, with decreasing activity coefficient γ . All salts increase ionic strength of solution and reduce the γ value. Therefore, $CaCO_3$ dissolve in a NaCl solution better than in pure water. Hence it turns out that the solubility of $CaCO_3$ in sea water and in relevant marine, saline lagoon, and lake peloids will be increased. And vice versa, if ions are not formed while dissolution, for example, while dissolution of quartzite, then its solubility in the presence of electrolytes decreases due to hydrational binding of the solvent part in hydrated SiO_2 .

The activity of most ions in solution may be decreased due to the formation of complex ions. From this point of view, calcium carbonate in solution can be a typical complex ion, when the process runs by the scheme:



Other examples of similar processes for heavy metals: $\text{Pb}^{2+} + \text{HS}^- = \text{PbHS}^+$; $\text{Ag}^+ + 2\text{Cl}^- = \text{AgCl}_2^-$; $\text{Ag}^{2+} + 2\text{NH}_3 = \text{Ag}(\text{NH}_3)_2^{2-}$ show that such complexes influence the solubility in sea water and in relevant dispersions of pelagic sediments (peloids) of the NIASSM type. This creates additional problems for evaluation of the concentration level for heavy metals in oceans, in NIASSMs and peloids (Fig. 1.2).

NaCl , CaCO_3 and SiO_2 dissolve in water congruently, but the most of complex iron-aluminosilicates dissolve in congruently. For example, orthoclase KAlSi_3O_8 with iron compound impurities dissolves in water with the formation of a solution enriched with K and Si and a solid phase in the form of clay mineral:



The conducted experiment studies [12] showed that at Na-K-feldspar dissolution in water, an unbalanced composition of dissolved substances is formed due to the influence of CO_2 from the air. In the equilibrium conditions, Na and K bicarbonates, which regulate pH, will be present in the solution. On the other hand, the solubility of silicates, salts of a weak acid, depends on the pH value, which in its turn depends on the local concentration of CO_2 . Thus, silicates often have buffer influence on pH and on solubility of macro- and microelements both in sea water and in pelagic sediments of the NIASSM type. Therefore, this conclusion shows again, that in order to comprehensive lyassess the NIASSMs' behavior in natural and technological conditions, additional definitions of such phenomena as adsorption, ion exchange, colloid state of substance, nanostructural and nanochemical processes on the contact surface of nano- and microparticles of colloidal solution are required. Further more, the influence of microorganisms should be added as well. Their metabolism leads to the appearance of a number of complexing surfactant organic substances of the peptide series and of chemically active ferments.

1.6. Influence of colloids, adsorption, and ion exchange on nanostructuration processes of IASSMs and NIASSMs components

Sedimentation in seas and weat hering on lands with IASSMs and NIASSMs formation are accompanied not only by the processes discussed in the previous chapters. It is known that surface forces of disperse particles lead to ad-

Similar reactions are typical for magnesium minerals as well [10]. Here with, chemical interactions end with the formation of superfine dolomite, and the growth of crystals becomes limited by adsorption of magnesium ions on the crystallization surface centers.

Thus, for colloidal NIASSMs, the most characteristic processes are the nanostructuring processes in compounds of Fe, Al, Si, Ca, Mg and other elements and also of impurity elements and heavy metals in the conditions of simultaneous adsorption and ion exchange. They lead to chemical and microbiological transformation of such compositions. Here with, a complex superfine polymineral NIASSMs, suspensions of pelitic sediments and peloids are formed [9-15, 18, 19, 21, 22, 24-31, 40, 55-61].

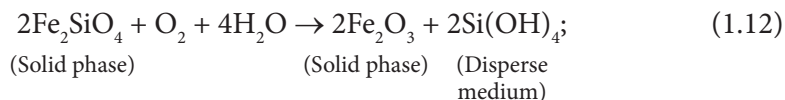
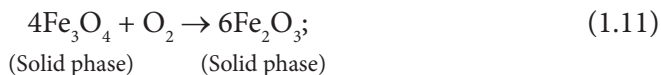
Except the mentioned features of element transfer process in NIASSMs in the conditions of their colloidal state, fine dispersion of minerals can complicate their sedimentation according to Stoke's law. Their very small particles with sizes of 10^{-8} - 10^{-7} m, namely ultradisperse colloidal particles, can obey the conditions of the Brown motion and behave as large molecules, which is more typical for nanosized particles (10-100 nm or 10^{-8} - 10^{-7} m). Such particles, mostly characterized by rather amorphous than crystalline state and by increased surface area, show increased chemical activity in comparison to similar crystalline particles, and they have very low sedimentation rate.

In the conditions of geochemical and geophysical transformation of rocks with the formation of NIASSMs, pelagic sediments and peloids, there are two problems arising: how colloids are formed in nature and how stable they are [10, 12, 18, 20, 23]. It is rather easy to obtain a colloid system in the laboratory conditions, but it is not always clear how much and for what period of time the colloidal material can be formed in the natural conditions of mechanical grinding and under weathering, which is practically always accompanies with the formation of supersaturated solutions [12, 20]. For example, silicates and iron oxides in the conditions of weathering give unstable solutions, supersaturated relatively to crystallized Fe_2O_3 . Such processes are typical for formation of iron-containing clays and of clay minerals containing feldspars. In general case, when the crystallization rate is very low, there is a possibility of receiving very small particles, among which, as shown in [20, 90-104, 106], there are nanosized ones as well. So, it is not unexpected that natural waters contain much higher amount of colloidal iron oxide-hydroxides, than at equilibrium with crystalline hematite, goethite, magnetite and quartz.

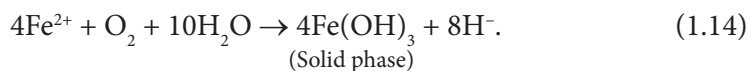
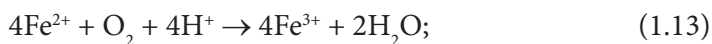
Surface ionization of colloidal particles leads to the appearance of surface charge. It is known, that colloidal iron hydroxide has a positive charge, and hydrated colloidal silicon dioxide has a negative one. Therefore, by theory, such particles should actively interact in a disperse medium with the formation of sedi-

mentary unstable compounds or aggregates of particles. However, particles can be stabilized under the action of different factors: protective action of organic surfactants, which appear as a result of biogeocenosis activity; adhesion interaction with microorganisms; influence of temperature and salinity of water; chemical reactions on particle surface, *etc.* The influence of such factors complicates the prediction of some NIASSMs behavior and needs experimental specification of their behavior in different conditions. But it is not always possible to separate the processes of adsorption and formation of surface chemical compounds, which makes it difficult to interpret experimental facts without additional physicochemical researches in different directions. It should also be taken into account, that in the conditions of geochemical and microbiological transformations of NIASSMs, iron and silicon bonded in silicate minerals can be separated and form new compounds. This is due to the fact that iron transits into disperse media in the form of $\text{Fe}(\text{OH})_3$ colloids, and silicon is often in the form of ions in solution, but not in the form of colloid particles [23].

As natural pelitic sediments are polymineral and have iron (Fe^{2+}) compounds in their composition, disperse fracturing of such compounds according to the laws of physicochemical geomechanics occurs under the conditions of adsorption of oxygen from the air or owing to the microfaunavital activity. For example, it proceeds by the following schemes:



or according to the chemical interactions in a disperse medium:



As follows from equations (1.11)-(1.14), processes of Fe^{2+} in Fe^{3+} transformation with simultaneous disperse fracturing of dense NIASSMs depend on pH. Since the hydrogen index is regulated by the vital activity of microorganisms, the role of dispersing processes of dense NIASSMs according to the laws of physicochemical mechanics and geomechanics [7, 20, 54] and as the result of metabolism processes [16-18, 90-104] should be prominent and considered separately in such biocolloidal nano- and microinteractions.

1.7. Role of microorganisms and nanostructures in formation of iron oxide-hydroxides and biogenic minerals in biocolloidal transformation of IASSMs and NIASSMs

Biogenic minerals, which also contain iron oxides and hydroxides, are characterized by small particle sizes in the nano- and colloidal range (from 2 to 500 nm) as well as by the presence of other structural impurities, such as SiO_2 , Al_2O_3 , sulfates and sulfides, As and P in the form of arsenates and phosphates and other compounds [1, 11-13, 19, 24, 25, 105, 107, 109, 110]. The most important factors influencing on the processes of chemical and microbiological oxidation or reduction of iron in disperse polymineral phases and in a disperse media are pH and the presence or absence of an oxidant, as well as additional factors such as metabolism of microorganisms, the rate of sedimentation and transformation of disperse phase under the action of geomechanical and hydrogeochemical transformations [110-114].

At the neutral pH in the anaerobic conditions, redox of iron can take place with the participation of autotrophic bacteria, which chemically recycle CO_2 with the help of light energy with liberation of O_2 . The process may be accompanied by reduction of nitrates with parallel reduction of iron by iron-reducing microorganisms [115]. Different groups of microorganisms that oxidize Fe^{2+} are found in soil and hydrothermal waters [111], in depths of ocean [112], and in marsh pe-lagic sediments [113]. In neutral media, *Gallionella* spp. and *Leptothrix* spp. bacteria are the most active. In an acid medium, the rate of Fe^{2+} oxidation almost does not depend on pH, and catalytic transformation occurs through various types of iron oxidizing microorganisms. The main ones are *Acidithiobacillus* spp. (γ -Proteobacteria). In a strongly acidic (pH 0.7-1.0) medium, the oxidation of Fe^{2+} sulfides is catalyzed by *Leptospirillum ferrooxidans*, and at pH = 0.5 — by Archean iron oxidizing bacteria *Thermoplasma* spp.

Addition of magnetite to the biomineral systems results in reducing duration of microbiological processes by dissolving magnetite with release of Fe^{2+} . Subsequently, Fe^{2+} serves as a substrate for autotrophic bacteria, which transform Fe^{2+} into Fe^{3+} . Other bacterial reactions occur simultaneously with those processes, they lead to formation, depending on pH, of various sulfides, carbonates and minerals, such as siderite, magnetite, rhodochrosite, apatite, phosphorite (vivianite), etc. (Fig. 1.3). There are also possibilities to separate heavy metal compounds, as well as phosphorus and arsenic from polymineral iron oxide silicate suspensions. In general, these processes are reflected in Table 1.5 [109].

Bacterial reactions can solve many practical problems as we can see from the given data. But the mechanisms of such reactions are complex, and they have been investigated only in general terms. At the same time, it is clear that understanding of such

mechanisms gives the opportunity of scientific forecasting and creation of effective biogeotechnologies for purification of NIASSMs from impurities of heavy metals, arsenic and phosphorus, to produce many minerals from them with specified properties, and also to design reduction processes for obtaining metallic phases of noble metals.

To sum up, the research of fundamental problems associated with colloid-chemical, nanochemical and biocolloidal features of the mechanisms of bacterial reactions is relevant and timely.

In addition to the processes considered, the attention of researchers are attracted by the chemical and bacterial reactions, which in the laboratory conditions, in the environment, or in technogenic sludges from metallurgical and other industries lead to the formation of unstable structures such as Fe^{2+} — Fe^{3+} LDH (Layered Double Hydroxides, or Green Rust), which easily transform into lepidocrocite, goethite, and magnetite [116-122].

The process of Green Rust transformation of the $\text{GR}(\text{CO}_3^{2-})$ and $\text{GR}(\text{SO}_4^{2-})$ types into γ - FeOOH (lepidocrocite) is considered in [116-118]. And there are the processes of phase formation with the participation of microorganisms consid-

Table 1.5. Bacterial reactions, which lead to the formation of new inorganic compounds in IASSMs and NIASSMs with the separation of ion-impurities

Ion-impurities	Form of metals after the transformation	Culture of microorganisms; process conditions
<i>Mineralized forms</i>		
Pb^{2+} , Zn^{2+} , Cu^{2+} , Ni^{2+} , Cd^{2+} , Hg^{2+} , Ag^+ , As^{3+}	In the form of sulfides: PbS , ZnS , CuS , SrS , NiS , CdS , TeS , HgS , Ag_2S , As_2S_3	<i>Alcaligene ssp.</i> ; sulfate reduction bacteria, acidic medium, anaerobic conditions
AsO_2^-	In the form of crocodile: FeAsO_4	<i>B. arsenooxidans</i> , <i>Pseudomonas sp.</i> , <i>Achromobacter sp.</i> , <i>Xanthomonas sp.</i> ; alkaline media, aerobic conditions
Co^{2+} , Cu^{2+} , Zn^{2+} , Ni^{2+} , Mn^{2+} , Fe^{2+}	In the form of carbonate, phosphate minerals: apatite, siderite, magnetite, rhodochrosite, vivianite: CoCO_3 , CuCO_3 , NiCO_3 , MnCO_3 , SrCO_3 , $\text{Fe}_2(\text{CO}_3)_3$, $\text{Fe}_3(\text{PO}_4)_2$	<i>Alcaligenes eut.</i> , <i>Shewanella putrof.</i> , <i>Geobacter metal</i> , <i>Aquasperillum magnetotacticum</i> ; alkaline or buffered neutral medium, aerobic or anaerobic conditions
Cr^{6+}	Cr^{3+} , $\text{Cr}(\text{OH})_3$, Cr_2O_3	<i>P. dechromaticans</i> , <i>P. chromatophile</i> ,
U^{6+}	U^{3+} , UO_2	<i>P. fluorescens</i> ; neutral medium
<i>Reduction to metal</i>		
Au^{3+}	Au^0	<i>B. cereus</i> ; neutral environment, aerobic conditions
Hg^{2+}	Hg^0	
Ag^+	Ag with $\text{Ag}(\text{OH})$	

ered in [119-122]. In [121], the interaction of microorganisms with minerals and organic substances in natural ecosystems has been investigated. A disadvantage of these studies is the absence of necessary attention to the colloid-chemical mechanisms of the transformation of iron oxide-hydroxides in NIASSMs in the conditions of geochemical bacterial processes and their role in the appearance of more complex mineral and polymineral systems and pelitic sediments.

Thiobacillus ferrooxidans and *Leptospirillum ferrooxidans*, which contribute to the formation of Fe^{3+} in an acidic medium, should be noted among the types of bacteria taking part in the geochemical bacterial reactions of GR formation. *Bacteria Gallionella ferronea* are effective in a neutral medium in the aerobic conditions. Non-fermenting bacteria, which breath at the expense of iron and fermenting bacteria such as IRB, DIRB (dissimilation iron-reducingbacteria) are adapted to the bacterial mechanism of iron reducing. In addition, formation processes of Fe^{2+} — Fe^{3+} LDH in the natural conditions have been investigated, complex research of reducing processes, dissolution and liberation of highly disperse iron oxide silicate minerals has been performed; the leading role of IRB in the formation of GR in the natural conditions [123-126] has been disclosed. The mechanisms of such processes are related to the reducing of Fe^{3+} with the simultaneous dissolution of minerals and the interaction of Fe^{2+} ions with mineral structure. Cosedimentation of Fe^{2+} is also possible with the structures including iron oxide-hydroxides in their composition [127]. However, the role of geomechanical and nanochemical structural processes as a consequence of microorganism vital activity in [123-127] has not considered yet.

Sea water processes have their own peculiarities. Bacterial reactions in such conditions occur with the participation of both iron-reducing bacteria *Clostridium* spp. uncultured, and sulfate-reducing bacteria *Desulfovibrio caledoniensis* (SRB). The life activity of SRB activates due to intermediate formation of FeS_2 pyrite particles with formation of GR (SO_4^{2-}) [128-131]. But DIRB slows down this process [132]. The mechanism of interaction between SRB and DIRB was considered in [133, 134].

The results obtained in [133] showed that $\text{GR}(\text{CO}_3^{2-})$ and $\text{GR}(\text{SO}_4^{2-})$ are formed in the presence of DIRB, their ratio depends on the ratio of concentrations (C) of carbonates and sulfates in the solution. Single GR (CO_3^{2-}) is formed at $C \geq 0.17$, and at $C < 0.17$ there is a mixture of $\text{GR}(\text{SO}_4^{2-})$ and $\text{GR}(\text{CO}_3^{2-})$ [133]. Hence, it turns out that in the conditions of solutions contacting with air, it is quite complicated to obtain pure structures of $\text{GR}(\text{SO}_4^{2-})$, and that can affect the results of kinetic studies of the $\text{GR}(\text{SO}_4^{2-})$ formation in sulfate solutions due to the uncontrolled transition of CO_2 from air into the solution. This also complicates single-valued modeling of GR formation in the presence of certain types of microorganisms, whose life activity product is CO_2 .

Thus, literature analysis of the data shows that in natural conditions with a lack of oxygen (deep processes in seawater, in groundwater and underground water), the formation of Green Rust is due to the vital activity of microorganisms, primarily iron-reducing. Since aqueous solutions in natural conditions mostly have low concentrations of SO_4^{2-} ions, and Fe^{2+} — Fe^{3+} LDH of GR (CO_3^2) type are mainly formed. The latter are unstable compounds and therefore they are active reducing agents. Their chemical activity is also increased, because Green Rust particles are in the range of typical nanosized structures (10-100 nm) [109, 110]. All this leads to series of yet unexplored nanochemical reactions, the cause of which is metabolism processes, occurring in disperse IASSMs and NIASSMs in certain geomechanical conditions [20]. Mechanisms of such processes are important for scientific substantiation of the latest biocolloidal nanogeotechnologies, and that makes such studies very relevant.

1.8. Microorganisms in pelitic sediments and peloids; biocolloidal processes

1.8.1. Features of pelitic sediments and peloids, and their physicochemical and other properties

Peloids, or otherwise — therapeutic muds, formed under the conditions considered in [135-158] are the most valuable among the pelitic sediments. According to [135], they are modern or relatively young natural formations, which consist of water, mineral component (primarily clay) and organic substances, and are characterized by a fine disperse structure, homogeneity and, in most cases, pasty consistency. Due to this, they can be used in balneology in heated state for therapeutic purposes in the form of baths and local applications. Peloids have a various chemical composition, and they are enriched with biologically and chemically active components. The medical use of peloids determines high demands for the content of unwanted nanoparticles, toxic substances and pathogens. Therefore the importance of a specific examination of their suitability for therapeutic purposes arises [136-143]. The process of regeneration and activation is one of the methods for purification of muds from pollutions [144-146]. Peloids are formed in various reservoirs (seas, estuaries, lakes, ponds, swamps) as well as in areas of the Earth's crust, where the outcrop zones of disperse clay rocks, underground waters, and gases on surface are formed as a result of tectonic processes. That process causes formation of knoll (volcanic) peloids. Hydrothermal peloids are formed in the areas of volcanism [147]. Assessment of pelitic sediments suitability as peloids for practical use is given in [148, 149].

The composition of peloids and pelitic sediments depends on the natural conditions of their formation. However, all of them are characterized by general struc-

tural properties and heterogeneous physicochemical structure, which consists of liquid and solid phases. The last ones are in equilibrium among each other [145, 148-154]. The liquid phase is a mud complex, which is an aqueous mineral solution that impregnates crystalline skeleton and colloidal mass of peloids [135, 148].

The mud solution content is from 25 to 97 wt.% of peloids. Since it is a derivative of brine covering deposits, the mud solution, by its ionic composition, reflects, within limits, the brine composition. The main mass of ions in the mud solution is presented by sodium, magnesium, calcium, chlorine, sulfate and bicarbonate ions. The gases in the muds are contained mainly in the dissolved state. The source of their formation are biochemical processes generally, which result in formation of hydrogen sulfide, carbon dioxide, nitrogen, hydrogen and methane. The total mineralization of mud solution varies from 0.01 to 0.05 g/dm³ (for peat deposits) and up to 250-300 g/dm³ (for sulfide oozes). The mud solution pH value depends on the chemical composition and direction of occurring biological processes there. Classification of muds by pH are ultra-acid (pH <2.5), acid (pH 2.6-5.0), slightly acid (pH 5.1-7.0), light-alkaline (pH 7.1-9.0) and alkaline (pH >9.0) [135]. The solid part of peloids consists of two components, namely a coarse-disperse or crystalline matrix and a fine-disperse hydrophilic colloidal complex. The crystalline matrix of peloids consists of clay and sandy particles with a diameter above 0.001 mm, as well as of insoluble in water salts: gypsum, carbonates, phosphates, and sometimes coarse organic residues. Dispersity of crystalline skeleton has an important therapeutic value, because the larger the content of small silicate particles, the better quality of peloid systems. Important physical properties of peloids, such as viscosity, plasticity, mass fraction of moisture, and moisture content, are also associated with the crystalline matrix. The thinner peloid matrix, the greater their moisture content [135]. The colloidal complex (nano-, ultra- and microdisperse part of the mud) is presented by various mineral particles smaller than 0.001 mm, organic materials, complex inorganic iron- and aluminosilicate, and organomineral compounds on the basis of sulfuric iron, iron hydrosulfide, silicic acid, aluminum oxide hydrates, iron and manganese, sulfur, *etc.* Iron compounds color the mud in black and dark gray. The content of colloids in different types of the therapeutic muds is different: in ooze muds it is 4-20%, in peat muds and sapropel — up to 80%. Adsorption capacity of muds allows the removal of pathogenic microorganisms during mud treatment from the skin surface or mucous membranes. The colloidal complex, in addition to the crystalline matrix, determines plasticity, moisture capacity, thermal properties and adsorption capacity of peloids. Thus, it can be assumed that peloids, in contrast to pelagic sediments, are a homogeneous plastic mass of a dense consistency. They are characterized by a high fraction of moisture, high heat capacity and low thermal conductivity, and also a high adsorption capacity [135].

Peloids used for therapeutic and prophylactic purposes must meet certain requirements. The assessment of mud quality and its suitability for medical treatments is based on the composition characteristics and properties (humidity, clogging, mineralization, plasticity, content of organic substances, etc.) as well as their sanitary state [144, 155-157]. Such properties have been investigated in papers [148, 152, 153, 158]. At the same time, pelitic (pelagic) sediments, which are much more prevalent than peloids (Tables 1.1-1.4), exhibit physicochemical properties only partially the same as those of the latter [1, 4-15, 18, 19, 23], and that is what their classification testifies.

1.8.2. Classification and characterization of the main types of pelitic sediments and peloids

Pelitic sediments formed mainly in lagoons, seas and oceans are divided into deep-water and shallow-water ones [12]. Some of the Ukrainian pelitic sediments with acceptable balneological tests are considered as therapeutic muds (peloids), and they, especially deep-water peloids, have been investigated only recently [16, 17, 106]. The following classification of peloids is usually used: peaty, sapropelic, sulfide, freshwater clayey, volcanic and hydrothermal oozes [135].

Peat peloids are marsh deposits, characterized by a high degree of plant component decomposition (above 40%). Peat deposits in the territory of Ukraine are located in the forest and forest-steppe geographical zones [152, 159, 160]. Since they contain iron-silicate components of the NIASSM type, their colloid-chemical and balneological properties are regulated by them.

Sapropels are organogenic bottom sediments, mainly fresh water ones. They are formed as a result of reservoir flora and fauna decomposition under the microbiological activity influence. They consist of organic and mineral substances of the NIASSM type with a neutral reaction of the medium, low mineralization of the solution (up to 1 g/dm³), and high mass fraction of moisture (up to 97%). There are low-ash and high-ash sapropels known. The low-ash sapropel is subdivided into algae and zoogenic, humus and peatland. The high-ash sapropels are divided into calcic and clay ones. Their therapeutic significance is determined by high thermal properties, the presence of a large number of organic substances, and biostimulants like vitamins, enzymes, hormones. Sapropels in Ukraine have not been sufficiently studied for its application in therapeutic practice yet [135, 160, 161].

Ooze sulfide peloids are bottom sediments of saline basins, primarily of seas and oceans. They are formed as a result of flora and fauna decomposition by microorganisms in the presence of NIASSMs, they contain hydrogen sulfide and sulfuric iron, but poor in organic substances (1-3%). Their thermal properties are significantly inferior to those of peat and sapropelic muds, but the content of iron

sulfides and water-soluble salts is much higher. An important feature of ooze muds is the content of various gases in them, such as hydrogen sulfide — up to 200 mg/1000 g of therapeutic mud, as well as methane, carbon dioxide, ammonia, and organic (humic) substances. They give the peloids a significant therapeutic effect. Among other organic substances, with important antimicrobial properties, it is necessary to distinguish different acids, pigments, penicillin-like products produced by different bacteria, mold fungi and actinomycetes. Continental sedimentary sulfidic peloids are also found in salt lakes of continental origin in salt-water provinces, for example in the Dead Sea (Israel, Jordan). In Ukraine, they include peloids of lakes Gopri, Salt Estuary, and Prokofievskiyi. Peloids are also divided into coastal ooze sulfide muds of sea bays, coastal lakes and estuaries, and marine ones located in the Black Sea basin. They are being characterized by high content of sulfides and mineralization of the solution. Their ionic composition is close to sea water, sometimes much more concentrated. They are found only near the shores of southern seas and estuaries. The mineralization of their mud solution is almost identical to sea water salinity. Deposits are located in the Berdiansk and Yalta bays [135, 148, 160, 162]. Deep sea salt peloids are characterized by high antifungal activity [21, 53].

Volcanic (knoll) peloids are formed on areas of tectonic disturbances in oil and gas-bearing regions, which are composed of layers of clay rocks, typical representatives of NIASSMs. They have nano-, ultra- and micro-disperse composition, as well as high plasticity and adhesiveness. Since they relate to clay peloids, they have significant moisture and heat-holding capacity. Knoll peloids are alkaline (pH is 8.2-8.8). Among the microorganisms of such peloids, sulfate-reducing and denitrifying biogeocenoses are widely distributed. They decompose organic substances with gas formation under anaerobic conditions. The most well-known deposits of peloids of this type are located on the Kerch peninsula and the Bulhanak knoll field [162].

However, colloid-chemical studies of pelagic sediments are still insufficient [16, 17, 106]. They should be significantly expanded in connection with the established important spheres of their application.

1.8.3. Microflora of pelitic sediments and peloids

Among the mentioned types of NIASSMs, there is a huge number of microorganisms — billions per 1 g of ooze or sediment [163]. Pelagic sediments testing for use as peloids, in addition to sanitary-microbiological tests [149], also include characterization of their microbial cenosis, since microorganisms of peloids represent an important component of biota [159, 161-164]. The autochthonous microflora of peloids is characterized by polyfunctional enzyme systems,

high biochemical activity, and ability of rapid reproducing. It plays an important role in the biocolloidal functioning of such ecosystems as peloid deposits [47, 159, 163, 165-170].

Physicochemical properties of peloids and their microbiological composition are closely correlate and mutually conditioned with biocolloidal processes [8]. The direction and activity of biocolloidal processes depend on the ratio of different microorganism physiological groups in biogeocenosis and physicochemical conditions of their habitat. These conditions can negatively affect the activity of pathogenic and opportunistic pathogens [145, 163, 168]. The necessity to justify the requirements for quality of peloids, taking into account their microbial biogeocenosis, is established in [171].

Therefore, using various methods in various microbial biogeocenosis of peloids and pelagic sediments, biocolloidal processes which are capable of influencing the physicochemical composition, and producing biologically active substances are investigated [48, 172, 173]. Biochemical substances released by microorganisms in biocolloidal processes of their vital functions, determine the physicochemical properties of peloids. They include some of colloidal fractions of peloids, for example sulfur iron hydrate and biocolloids, which, along with inorganic colloids of NIASSM type, create plasticity and viscosity of peloids. They are produced by microorganisms [163], which also affect the inorganic base of NIASSMs in accordance with the laws of physicochemical geomechanics. An important role in peloidogenesis is played by the processes of sulfate reduction, rotting, denitrification, and butyric fermentation. Sulfatereduction is the main source of hydrogen sulfide in peloids and pelagic sediments. There are data, that sulfate-reducing bacteriadetected in up to 105 CFU/g amounts are capable of producing 15.6 mg/kg of hydrogen sulfide per day. With increasing depth of peloid deposition, the number of sulfate-reducing microorganisms decreases [47, 49, 145, 157, 161, 163, 166, 168, 175].

Marine bottom pelitic deposits are transformed into peloids due to biocolloidal processes involving NIASSMs because of a specific microflora vital activity [8, 148, 149]. Significant role in functioning of marine peloid ecosystems is played by heterotrophic microorganisms (bacteria, yeast, and fungi), which take part in organic matter cycle in ocean, in regeneration of biogenic elements and other substances [154, 176], and, as it was recently established, in biocolloidal mineral transformations [16, 17].

Microorganisms also play a significant role in processes of humus formation. Humic substances give peloids a dark color and they are a nutrition source for microorganisms [175, 177]. Moreover, they indirectly participate in processes of biocolloid transformation of minerals. It was established [177] that humic acids exert anti-inflammatory and astringent effects due to their nano- and microcolloid structure. In addition, the presence of bactericidal effects in

marine peloids and pelitic sediments provides the possibility of their use as natural antimycotic agents for fungal skin contamination caused by dermatophytes [168, 172, 178-182].

Thus, the presence of microorganisms and disperse NIASSMs in pelitic sediments is a prerequisite for peloidogenesis with therapeutic mud formation. However, such processes in terms of colloidal nanoscience have not yet been systematically and comprehensively investigated.

1.9. Mechanical deformations of dense rocks prior to formation of IASSMs, NIASSMs, pelitic sediments, and peloids (classic mechanics, physicochemical mechanics, and geomechanics)

Along with colloidal and biocolloidal effects [9-20], according to the classic mechanics laws of deformation processes earth materials [183], physicochemical mechanics and geomechanics [12, 20, 89], mechanical effects always play a leading part [9-15, 19, 20] in many processes which take part in the Earth's crust deformation (up to 30-35 km depth). Their thorough investigation with methods of classic mechanics showed [183-214] that rocks, including iron-aluminosilicate ones, are similar to stressed elastic and brittle materials, when their length is changed. The length change is directly proportional to the moderate stress. Upon ceasing the stress, an instant elastic length recovery up to the initial state happens. Beyond a certain stress limit, an unexpected brittle fracturing occurs, like a geological hammer impact [12]. In other cases, besides of brittle dispersion, in physicommechanical and physicochemical conditions there can also occur viscous flow of rocks [11-15, 215-223], or their creeping (sliding down in tectonic and technological conditions) [224-236].

There are known four mechanisms of rock deformation [12, 183-186]: fracturing, [237-263], frictional sliding (creep) [264-285], plastic deformation [271, 274], and recrystallization [282-285] which occurs with grain growth. The effect of water is reviewed in [286-291], of multiphase deformation in [292-299], and chemical effects in [300-305]. Cracks formed while fracturing have different length and thickness. Their length range can be from few grain lengths up to kilometers, and thickness varies from nanometers (10-100 nm) [20, 89] up to micro- and macrocracks. Frictional sliding is very close to fracturing process and is usual for layered rocks. The rock plastic flow is possible in special conditions, and at increased temperatures (400-650 °C at 15-35 km depth), the recrystallization and initial grain coalescence or crystallization of new phases take place [12-15].

There are three types of rock deformational behavior: brittle, intermediate and fluidic. The plastic flow (Figs 1.4 and 1.5) is the most attractive for developing

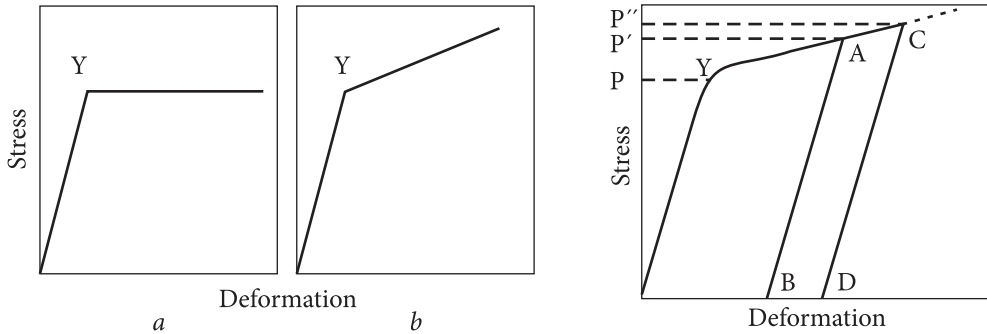


Fig. 1.4. Deformation diagrams for ideal elastoplastic materials: *a* — without deformational strengthening; *b* — with deformational strengthening. Y — flow limit

Fig. 1.5. Curves for loading and unloading of fluid material: P — initial flow limit; P' — increased flow limit after unloading in point A; P'' — flow limit after unloading in point C

rheological laws of deformation processes, it has been studied quite successfully not only by means of mechanics of the Earth material deformation processes [12, 183-214], but also by physicochemical mechanics and geomechanics (PCM and PCGM) [20]. PCM and PCGM usually study colloid-chemical and rheological laws of deformational processes in rocks and disperse solid-like IASSMs, NIASSMs, pelitic sediments and peloids [16, 17, 20].

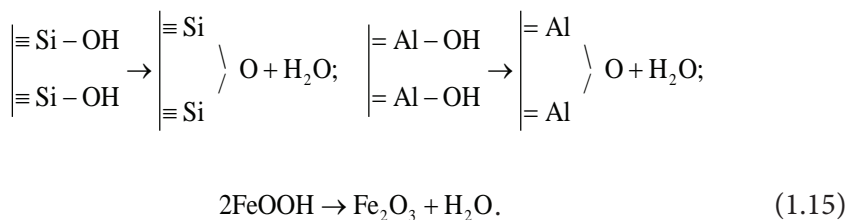
The curves in Figs 1.4 and 1.5 show that the transition process from elastic to plastic state under the influence of increased stress P depends on specific physical conditions. Thus, tests showed that the rocks became fluidic, in first place, under the influence of just a pressure. But the word 'fluidic' here is not a synonym of 'plastic' in a physical meaning. In addition, some rocks flow are accompanied by microscopic fracturing and shifting along with simultaneous friction. At that, it was found recently that such fracturing occurs at the nanolevel and helps a polymineral structure to acquire new physicochemical properties characteristic for ultracolloidal systems [16, 17]. The plastic flow is considered to start near the flow limit (point Y in Figs 1.4 and 1.5). To keep such a process, the stress needs to grow continuously in a sample, that is to be testified by the angle of the third diagram segment in Fig. 1.5. For example, if stress ceases in point A, an elastic aftereffect, i.e. decreasing of deformation value on the AB line can be seen. However, if stress is applied again, plastic deformation starts again, but at higher stresses than for point A. The same situation takes place with unloading stress in point C. This way, deformed sample becomes harder than it was before deformation. Such an effect is connected with deformational strengthening. But in most rocks, the pressures required for plastic flow exceed pressures usual for the Earth's crust. The same concerns additional pressures needed for deformation of rocks. However, in

many cases, such and even faster deformational processes run in the Earth's crust. Developments in physicochemical geomechanics remove mentioned contradictions and explain deformations of earth materials by the influence of water, sometimes even by its traces [12, 20]. The mechanism of this phenomena consists in occurring hydrational processes on the nanocapillary level, and in colloid-chemical and nanochemical transformations in nano- and micropores of rocks [16, 17, 89]. However, the mechanisms of these processes have not yet well developed, so further investigations and considerations are required.

The same concerns nanochemical processes with the influence on elastic properties of rocks. There are no resumptive ideas about contact interactions in nanostructured rocks [237-239] of the NIASSM type and other solid-like concentrated sediments [240-265].

In addition to mentioned physical phenomena, huge influence on rock deformational processes is exerted by diffusion and temperature, which reaches 400-650 °C at 15-35 km in the Earth's crust depth [11-15, 266-285]. According to the results of many experiments, in almost all crystalline materials, no matter what pressure is, the temperature increasing leads to lowering flow limit which interfere crack formation. In materials where chemical reactions proceed at increased temperatures, the influence of temperature on chemical properties under the concurrent stress can be different [12, 286-291]. Thus, according to such concepts for natural serpentinite (magnesium silicate with admixtures of iron oxides), the fluidity increases and deformational strengthening — decreases. At higher temperatures, there is a gradual transition into the brittle state. At above 650 °C, the typical brittle state fracturing occurs by a single crack. That is explained by formation of forsterite and talc from serpentinite [12].

However, this explanation doesnot describe the mechanism of processes at temperatures in the 500-650 °C range. Formed changes are connected mostly not with chemical reactions of silicate phases formation, but with known chemical dehydration reactions [19, 20]. Majority of rocks have a liquid aqueous phase which fills pores or wraps rock grains. In the case the rock is dry, the process of mechanochemical dispersion and transformation of rocks proceeds due to the dehydration reactions at increased temperatures, for example, like the following:



That is why, the behavior features of iron-aluminosilicate and silicate rocks are related to the presence of adsorptive or chemically bonded aqueous phase [20, 268-291], actively released from silicates just in the temperature interval of 500-650 °C, i.e. at the 15-35 km depth, owing to reaction (1.15) of structural dehydration [12, 20].

Such water remains in rock samples and covers mineral grains in the form of nano- and microfilms or locates in microcracks and capillaries. Released water while dehydration process actively affects deformation processes of rocks, changing their mechanical properties. However, hydration water influences on minerals not only physically, but also by its participation in chemical transformation processes. Here, chemical processes of colloid-chemical, adsorption, and ion-exchanging interactions (see Section 1.6) between solid and liquid phases proceed with the formation of new minerals. It's evident that the new chemically formed NIASSMs have new mechanical properties as well. A change in rock sample strength in such conditions can occur in two ways: with dissolution of highly stressed grain parts and simultaneous transportation of the dissolved phase into other less stressed grain regions (physical way) [292-299] or with new phases formation due to nanochemical reactions [300-305]. These phases are more stable in such metamorphic conditions, and they change mechanical properties of rocks. With quartz as an example, it was shown [12, 294, 297] that a presence of water significantly changes mechanical properties of the crystals. In its absence, quartz crystals retain their almost ideal elasticity and brittleness. But, in the presence of water with a certain temperature and pressure ratio, the quartz and other silicates lose elasticity and fluidity. It can be explained by the outcome of chemical hydrolysis of $\equiv\text{Si}-\text{O}-\text{Si}\equiv$ bonds, which border with migrating in the structure aqueous dislocations. This flow mechanism is considered to be the most important in the rock transformation and metamorphism [20].

There are other less important mechanisms affecting strength of rocks, which have not chemical, but physical, physicochemical or colloid-chemical nature [12, 20]. They are conditioned by the appearance of aqueous intergranular liquid phase itself. In addition, if the rock penetrability is quite high, then the pressure in a porous liquid is equal to hydrostatic pressure. However, according to the geological investigations [9-15, 25, 26], the pressure of porous liquid even in relatively low Earth's crust depth considerably overrides the equilibrium pressure:

$$P_{\text{liq}} > \rho_w gh, \quad (1.16)$$

where P_{liq} is the pressure of porous liquid; ρ_w is the water density; h is the water column height.

It can verge towards the lithostatic pressure:

$$P_{\text{liq}} = P_1 = \rho_r gh, \quad (1.17)$$

where P_1 is the lithostatic pressure, ρ_r is the rock density.

Factors like dehydration reactions, partial thermal sintering on a low Earth's crust layer, metamorphism, action of some rock layers as semipermeable membranes, and tectonic forces locally or regionally increase the pressure of porous liquids. Herein the pressure between solid grains does not conform to the lithostatic pressure, but it is lower by a value that depends on the pore pressure and geometrical aggregate features including not well investigated yet nanostructural effects.

If the lithostatic pressure is equal to P_1 , porous pressure to P_p , then the effective pressure will equal:

$$P_e = P_1 - \eta P_p, \quad (1.18)$$

where η is a coefficient which depends on the grain size and shape, penetrability, liquid viscosity and ranges between zero and one. Most researchers suggest that $\eta \rightarrow 1$.

Mechanical investigations have shown [12] that a chipping phenomenon occurs here. Increasing porous pressure can result in decreasing of effective pressure between grains lower than the hydrostatic pressure, and the layer frictional shear resistance decreases as well. If the porous pressure is high enough, then instead of fracturing of rock grains, an intergranular friction occurs. Thus, formation of chips and probability of bursting brittle dislocations are eased.

Natural bursting surfaces in rocks in general are classified as cracks (rupture without dislocations). Experimental data testify that such cracks are formed during brittle fracturing. Positively, the connection between the initial position of rupture surface and the stress state before this rupture has to exist. Thus, this process of crack formation is of the sheer brittle fracturing type. It can be easily imagined that crack formation is possible in case of normal stretching stress on the surface that is perpendicular to the stretching axis, exceeds the P_t value (material stretching strength limit). However, it is hard to imagine that squeezed rock is simultaneously stretching and how the cracks are formed here. Another contradiction to the theory arises while considering possible P_t values. It is known, that $P_t \approx E/10$, where E is the Young modulus. Experiments testify to disagreement of found P_t values to theoretically calculated ones. Thus, for example, most monolith rocks have E of about 1 Mbar, where as the theoretical value of P_t equals 100 kbar. However, practical results show that P_t does not exceed 1 kbar [12].

This disagreement is removed by the Griffith brittle fracturing theory, which appeared above 150 years ago and today is being developed in the laws of modern physicochemical mechanics and geomechanics [20]. According to the theory, a solid rock body is considered to be a monolith material not any more. Experiments showed that rocks have fine cracks, including nanosized ones, and heterogeneities, which influence the stress distribution. The found defects are located on the grain boundaries and in grain depth in the form of tiny cracks and gaps, usu-

ally of nanometer sizes [20]. They are slightly open during plastic flow. Most of them are irrevocably closed at increased stress, and some of them remains open. Such pores are not held by anything from inside due to the lack of pore liquid. That is why the stress concentrates in zones close to them.

Such regulations compile the theory of brittle fracturing of solid body rocks, which considers the presence of microscopic structural defects, and is used for development of logically concerned ideas on formation of cracks in rocks with their transition into ground, pelitic sediments and peloids after complex fracturing processes. According to the Griffith theory, the solid body contains developed structural defects of mechanically weakened areas due to huge amount of fine elliptical cracks. When the stretching forces are applied to such a body, the local increasing stresses occur around the elliptical cracks. On the basis of the data about such crack growth conditions, a mathematical model has been designed which does not contradict the found real low values of bursting stresses. Here, the velocity of crack propagation v_c satisfies the expression:

$$v_c = kv \left(1 - \frac{C_0}{C} \right)^{1/2}, \quad (1.19)$$

where v is the velocity of sound propagation in the material; C_0 is the size (half the length) of the crack needed for its spontaneous propagation; C — is half the crack length at any stage of the tearing process; k is a dimensionless coefficient.

This expression shows that crack propagates with acceleration. Crack development velocity accelerates significantly when the crack reaches its maximum sizes. Coefficient $k < 1$, so the crack propagation velocity does not exceed the sound velocity [12].

Every real material or iron-aluminosilicate rock contains cracks and gaps of various sizes, forms, and orientations in volume. Even under simple compression in such conditions stretching stresses appear at the ends of some cracks. This conclusion pulls off contradictions in the theoretical ideas of Griffith's predecessors which were discussed earlier. Cracks with stretching (induced) stresses grow gradually. There was proved that they grow through curved surfaces while compressing until they become parallel to the compressing axis. Then their growth stops. If a sufficient number of cracks of that direction have formed, they can unite in some places forming one large tearing surface, which can be developed, crossing the whole body at long distances. Real similar cracks investigated in natural conditions attained hundreds of kilometers, and their formation rate reached up to half the acoustic velocity, which, as known, equals 600-800 m/s for dense IASSM minerals.

Few important factors should be considered among the features of tearing cracks formation. Most rocks are stronger in compressing than in stretching. Hence, according to the above mentioned mechanisms, stresses induced in com-

pressing have to be lower than in stretching. So, typical tearing cracks formed in compressing are formed under the induced stretching forces localized around the structural defects and initial cracks. Most possible that tearing cracks are formed in some solely part of sample or rock in a zone of few initial cracks growth or other structural defects. A big crack formed at that develops further with high velocity, forming a surface which approaches a flat surface at the macrolevel. However, such a surface looks ribbed and groovy at the micro- and nanolevel because of the huge number of microdefects in the rock structure. Thus, the big crack advances from defect to defect chaotically, according to the defect location. At that, a widespread surface type called a fleecy structure is formed.

From the viewpoint of classical mechanics and geomechanics, the term “crack” or “tearing crack” is used for characterization of various surfaces, whose formation occurs without visible traces of sliding or two-dimensional shifting. This feature and comparative smoothness of macrosurfaces, made many researchers conclude that the process under consideration is a process of structure embrittlement. Since such a process takes place not only at the macrolevel, but also at the micro- and nanolevels, then its final result is rock dispersion. Lately, such a mechanism has been proved theoretically and also confirmed experimentally via using methods of physicochemical geomechanics [20, 88].

However, it can be shown that accumulated knowledge of geological and colloid sciences, even before development of ideas of physicochemical geomechanics, allows making, like in the mentioned above cases, conclusions about rock dispersion under the compressing forces. But such conclusions are not possible by using only the ideas of geological sciences, without the advances of researchers of colloid-chemical processes in rocks using model systems of the NIASSM type [16, 17]. Indeed, to explain the laws of tearing crack development, there have been used a number of theoretical geological mechanisms, but none of them has become completely acceptable. In the opinion of some geologists, tearing cracks are formed in the course of rock formation. However, this opinion has its limitations as well. Such a process is theoretically possible for a layered stratum, where some cracks can be positioned perpendicularly to the stratum layers, formed during lithification and stratum compressing thickening. It is also theoretically possible for columnar structures in lava flows. It stops during lava cooling, where stretching forces appear. However, this theory cannot explain the formation of most cracks in metamorphic rocks, as they are formed only after the formation of folded and schistose structures. According to most geologists, tearing cracks are fatigue cracks formed under the influence of continuous cyclic Earth's crust stresses.

The most known theoretical idea is that tearing cracks are brittle cracks formed due to the stresses developed in rocks in the conditions of their elevation

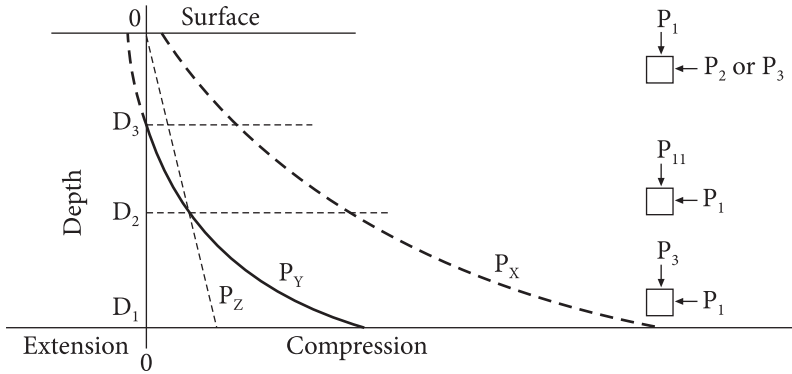


Fig. 1.6. Change in general stresses during rock elevation

from the Earth's crust depth. The elevation is followed under pressure of vertical tectonic forces by rising and erosion of rocks. As a result of that, a brittle dispersion of eroding solid material, generally of iron-aluminosilicate one, with the formation of NIASSMs on surface having polymineral nano- and microstructure of separate grains or their aggregates. During the elevation of some rock blocks from the Earth's crust depth, they can be conducted to side expansion, which can be estimated via a pure geometrical way.

Thus, the expansion of material with the horizontal size l in depth can be considered as stretching deformation $\Delta l/l$, where Δl is the gain of chosen horizontal size. If the body is elastic, then an extension is formed during its expansion $P_t = E \Delta l/l$. Further consideration of rock block in depth, where residual tectonic stresses remain, shows that they are horizontal compressing P_x , which works in the x direction of the rectangular coordinate system with the vertical axis P_z . This stress is added to the lithostatic stress $P_z = \rho g z$. Hence, three general stresses in the directions of coordinate axes can obey the following expressions:

$$P_x = p_1 = \rho g z \left(\frac{\nu}{1 - \nu} \right) + p \sigma'_x; \quad P_y = p_2 = \rho g z \left(\frac{\nu}{1 - \nu} \right) + \nu p x; \quad P_z = p_3 = \rho g z,$$

where ν is the Poisson coefficient.

During increasing stresses P_x , P_y and P_z change according to the variations of appropriate curves in Fig 1.6. As we can see, all stresses are compressing in depth D_1 , and P_1 and P_2 are horizontal.

There was assumed that disparity of stresses in depth D_1 are insufficient for shear defects formation. In the intermediate depth D_2 , the P_2 stress become vertical. And in more high layers, the disparity of stresses P_1 and P_3 can become suffi-

cient for formation of shear cracks in the conditions when most stresses are relaxed. At higher layer levels, for example at D_3 , the P_y stress can become stretching and lead to development of vertical tearing cracks.

The described order of stretching-compressing changes is hypothetical from different viewpoints. The other factors are important as well. For example, the influence of porous liquid at high pressures [20]. But such factors were investigated by geological science only superficially [12]. Results of colloid-chemical investigations testify that in the conditions of simultaneous action of liquid and cyclic pressure on rocks, the process of their brittle dispersion occurs only, not a mechanism of elastic-plastic fracturing [306], which confirms geological theories of compulsory preliminary formation of tearing cracks. Later these ideas were developed in the conditions of laws studied by such a borderline science like physicochemical geomechanics [20]. At the same time, the colloid-chemical and nanochemical laws of mechanical influence on rocks, and iron-aluminosilicates among them, were actively studied in the last decade [8, 16, 17, 23, 53, 88, 89, 105-108, 216, 217], and their generalization can give a big impulse to development of physicochemical geomechanics.

CHAPTER **2**

**NANOSTRUCTURAL
PHENOMENA IN IASSMs
OF THE EARTH'S CRUST**

2.1. Nanostructural effects in iron-aluminosilicate materials of the Earth's crust and surface

The solution of important problems in modern sciences concerning the Earth's crust rocks and their surface properties include crucial investigations of complex nanostructural effects. These effects and corresponding processes correlate with geomechanical, biocolloid, and nanochemical factors. But they have not yet considered systematically by means of colloid and biocolloid nanoscience, and physicochemical geomechanics [16, 20 55, 89, 183, 307, 308]. It should be also mentioned that about 90% of the Earth's crust rocks belong to fine-grained polymineral disperse iron-aluminosilicate systems and materials (IASSMs), generally nanostructured, which are presented both by dense nano- and fine-grained and by fine-disperse amorphous rocks, iron oolitic and polymetallic ores, pelitic clay-containing and other sediments from aqueous, generally marine, basins and soils. Thus, investigation, in the assigned task bounds, of mentioned above widely used in science and practice materials, in particular investigation of poorly studied biocolloid and geomechanical deformations in IASSMs aided with microorganisms and nanostructures are actual. That is why these problems are considered in this book. Various methods of physical chemistry and rheology of high-concentrated viscous disperse systems are used here. The main attention is given to disclosure of mechanisms of nanostructural-nanochemical effects in IASSMs aided by biogeocenosis. Analysis of their influence on geomechanical stress phenomena that occur with mechanodisperse deformations in IASSMs of the Earth's surface is considered as well.

Analysis of nanostructural phenomena in IASSMs of Earth's surface accompanied by geomechanical, nanochemical, and biocolloidal processes

Geochemical and nanochemical processes. Advances of physicochemical mechanics as part of colloid chemistry recently made it possible to define geological and geochemical development branches in areas of mechani-

cal, microbiological and nanochemical phase contact interactions in natural and technogenic materials as physicochemical geomechanics (PCGM) of rocks and disperse materials [8, 89, 308, 310]. This independent branch of colloid science analyses of geological and geochemical structural and nanostructural factors. It generally establishes the influence of mechanical, physicochemical, colloid-chemical, biocolloidal and nanochemical processes in contact zones of nanoparticles or their aggregates on geomechanochemical properties of the Earth's crust solids at large.

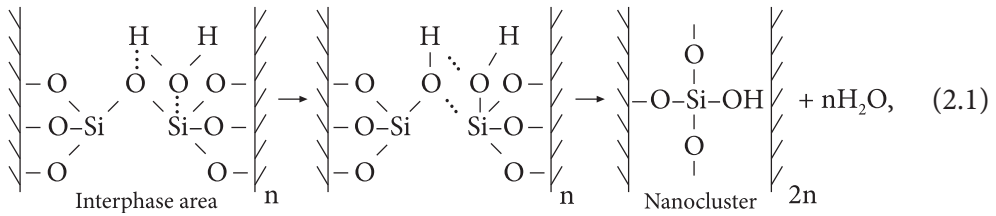
The development of fundamental investigations concerning water influence on geomechanochemical properties, dispersion, and disperse structure of rocks should be considered the most valuable achievement at times of PCGM formation [8, 89, 310-314]. The ideas about a special role of water in natural processes were formed ages ago, but its geological impact was concerned only in late XX century. It was studied from two viewpoints: chemical (geochemistry) and mechanical (rock mechanics) [308, 314]. Formality of such division is obvious. Mechanical properties were considered without physicochemical medium influence (i.e. nanochemical, colloid and biocolloid processes) until the end of the XXth century. That was due the fact that their integration into Earth science [20, 308] and integration of advances of other natural sciences occurred gradually. This was limited by development of fundamental basics of mentioned sciences, which are connected with geomechanical processes in the Earth's crust materials [89].

Since water is a usual component in dense and microdisperse rocks, which are generally in the polydisperse nano- and micrograin state, i.e. they are NIASSMs and since they are submitted to the common impact of mechanical stress and liquid medium, the water influence on such processes is by far essential. Besides, neither high solubility of rock-forming minerals, nor considerable amounts of liquid medium are obligatory for the appearance of mechanical effects occur in gas as a result of nanochemical and nanostructural processes while interaction of water with rock surfaces [314]. An obligatory condition here is the presence of a developed contact surface between nano- and micrograins of polymineral structure and a large rock contact surface connected to it [8, 89, 311-314]. The latter is formed by internal micro- and nanosized interphase boundaries of different mineral composition.

These principles substantially broaden a variety of geological and geochemical phenomena where water can play the role of an active component of dispersion processes, including many deformation and fracture processes of widespread in the Earth's crust IASSMs, which contain traces of water in grain-boundary layers. The effective water concentration, i.e., its thermodynamic activity, substantially depends on the quantity and chemical nature of dissolved components. It was shown [23, 88] that low quantity (0.05-0.1%) of alkali silicate nanoclusters dis-

solved in water can increase the dispersion water activity for rock materials of different nature, particularly for aluminosilicate and ironoxidesilicate rocks, by few orders of magnitude. It happens due to the action of mechanical external stresses and self-dispersion (internal stresses).

The breaking of hydrolytic siloxane bonds of silicate materials was considered as a general mechanism [23, 88, 315] of mechanochemical and nanochemical rock self-dispersion aided with water:



where /// — denotes the surface of nanoparticles; n — is the quantity of siloxane structures in interphase area of nanoparticles or nanoclusters.

The nanochemical reaction (2.1) accelerates gradually under the action of mechanical forces [23, 88]. That by-turn eases the development of fracturing nanocracks in silicate rock even with traces of water. Bond breaking frequency on the tip of a crack and its velocity (V) of enlargement correlate with the applied mechanical stress as follows [89]:

$$V = V_0 e^{-(U_0 - \gamma P)/RT}; \quad V_0 = \nu b, \quad (2.2)$$

where ν is the Debye frequency; γ is the active volume with included the over-stress factor $(c/b)^{1/2}$; c is the crack size; b is the crystal lattice parameter; U_0 is the process activation energy at $P = 0$.

Study of such rock fracturing mechanism in the presence of water and aqueous solutions is essential for geology and PCGM because it affects many dispersion processes of solids in zones of metamorphism and hypergenesis. It also influences physical chemistry and mechanochemistry of complex stress and tectonic phenomena, for example, sediment creeping in the conditions of earthquakes [183]. With a squeeze-loaded granodiorite as an example, it was experimentally shown [316] that its dispersion rate can increase by almost 10% within a month and nanocracks of initial 10-100 nm sizes can develop to cracks sizing from micrometer to part of millimeter with a 200 μm maximum.

In the beginning, the fracturing mechanism of hydrolytic siloxane bonds in silicate materials was considered as more specific for rocks containing quartz generally. But then the reaction (2.1) and other nanochemical water-aided reactions were shown to be essential for chemical processes in rocks and especially in

IASSMs and NIASSMs [23, 88]. Thus, one of the general mechanisms of rock fracturing aided with water and aqueous solutions is the mechanism of liquid phase penetration through nanoboundaries of grains. Such a process is considered as one of the most important dispersion ways for the majority of rocks based on the IASSMs and other minerals [315]. Besides, the energy gain in the case of grain boundary replacement by a liquid nanolayer was known to be the reason that make self-penetration of liquid through almost unporous dense rocks possible in processes of their metamorphism or weathering. Thanks to the development of nanochemistry [317] and understanding the role of nanoparticles for contact interactions in disperse polymineral rocks, this almost correct (from the thermodynamic point of view) conclusion was later improved [23, 88]. It was shown that for the start of almost any mechanism of mechanical rock fracturing, the chemical interaction of water with silicate rocks at the nanolevel is required, in particular like reaction (2.1). So, the rock mechanical dispersion mechanism starts from the above mentioned hydrolytic breaking of siloxane bonds and formation of at least nanocracks, according to reaction (2.2). Then, according to the Gibbs-Smith condition [314, 315], the grain boundaries between A and B crystals are replaced by liquid C:

$$\sigma_{AB} > \sigma_{AC} + \sigma_{BC}. \quad (2.3)$$

Here the energy of grain boundary appears to be higher than the sum of surface energies on the boundaries between crystals and liquid phase (water or aqueous solutions in our case). As a result, the process of surface reconstruction occurs on adjacent surfaces according to the chemical reactions described in general in [89, 306]. At the same time, growing fringes abut against neighbor grains and break the material along the grain boundaries under the crystallization pressure. The crack widens at the grain boundary by a step-wise nanochemical mechanism [23, 318]. When the average number of penetrated boundaries exceeds 1/3, the process runs continuously and obeys the linear-parabolic equation:

$$AL + BL = t, \quad (2.4)$$

where t is the time for the liquid front to move from the liquid source at distance L into polycrystalline rock [313, 314].

The linear part of equation (2.4) is defined by crystallization pressure P_{cr} growth kinetics:

$$A = \delta RT / D_{SL} C_0 P_{cr} \omega, \quad (2.5)$$

where δ is the average grain size; R is the gas constant; T is the temperature; D_{SL} is the diffusion coefficient of grain matter in liquid; C_0 is the mole concentration of liquid; ω is the molar volume.

The parabolic part of equation (2.4) is defined by limiting process of liquid viscous flow in a gap between rock grains, where the gap size is 10-100 nm usually.

The substitution of the Poiseuille equation for B value in equation (2.4) gives [315]:

$$B = 12\eta/\delta P_{cr}, \quad (2.6)$$

where η is the viscosity of liquid.

The value $1/B$ is considered as an effective (conditional) diffusion coefficient equal, by experimental estimations, to about 10^{-3} - 10^{-4} cm²/s. These values are many orders larger than diffusion coefficient in solids, because of the fact that a viscous liquid flow through nanocracks obeys the laws of physicochemical geomechanics and nanochemistry [20, 317].

The established phenomenon belongs to the area of interest of physicochemical mechanics and geomechanics, but in geological and technological aspects it proved to be valuable not only for the development of geomechanics, but also for the eco-security of production processes of oil, natural and shale gas. Indeed, the infiltration of water (injected during oil product extraction) from the depth of few kilometers is possible even through dense rocks. Thus, authors [23] showed that such a process can run faster by few orders of magnitude in porous disperse materials than in dense rocks.

In addition to considered water-aided processes of IASSMs fracturing and processes of liquid phase penetration through grain nanoboundaries, the quasi-spontaneous (nanochemical) dispersion of dense rocks under the action of water and aqueous solutions [315, 318] is possible. And the much more intensive natural and technogenic dispersion of porous materials in various surface-active mediums is possible as well [23, 88, 306]. This mechanism was analyzed from the viewpoint of physicochemical geomechanics, nanochemical dispersion, and subsequent nanostructural phenomena. It was shown that the dispersion process in polydisperse porous iron-aluminosilicate and aluminosilicate rocks can be completed within few hours in the case of external mechanical load application and alkaline pH of aqueous solution, so that it can be accelerated by orders of magnitude. The kinetics of such a dispersion process follows the equation [23]:

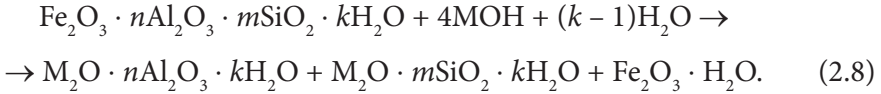
$$(S - S_0)^2 = kt, \quad (2.7)$$

where S_0 is the initial specific surface of porous body.

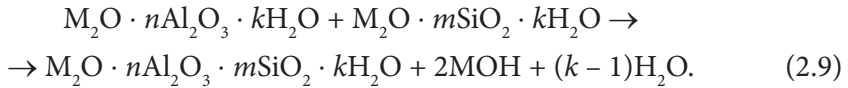
The processes by reactions (2.3)-(2.7) are of physical nature. At the same time, when the water influence on rock dispersion by equation (2.4) is interpreted, the crystallization pressure in nanopores is taken into account as well. This can be realized only with the help of nanochemical reactions of surface mineral nanophase formation. As mentioned above, the reactions in a general form are given in papers [89, 306]. That is why a more specific mechanism in comparison

with the described there is considered here. It takes into account the rising crystallization pressure in nanopores due to nanochemical reactions of formation of mineral nanophases of iron-aluminosilicates, aluminosilicates, and silicates, which results in wedging of nanocracks.

Thus, along with reaction (2.1), other nanochemical processes according to modified reactions (2.8) and (2.9) can occur in nanocracks about 10–100 nm:

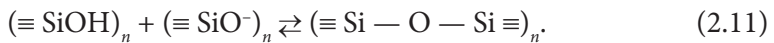
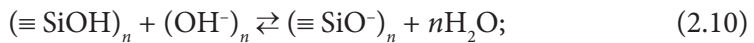


The products of reaction (2.8) react by the following scheme:



Then they take part in nanostructural contact phenomena along with $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$.

The products formed by reactions (2.8) and (2.9) have a bigger volume compared to the initial product of reaction (2.8). Therefore, obtained crystallization pressure tears (chemically wedges) the crack, and concurrent mechanical load help that to happen. The water, which enters the widened up to micrometers crack mouth, hydrolytically disintegrates the product of reaction (2.9) releasing an alkali, which diffuses into the new-formed secondary nanocrack in the form of solution. Thus, the self-dispersion process is proceeded and accelerated, according to the conclusions in [315, 318]. The process runs in the same way as in the case of liquid phase penetration through grain nanoboundaries, but faster by many orders of magnitude and lasts not years, but hours. It is also promoted by other nanochemical interactions in silicate structures, for example quartz-like ones, which complement interactions (2.1), (2.8), and (2.9). It is characterized by the following reactions [88]:



These reactions along with $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ (reaction (2.8)) give a beginning for a nanostructural transformation phenomena of forming fine dispersions as a result of coagulation-condensation processes in the contact zones of microparticles. The mechanism of this process is described below.

Hence, nanochemical reaction (2.11) is a reaction of polymerization. It leads to formation of polysilicate nanoclusters on the crack surface or on internal surface of dispersion microparticles. Released hydroxyl ions participate in reactions (2.8) or (2.10), or in formation of new phases along with FeOH . So,

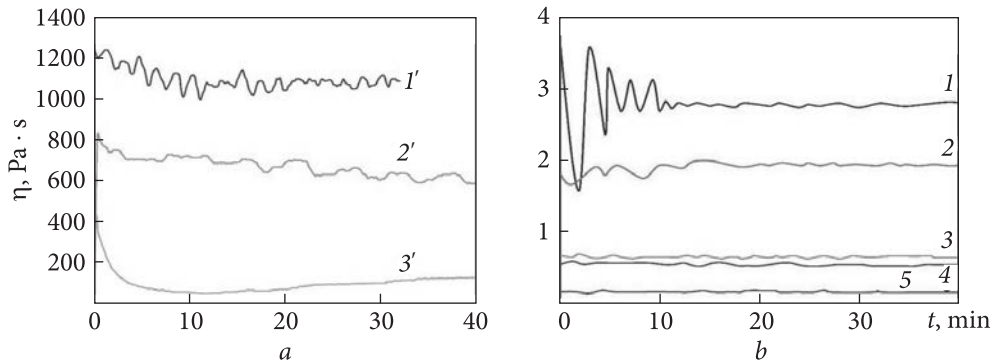
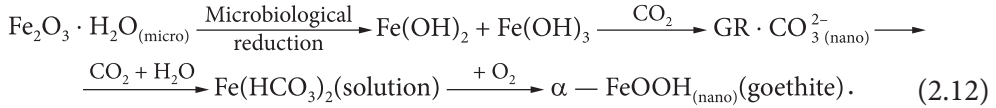


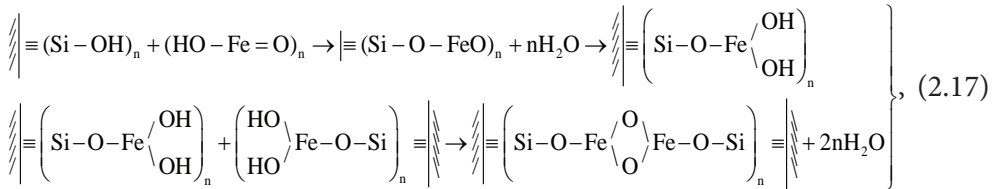
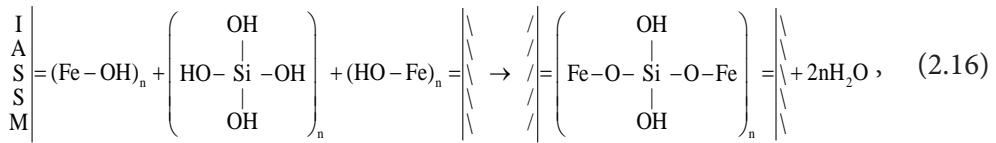
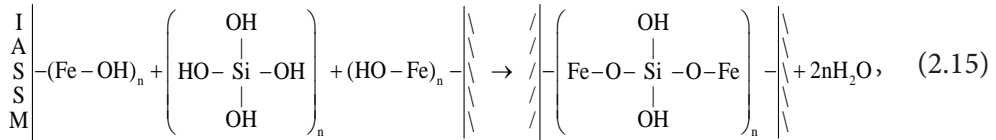
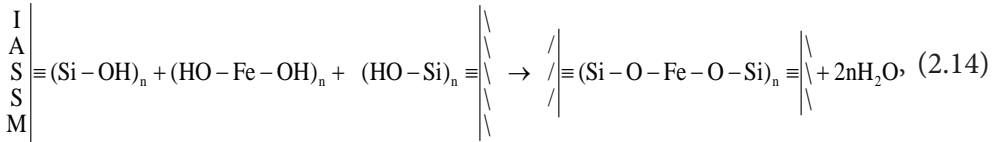
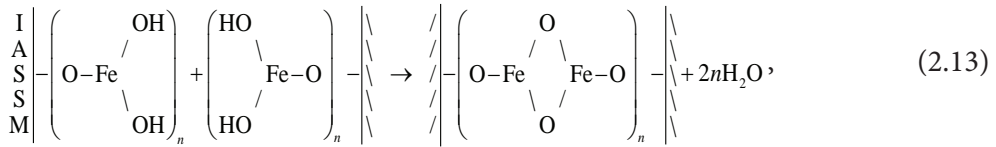
Fig. 2.1. Kinetics of dispersion flow (*a*) at shear rate $2,453 \text{ s}^{-1}$: (1') polyacrylic gel at $W_{\text{H}_2\text{O}} = 90\%$; (2') polyacrylic gel with 10% of quarts sand addition ($d < 63 \mu$) at $W_{\text{H}_2\text{O}} = 88\%$; (3') quarts sand at $W_{\text{H}_2\text{O}} = 26\%$; *b* — iron-aluminosilicate rock ($W_{\text{H}_2\text{O}} = 50\%$) with occurring of concurrent reactions (2.8) and (2.9) at shear rate (s^{-1}): 1 — 1.0, 2 — 1.8, 3 — 3.0, 4 — 27.0, 5 — 81.0

the reactions (2.10) and (2.11) complement not only the reaction (2.1), but they are also mediating in transformation processes of IASSMs and NIASSMs (2.8) and (2.9). And the colloid-chemical interphase interactions (which occur at the nanolevel on solid surface of formed silicate rock) are followed with nanostructural phenomena and nanochemical transformations in contact zones of particles, and further formation of new coagulation-condensation structures. The process runs gradually [318], as it was shown on the iron-aluminosilicate model system with an alkaline component [319]. The results presented in Fig. 2.1, *a* and 2.1, *b* testify that the gradual process is the most intensive in the conditions of low-mobility of porous disperse rock, and fades out with increasing plastic flow rate. This proves the partial breaking of contacts in interphase zones, further reformatting of the system and beginning of its restructuring. The mechanism of this process needs additional investigations and further consideration.

Biocolloidal processes. The interphase nanochemical interactions on the contact surface of silicate and aluminosilicate minerals comply with general nanochemical processes described by (2.1), (2.8)-(2.11) equations. But they have more complex additional features for iron-aluminosilicate minerals, which are part of ore materials and IASSMs [17, 306, 220]. There are models (2.12)-(2.17) proposed for interphase nanochemical interactions in iron-aluminosilicate minerals, which compose iron oxide-silicate (ferroclay) ore biocolloid materials. They allow to estimate more elaborately the nanocluster biocolloid mechanisms of such interphase interactions. Thus, the ferrite yielded by reactions (2.8) and (2.9) reacts with the help of microorganisms by the known scheme:



Then the following phase interactions in contact zones of microparticles occur:



where (...) is a nanocluster.

The models (2.13)-(2.17) demonstrate that interphase biocolloid interactions are accompanied by formation of coagulation-condensation bonds between surfaces of similar or different disperse phases, which leads to compaction of previously dispersed iron-aluminosilicate materials. Such mechanisms of contact interactions prove that interphase interactions with Fe^{3+} are stronger than that with Fe^{2+} . It is fair as the microbiological oxidation of Fe^{2+} into Fe^{3+} is possible for Fe^{2+} , which is typical for models (2.14) and (2.15). This leads to breaking of interphase $-\text{O}-\text{Fe}-\text{O}-$ bonds with the formation of goethite according to the model (2.12). Thus, the biocolloid mechanism differs from the inorganic one (2.11) described earlier for formation of intermediate Green Rust (GR).

According to analysis of the multistage process (2.17) of goethite participation in contact interactions of disperse phases by inorganic and biocolloidal mechanisms, it is close by the reaction rate (Fig. 2.1) to single-step interactions described by model schemes (2.13) and (2.16), and in some cases, it is even more rapid.

Besides of considered mechanisms of the Rebinder phenomenon realization in the Earth's crust, the plastification (creeping) of ironsilicate rocks in some conditions (low shear rates) is possible [314]. The creeping can proceed in two ways. First, the rate of creeping can be increased by few orders of magnitude under the action of surface-active substances. This is shown in equation (2.2) by an increase in the structural factor (γ). Second, if the Gibbs-Smith condition (2.3) is met, a specific and effective mechanism is possible. In the second case a mechanically loaded areas with the excess chemical potential dissolve according to equations (2.8)-(2.17). Then the latter, dissolved or chemically transformed into nanoclusters matter, precipitate on other loaded areas. Theoretical and experimental physical investigations of this process showed that the rate of creeping in the conditions of recrystallization is described by a modified equation [314, 315]:

$$v = D_{SL} \omega P C_0 \delta / RT d^2, \quad (2.18)$$

where d is the average grain size in the polycrystal.

The results allowed us to use the methods of physicochemical geomechanics and biocolloid chemistry in analysis of technological and ore-genic processes with rocks. The general aim of physicochemical geomechanics of ore genesis is to determine laws and mechanisms of successive changes of rock structure-mechanical properties in the conditions of complex polychronic ore-genic processes. It also depends on: the type of surface contact interactions on interphase boundary (phase interactions); chemical composition and structure of polymineral ore material; temperature and character of loaded state; the presence of microorganisms [8]. At that, the most interesting from the viewpoint of physicochemical geomechanics are numerous natural and technogenic IASSMs and NIASSMs. An essential role in them is played by surface physicochemical and chemical processes and interactions, which determine their lyophilic/lyophobic properties. Such processes and interactions accompanied by structural phenomena include rheological, nanochemical, mechanical, mechanochemical, microbiological, adsorption, contact adhesion-cohesion processes and interphase surface interactions. The development of this scientific branch has promoted in recent years a better understanding of ore genesis in solid, sedimentary, and porous rocks and disperse materials in particular. It also promoted the development of effective related technologies for transformation of dispersions, its processing and application in large-scale production processes, and also the

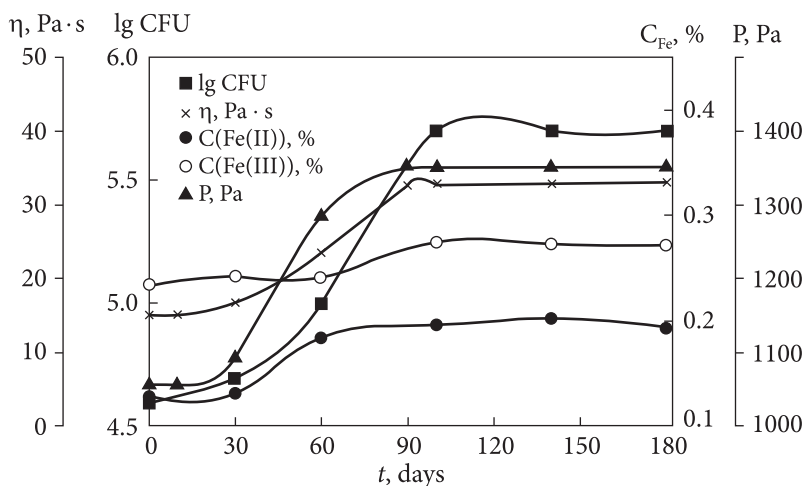


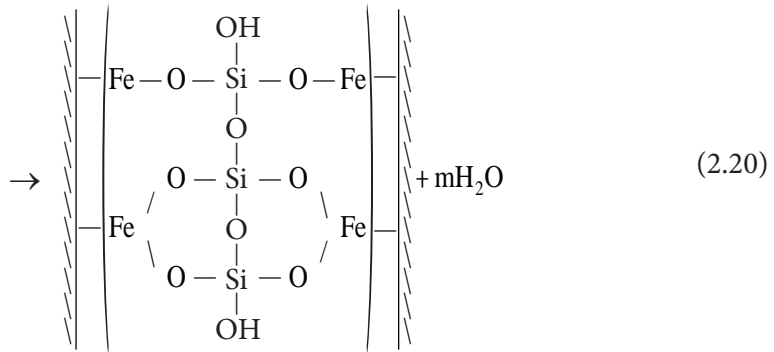
Fig. 2.2. Correlation of viscosity (η), shear stress (P), concentration (C , %) of Fe^{2+} ($C(\text{FeII})$) and Fe^{3+} ($C(\text{FeIII})$), and colony forming units ($\lg\text{CFU}$) with the exposure time for the Black Sea nanostructured pelagic sediments picked up from 1800 m depth with 46% moisture

Table 2.1. Physicochemical indexes of marine pelagic sediments, 46% moisture

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
Content of <250 μm particles, %	0.8	0.8	0.7	0.6	0.5
Content of nanoparticles, %	0.1	0.1	0.3	0.4	0.4
$\lg\text{CFU}$	4.6	4.6	4.7	5.1	5.7

development of ideas concerning structural mechanisms of stress phenomena (creeping, earthquakes, etc.).

The largest development in that direction has got investigations of biocolloid, microbiological and biochemical processes based on application of selective heterocoagulation [8, 17] of mineral matter with microorganisms. The same concerns the processes in ocean concretion recrystallization [312]. Onward development of these directions allowed estimating dependences of nanochemical, microbiological and physicochemical features of self-dispersion processes in dense, porous or disperserocks and in their derivatives (peloids and pelitic sediments) and their further structural compacting in specific conditions [16, 20, 17]. These processes, considered in further chapters, substantially depend, in the case of peloids and pelitic



It is evident that structures formed by schemes (2.19) and (2.20) bond the aggregates of IASSM, NIASSM, aluminosilicates, and silicate materials in water dispersions most strongly, which is clearly confirmed by increasing viscosity and shear stress.

Thus, biocolloidal interactions are activated, along with physicochemical and nanochemical processes in dispersions of iron-aluminosilicate sediments and peloids, under the action of surface-active substances (microorganism metabolites), which affect the production of nanodisperse structural organo-clay-carbonates. The latter enrich bottom peloids and pelitic sediments with organic substances, iron oxides, clays, and calcite [16], which results in transformation of derivative dense rocks into concentrated compositions of pasty watertight bottom sediments, generally in seas and oceans. These compositions are structured by nano- and microparticles of iron oxides, clays, carbonates, and organic substances. They form a strong coagulation-crystallization contact nanophase bonds due to realization of (2.12)-(2.17) and (2.19)-(2.20) schemes. The general scheme of rock transformations is presented in Fig. 2.3. Rheological behavior of forming pelitic sediments is considered below [306].

Analysis of nanostructural phenomena in IASSMs and NIASSMs related to rheological processes. According to the data of [306], clay minerals, especially montmorillonite as a component of bentonite clays, exert the largest influence on the properties of nanostructured IASSMs and NIASSMs [220]. They are self-dispersing partly up to nanoparticles in aqueous suspensions. Their behavior does not correlate with the dispersion water content in them (humidity) but exhibits a significant correlation with nanostructuring processes, which depend on the chemical structure and nanochemical properties of montmorillonite nanoparticles. Thus, according to [220], suspensions of calcium bentonite at 50% of water content show the so-called hyperanomalous viscosity change, but at 75% of water content this effect disappears. At the same time, after nanochemical processing of the clay with sodium bentonite formation, it appears again, but at 90% humidity. This effect is related to the increased number of smaller Na-montmorillonite nano-

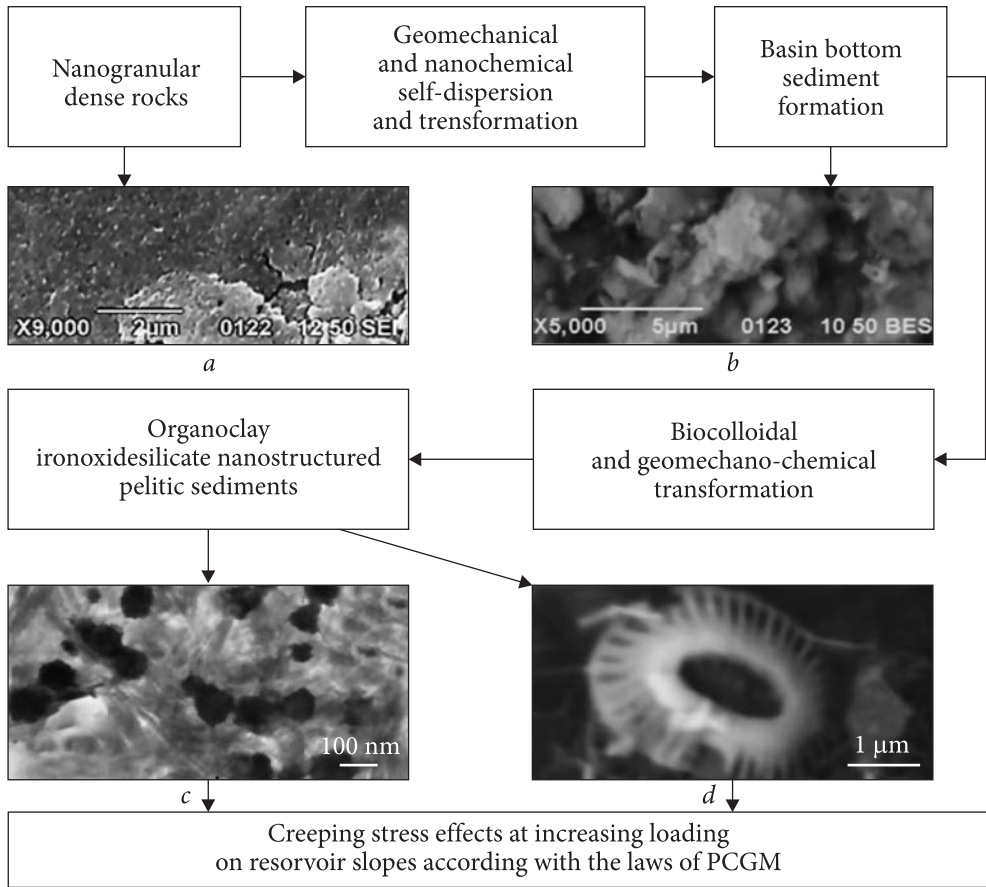
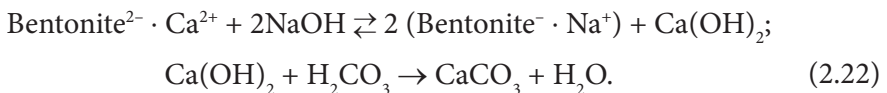
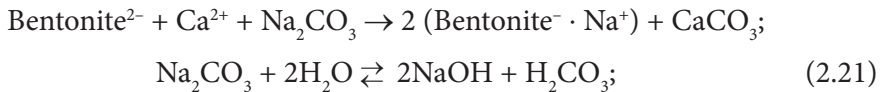
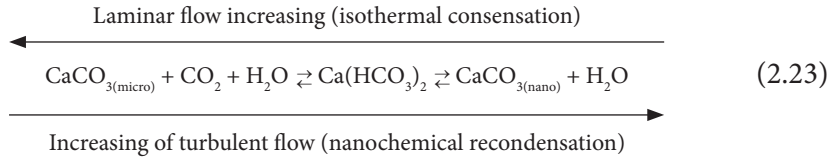


Fig. 2.3. General scheme of rock transformation: *a* — SEM images of nanogranular rocks; *b* — bottom sediments of crushed rocks; *c* — pelitic organoclay-ironoxide-silicate sediments and peloids; *d* — pelitic sediments with carbonate residue of *Foraminifera*

particles in the bentonite composition according to the following nanochemical process [17]:



Natural bentonites usually contain calcium. Therefore, another process of formation of CaCO_3 nanoparticles aided with CO_2 from air is possible, concurrently to formation of Na-montmorillonite nanoparticles [17]:



The direct reaction (2.23) of nanochemical recondensation takes place at high speeds of turbulent mixing of bentonite suspensions (high shear rate in a reoviscometer), where as the reverse reaction does at low mixing speeds (laminar flow) [17].

Thus, it should be noted that the nanostructuring processes in clay suspensions, nanochemical processes of formation of nanoparticles in them, including biocolloidal processes, and chemical structure of nanoparticles play a significant role in rheological behavior of suspensions.

Based on the above considerations and the loading and unloading curves for elastic-plastic materials in [306] (which, according to the authors [220], include suspensions of bentonite in the conditions of hyperanomalous viscosity), Fig. 13.11 in [306] can be presented like Fig. 2.4.

The curves (Fig. 2.4) show that the hyperanomaly of viscosity is usually characterized by curves 1 and 3, and the effect of ultraanomalous viscosity unknown before — by curves 1 and 2. Both effects were experimentally confirmed by the mass of rheograms for various types of clays, peloids and pelitic sediments presented in [17, 55, 89, 306], but with lack of interpretation. So, a tentative conclusion can be made from these data: the effect of viscosity hyperanomaly is more usual for less concentrated suspensions or at lower iron content in them [17]; the ultraanomalous viscosity effect is more usual for more concentrated suspensions or at lower shear rates if the other previously mentioned factors remain the same. Here with, the dispersion moisture (W) changes in such a way: $w_{1-3} > w_{1-2} > w_{1'-2'}$. Thus, Fig. 13.4 in [306] reveals that the $\eta = f(P)$ dependence for the Black Sea pelagic sediment suspension at 65% moisture shows hyperanomaly of viscosity in the interval of high shear rates ($P = 500\text{-}2300$ Pa), but at relatively low shear rates ($P = 50\text{-}500$ Pa) it shows ultraanomalous viscosity, i.e. corresponds to the transitional mode [306] (Fig. 13.4, *a*). At moisture above 77% (Fig. 13.4, *b*) [306], the suspension flow is characterized by hyperanomalous viscosity effect only. At the same time, the rheogram of NIASSMs shown in [17] testifies that hyperanomalous viscosity is typical for NIASSMs with high content of iron in the form of nanogoethite and at 46% humidity. At a lower moisture $W = 55\%$ (Fig. 13.5) [306], the flow of peloid suspension of the Black Sea type (Kuyalnik Estuary, 20 m depth) is characterized by the effect of viscosity ultraanomaly. Thus, the mentioned data and a large number of other data for various sediments, soils, and sands indicate a significant role of rheological effects in stress processes occurring in the Earth's crust. But these findings need more detailed analysis.

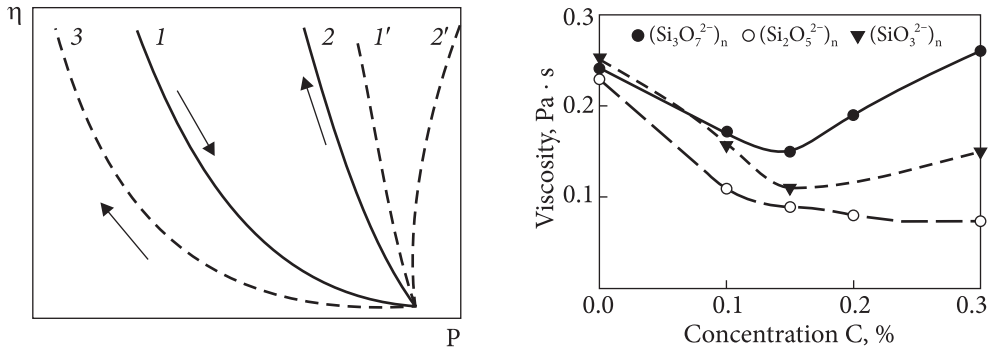


Fig. 2.4. Loading and unloading curves (1, 2), respectively, in the conditions of plastic flow of elastoplastic material [306]; unloading curve (3) in the conditions of viscous hyperanomalous effect [220]; (η — viscosity, P — shear stress)

Fig. 2.5. Influence of contact silicate nanocluster chemical structure on viscosity of 50% aqueous suspension of disperse iron-aluminosilicate clay rock in dependence from concentration (C) of anionic inorganic nanoclusters of various chemical composition

Established regularities for nanostructural phenomena in dense and disperse materials of the Earth's crust also made it possible to develop and implement a number of methods for aimed controlling the structure of IASSMs and NIASSMs. They are based on achievements of physicochemical geomechanics, biocolloid chemistry, and laws of nanochemical contact interphase interactions [306]. For example, the validity of methods for controlling the physicochemical properties of barrier structures, soils, and rocks [320] using various active mediums of natural and technogenic origin was explained with the help of ideas of colloid-chemical material science [8, 88, 23].

As an example, Fig. 2.5 shows investigation results for the influence of surface-active in organic nanostructured medium on rheological properties of disperse clay rock treated with microorganisms for formation of organic surfactants. The developed technology was used to decrease mineralized water filtration through the basin bottom. These results are similar to other analogous data [306, 320] and allow tentative consideration of denudation processes of marine and ocean land slopes involved by biogeo- and nanochanges in elastoplastic properties of underwater sediments on slopes, and give a possibility to prevent the stress phenomena in them [8, 16, 20, 23, 88, 89, 106, 108, 306-308, 310-316, 318, 320]. These results well correlate with recent conclusions in [321, 322]. Some of those data are presented in Fig. 2.6 with addition of denudation processes on land slopes, which occur up to nowadays under the action of increasing mass of upper layers of elastoplastic weathering rock material, comprising generally disperse quartz and iron-aluminosilicates. They creep when the pressure reaches $P > P_{\text{critical}}$

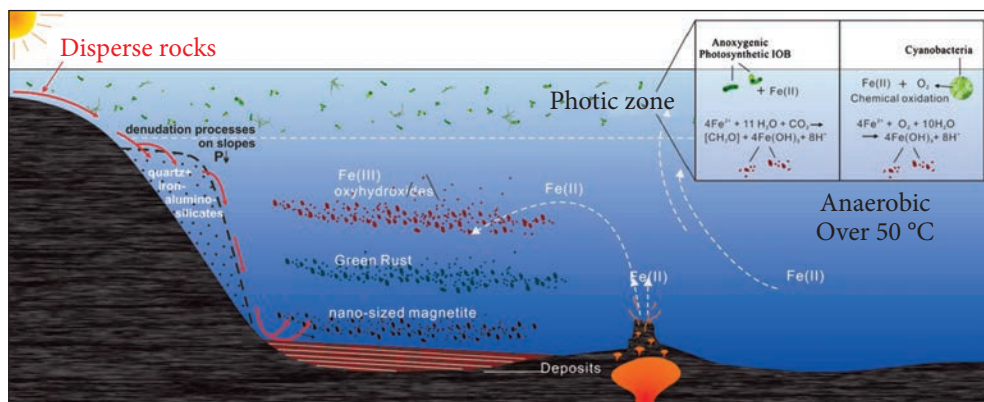


Fig. 2.6. Transformational model of iron compounds in the Archean ocean [321, 322] and up to our days continuing denudation processes on its land slopes due to creeping of sediments under the action of pressure force (P) of accumulating masses of quartz and iron-aluminosilicates

and provoke stress phenomena by the laws of physicochemical geomechanics according to earlier described mechanisms in [306].

To sum up conclusions of studies of nanostructural phenomena in iron-aluminosilicate materials of the Earth's crust, including stress phenomena, and additional experimental data obtained for rocks and disperse IASSMs concerning the influence of nanochemical and microbiological processes on those phenomena, the science-based capability to provide rather accurate description of many nanochemical and rheological mechanisms of the majority of physicochemical stress and catastrophic processes occurring in the Earth's crust and in technogenic conditions should be emphasized.

Conclusions. The above results allowed us to consider kinetics, thermodynamic basics, and mechanisms of rock transformations including their self-dispersion aided with nanochemical and microbiological processes forming new disperse structures with thermodynamically stable mineral phases. The ideas of mechanisms of rock creeping due to recrystallization of mechanically loaded areas, and nanochemical transportation of liquid phase substances through grain boundaries into other loaded surface are as have been developed. The basic principles of nanochemical and physicochemical regulation of disperse porous sediment structural properties in natural and technogenic conditions, which can be used for preventing stress and catastrophic phenomena have been established. On ward ways for the solution of mentioned fundamental problems were determined with application of the revealed laws in geological sciences, and in biocolloid and colloid chemistry for the development of up-to-date technological processes. These processes are crucial for advancement of their applications in

environmental protection, ecobiotechnologies, metallurgical, ore processing, gas-and-oil producing, ceramic, building, and other industries, in agriculture, in medicine for developing new rehabilitation methods and spa-therapeutic curing, prophylaxis of hemophilia, developing wound-healing, therapeutic and cosmetic remedies etc.

2.2 Nanostructural, biocolloidal, and physicochemical stress phenomena factors in aqueous iron-aluminosilicate dispersions

Nanochemical, geomechanical, biocolloidal, and other physicochemical factors of nanostructural transformations in iron-aluminosilicate and polymineral formations (Fig. 2.7) have been actively investigated recently. These formations consist of dense ironoxide-aluminosilicates or nanocrystalline disperse rocks and additives of different iron oxide-hydroxide and organic compounds, carbonates, phosphates, *etc.* [10, 11, 88, 319, 323-325]. Such formations based on nanostructural iron-aluminosilicate systems and materials (NIASSMs) exhibit features characteristic only for them. For example, it was established that intermediate chain phase bonds from a number of nanoparticles play a significant role in contact arrangement of NIASSM microparticles, which help to unite separate colloid particles and microparticles into aggregates or disconnect them depending of the velocity of laminar or turbulent dispersion flow, and they are also responsible for strength and rheological characteristics of polymineral macrostructures [16, 23]. The state when individual nano-, micro- and macroparticle aggregates of polymineral substances disconnect one from other can be reached owing to geomechanical tension or in the conditions of plastic flow of such structures. Under the action of big loads, a complete breaking of NIASSMs structure and uncontrollable dispersion flow with increscent velocity can be reached, i.e., catastrophic phenomena can occur in both natural and technogenic NIASSMs [323]. However, mechanisms of such mainly nanochemical and biocolloid transformations (Fig. 2.7), separation or secondary structuring of nanophase formations, partially developed for lake and ocean pelagic sediments and peloids [10, 11, 16, 23, 323], have not yet been properly explained for concentrated nanostructured dispersions and other sediments and soils in theconditions of stress processes [323].

So, the investigations of mechanisms of nanochemical and biocolloid processes with transportation of nanostructured microaggregates formations make it possible to expand the opportunities to form nanocomposites with improved mechanical characteristics for prevention of stress phenomena in different sediments and soils. From this point of view, the most attractive are NIASSMs of biocolloidal origin, which include clays important for practical application, and iron ores.

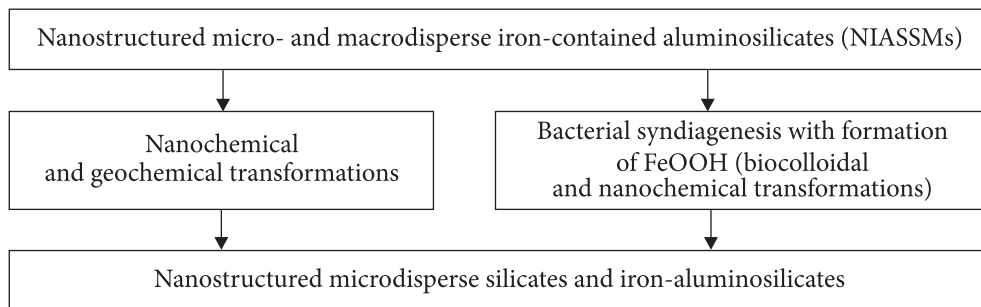


Fig. 2.7. Scheme of nanochemical, geomechanical and biocolloidal transformations of nanostructured iron-aluminosilicates

It should be mentioned that clays are structures with prevailing aluminosilicate content in comparison with the content of iron oxide additives, organic matter, carbonates, *etc.*, and that iron ores are structures with prevailing content of iron oxides in comparison with the content of silicates and other additives. The main structure formation additives of such natural polymineral nanocomposites are usually not only iron hydroxides, but also calcium compounds in the form of carbonates and organic substances, the products of microorganism metabolic processes [23, 321, 325]. That is why the complex task of current study was primarily to explain the mechanism of nanochemical and biocolloid processes aided with nanoclusters and nanoparticles of various origin; their contacting with microparticles, and their influence on geomechanical stress phenomena and technology specifics of controlling such phenomena.

Analysis of the main physicochemical properties of different representatives of IASSMs and NIASSMs and preliminary modeling of stress and catastrophic processes on marine slopes and ocean bed

The main experimental and model data for different IASSMs and NIASSMs are presented in Figs 2.7-2.19 and in Tables 2.2-2.4. According to [16, 23, 309, 322, 325], the NIASSMs in general are colloid disperse oozes, bottom sediments and so on, consisting of mineral and organic substances, which have been significantly transformed owing to geological, physicochemical, chemical, biological and biocolloid processes (Fig. 2.7). They are a homogeneous fine-grained plastic mass. Natural colloid and biocolloid formations of different genesis can belong to them, for example, iron ore formations with huge amount (40-70%) of iron oxides and aluminosilicate admixtures (Fig. 2.8, Table 2.2) and clay minerals with iron oxide admixtures, as well as fresh-water clay soils, sands and salt-water iron-containing disperse sediments. Recently, the sea muds (Figs 2.9-

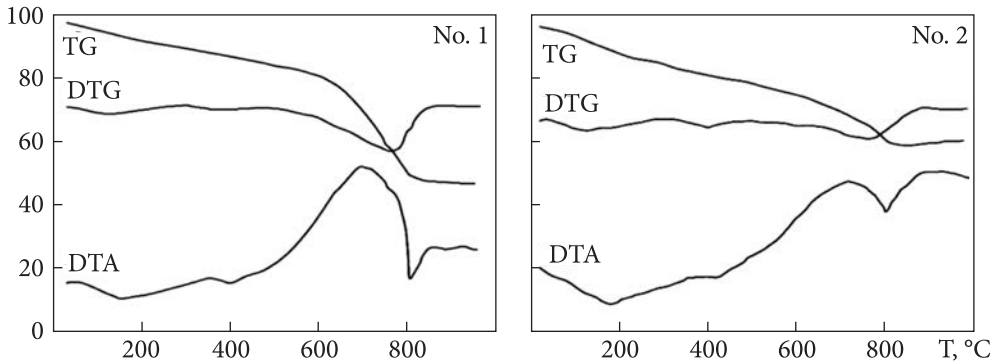


Fig. 2.8. Thermograms of micropolycrystalline jaspilite samples No. 1 and No. 2 from the Azov sedimentary oolitic iron ore deposits (see Table 2.2)

Table 2.2. Granulometric composition of NIASSMs suspensions of Azov (sedimentary oolitic iron ores milled in water) consisting of iron oxides, iron-aluminosilicates, clay minerals, and carbonates

Sample number (see Fig. 2.8)	Particle sizes in fractions (μm) and their content(mass %)								
	≥ 1000 μm	500- 1000 μm	250- 500 μm	100- 250 μm	50- 100 μm	25- 50 μm	10- 25 μm	1- 10 μm	≤ 1 μm
1	0.02	0.02	0.03	8.12	17.8	64.78	5.70	1.98	1.22
2	1.0	2.33	16.64	64.91	19.89	10.97	1.24	0.88	0.65

2.12, Tables 2.3, 2.4) or pelitic sediments of coastal and deep-water origin, whose part among the known NIASSM reaches 70-80% [17, 89, 306, 308, 326], have been actively investigated as the main representatives of NIASSMs. The determination of nanostructural, biocolloid, physicochemical and geomechanical mechanisms of their formation can give answers to the questions of participation of NIASSMs in stress phenomena both in underwater slopes of seas and oceans, and in concentrated soil dispersions in natural geomechanical and technogenic processes [8, 20, 327, 328].

From the practical view point, clays, iron ores and pelitic deposits (peloids) are the most important among NIASSMs. Clays are combined uncemented sedimentary rocks of biocolloid origin composed of clay minerals with admixtures of iron oxides. Pelitic deposits (peloids) are sediments of lakes, seas and oceans consisting of planktonic organism remains, fine disperse mineral particles, cosmic dust and products of chemical transformations in fresh and salt water. From the viewpoint of geomechanical and nanochemical processes, their nanostructural behavior is reliably connected with destructive work of water fluctuations and

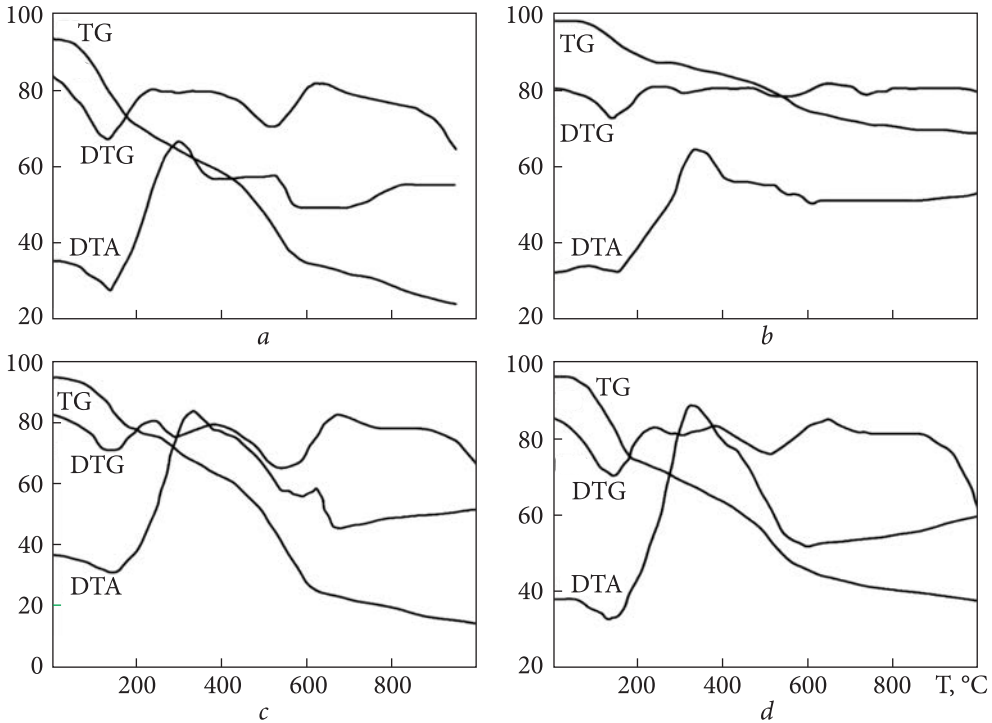


Fig. 2.9. Thermograms of nanostructured disperse pelitic sediments for muds from: *a* — the Kuyalnik Estuary (sample 1); *b* — the Azov Sea 10 m depth (sample 2); *c* — the Black Sea 1800 m depth (sample 3); *d* — the Black Sea 2000 m depth (sample 4)

Table 2.3. Granulometric composition of samples of nanostructured pelitic sediments

Sample (see Fig. 2.9)	Percentage composition in fractions, %				
	≥500 μm	500-100 μm	100-5 μm	5-1 μm	≤1 μm
1	6.32	58.79	10.41	4.07	20.42
2	27.89	44.83	13.64	1.55	12.09
3	10.39	14.24	8.21	37.96	29.20
4	12.24	20.18	15.33	28.47	23.78

displacement of sediments in reservoirs [220, 323]. The scheme of mentioned processes in sea sediments is given in Fig. 2.13, according to which, while retreating from the coastline and increasing depth, surface destructive processes in reservoirs, especially marine ones, are replaced by gravity precipitation and nanochemical and biocolloid structuring of sediments. At that, sediment forming material may be of various origin. Its main mass comes from the land, generally due to soil erosion in the form of dissolved components and solid particles of different

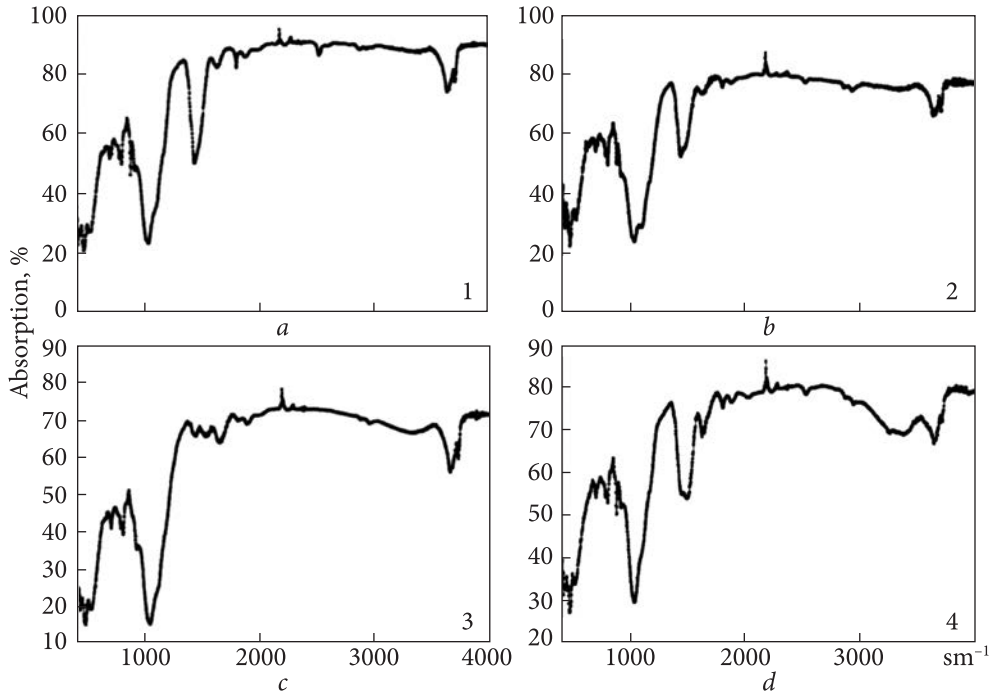


Fig. 2.10. Infrared spectra of bottom muds from: *a* — the Kuyalnik Estuary; *b* — the Azov Sea (depth 10 m); *c* — the Black Sea (depth 1800 m); *d* — the Black Sea (depth 2000 m)

Table 2.4. Characteristics of pelitic sediment samples

Parameter	Sample (see Fig. 2.10)			
	1	2	3	4
Volume of 1g dry sample, cm ³	0.8	0.8	0.8	0.9
Volume of sample after swelling for 20 h, cm ³	0.9	0.9	1.0	1.05
Swelling coefficient in water, cm ³ /g	0.1	0.1	0.2	0.15
Wetting rate, W_{water} , cm ³ /s	$3.8 \cdot 10^{-3}$	$6.5 \cdot 10^{-3}$	$2.5 \cdot 10^{-3}$	$2.3 \cdot 10^{-3}$
Wetting rate, W_{decane} , cm ³ /s	$7.7 \cdot 10^{-3}$	$7.4 \cdot 10^{-3}$	$6.7 \cdot 10^{-3}$	$6.8 \cdot 10^{-3}$
Interparticle porosity, %	61.3	56.7	62.2	64.7
Wetting heat by water, J/g	23.3	19.2	19.9	26.4
Wetting heat by decane, J/g	23.6	8.1	11.7	19.6
Lyophilic coefficient, β	1.0	2.4	1.7	1.3

size, including nanoparticles. Sediments may also be formed by organogenic (biocolloidal) way as a result of the death of living organisms. According to this, terrigenous, organogenic and chemical sediments with organogenic (biocolloidal) for-

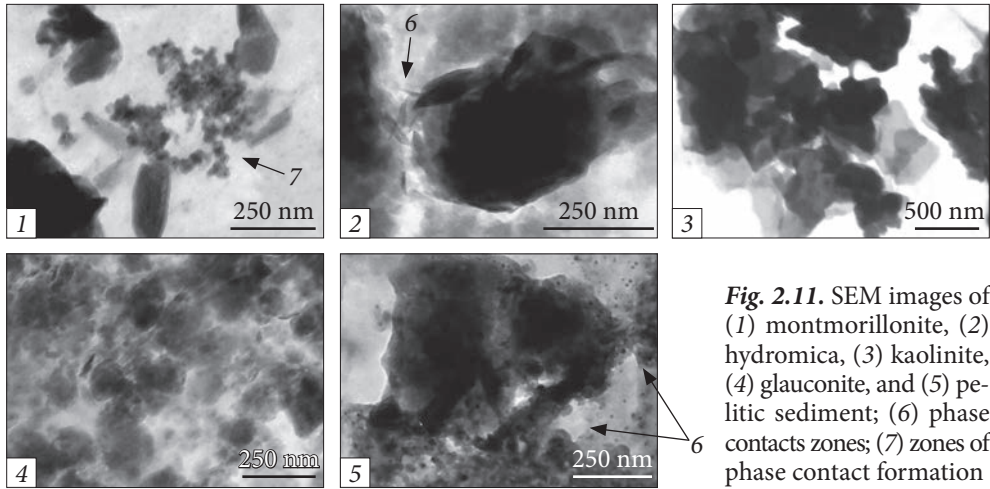
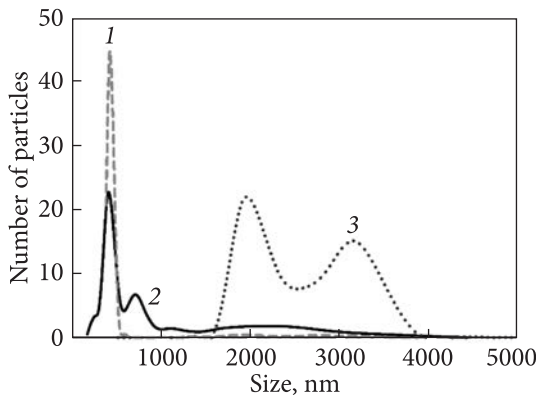


Fig. 2.11. SEM images of (1) montmorillonite, (2) hydromica, (3) kaolinite, (4) glauconite, and (5) pelitic sediment; (6) phase contacts zones; (7) zones of phase contact formation

mation owing to the death and transformation of living organism remains can be distinguished [10, 11, 16, 17, 23, 88, 89, 308, 309, 321-326]. The sediments of the mainland slope (bathyal area), whose surface shifts, are often a factor of stress phenomena, can be met up to 3000 m depth and are characterized by high heterogeneity. Fine-grained terrigenous clay sediments sharply dominate. Those are oozes, which have different colors depending on the polymineral composition and medium, but they have common surface structures, which take part in contact geomechanical interactions (Figs. 2.10 and 2.11). Organogenic carbonate-containing sediments play an important role in analyzed processes. They are formed along with iron hydroxides (Fig. 2.13) as a result of conglomeration and further mechanical and nanochemical dispersion of carbonate shells of planktonic organisms, and also due to dispersion of volcanic oozes and clay soil carry-overs from rivers and continental slopes [10, 88, 89, 306, 323]. So, from analysis of NIASSMs behavior (Fig. 2.13), it comes out that the initial stage of their transformation is



the so-called mechanical denudation processes [88, 306]. The initial mechanochemical, nanochemical and geomechanical transformations, widespread in different reservoirs but mostly in

Fig. 2.12. Particle size distribution of mud fine-grained fraction (see Fig. 2.9): 1 — muds from the Azov, sample 2; 2 — muds from the Black Sea, sample 3; 3 — muds from the Black Sea, sample 4

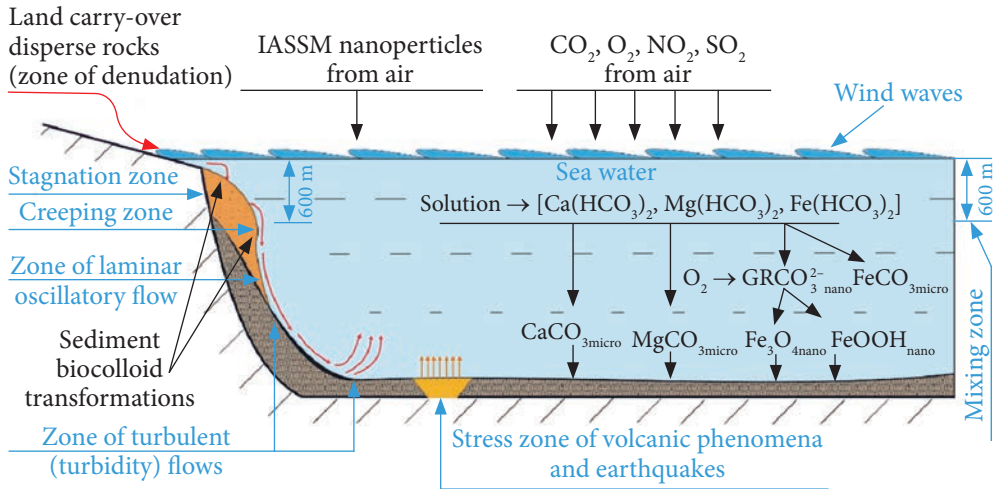
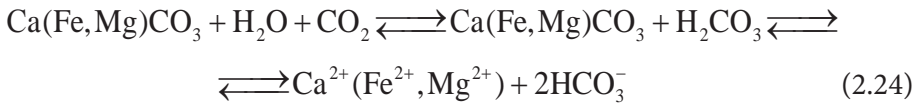


Fig. 2.13. Model of transformation processes in reservoirs (seas and oceans): carry-over, denudation, stagnation, creeping, biocolloid interactions, laminar oscillatory flow, turbulent flows, stress volcanic phenomena and earthquakes, chemical nano- and microinteractions. GR — Green Rust

seas and oceans (in shelves and continental slopes) also belong to them. Three main categories distinguished among such complex processes are: activity of waves and flows, underwater crashes, and work of the so-called turbiditic flows [88, 306]. According to Fig. 2.13, the waves of muddying water influence the conditions of marine sediment conglomeration and dispersion up to depths of about two wavelengths, i.e. 600-800 m. But the main denudation work is done by waves in shallow water only, near the coast [88, 306]. Underwater landslips are widespread enough and they take fresh bottom mud sediments from even small-angle slopes (down to 2-5°). On the steeper slopes, the creep of sediments already partially compacted also can occur. They are real avalanches but less intensive than on the land if their velocity does not cross the border of hyperanomalous current. Big and fast muddy (turbiditic) flows are formed in the areas of continental slopes and in areas at the bottom with a relatively steep slopes covered with fine-grained thixotropic muds in the conditions of flow transformation from a hyperanomalous to a low thixotropic one. The waves penetrating to the depth up to 600 m during storms exert the effect of a hydraulic impact that instantly rarefy thixotropic muds turning them into a viscous liquid, capable to active nanochemical and geomechanical transformations. Thus, the formed suspension flows down the slope without mixing with water due to the high specific mass. In particular, the appearance of clay terrigenous sediments at great depths, chemically transformed due to the influence of pH change [8, 20, 327, 328] can be explained in this way. Besides, as shown in Fig. 2.13, the velocity of mud flows with mass up to hundred

millions tons of rocks increases significantly on the ocean slopes in seismic zones with length up to 2000 m and more. That can cause micro- and even macro-earthquakes when this mass hits the ocean bottom [89, 306, 308].

During the abovementioned processes, as it comes from the data shown in Figs. 2.7-2.12, nanostructural transformation of polymineral dispersions takes place, mainly with iron hydroxides, iron-aluminosilicates and carbonates. At the same time, in the beginning, nanostructuring at small depths leads to compaction of young clay-carbonate phaseolitic pelitic sediments with active microbiological dissolution of the most soluble structures and formation of more disperse material. Such processes usually last some dozens of days [8, 10, 11, 17, 20, 89, 306, 308, 309, 321-323, 326-328]. Dispersion processes in minerals proceed intensely at practical domination of HCO_3^- ions in water and end at alkaline pH values (over 7) [8, 20, 89, 220, 306, 308, 327, 328]. An explanation for this phenomenon can be found in the fact that iron, magnesium, calcium carbonates present in natural iron-oxide silicate materials (iron-containing peloids, sedimentary iron ores, iron-clays) react with carbon dioxide by the following equations:



The ratio $\text{HCO}_3^- : \text{H}_2\text{CO}_3$ close to 2 : 1 is provided here [22].

In salt water, the dispersion rate of NIASSMs based on natural clay and clay-carbonate rocks can be increased to a large extent, sometimes by tens of times, in the presence of carbon dioxide which regulates the alkaline pH value. Carbon dioxide is absorbed from the air in accordance with its partial pressure [220, 306, 308, 328].

The dipole moment due to the recharging of the side chips resulted from active coagulation and volumetric structure formation appears in the transition from alkaline to acidic environment in the clay particles of the NIASSM. This process is more typical for the most disperse mineral montmorillonite and the least significant for kaolinite (Fig. 2.11). Quite narrow pH range, within which the sediment structure change is the most important feature, which is explained by the presence of coagulation threshold at a certain pH value. Kaolinite particles lose their stability at $\text{pH} \approx 8$, montmorillonite particles at $\text{pH} \approx 6.5$, and hydromica particles at $\text{pH} \approx 6$ [220].

Water saltiness combined with changes in pH and partial pressure of carbon dioxide can also have a significant effect on the carbonate solubility. Thus, solubility product (K_{sp}) of calcium carbonate is described by the equation:

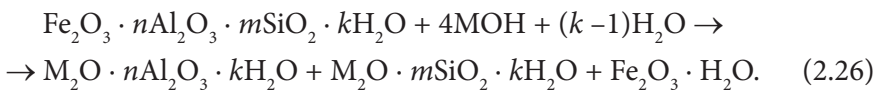
$$K_{sp}(\text{CaCO}_3) = [\alpha(\text{Ca}^{2+})][\alpha(\text{CO}_3^{2-})] = \\ = [m(\text{Ca}^{2+})] [m(\text{CO}_3^{2-})] [\gamma(\text{Ca}^{2+})] [\gamma(\text{CO}_3^{2-})], \quad (2.25)$$

where m is the molar concentration, γ is the activity coefficient.

Based on the postulate about constancy of K_{sp} value, it is obvious that with decreasing activity coefficients of the Ca^{2+} and CO_3^{2-} ions, their molar mass and hence the solubility of Ca, Mg, Fe carbonates increase. Since all salts with nomatched ions increase the ionic strength of solution and decrease the activity coefficient, the solubility of carbonates will increase in proportion to increasing the water mineralization degree. Here with, the solubility of CaCO_3 may be increased by several times [306, 308, 220, 328], which, in turn, leads to increasing mineral dispersion along with water salinity increasing. That fact is testified by experimentally shown increasing volumes of clay mineral sediments [220].

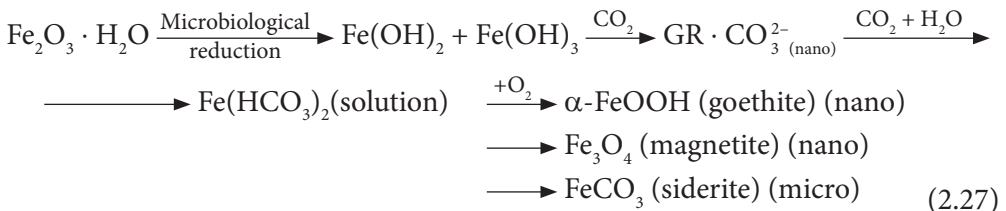
Thus, the role of a liquid phase in processes of natural and technogenic dispersion of iron-containing clay-carbonate dispersions of NIASSMs is very important. The intensity of the dispersion action of a liquid is substantially determined by the chemical and mineralogical composition of the rock [20, 23, 88, 319, 321, 323], pH, salinity degree of the dispersion media and by the nature of electrolytes dissolved in it [220]. It is also accompanied by the effect of compulsory mechano- and nanochemical dispersion, and the effect of biocolloid processes [16, 17, 89, 308, 309, 321, 322, 326].

Biocolloid nanostructural processes in NIASSMs aided by products of microorganism metabolism in slightly alkaline mediums last hours [23] on the contact surface of microcolloidal particles according to the modified common scheme [12, 308, 23] of the reaction (2.8):

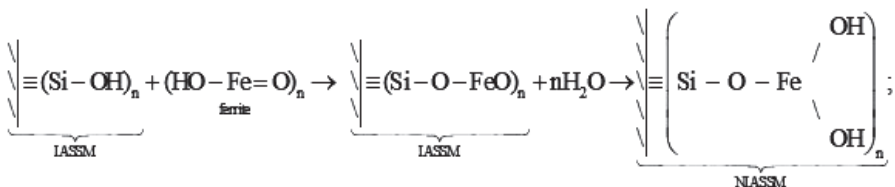
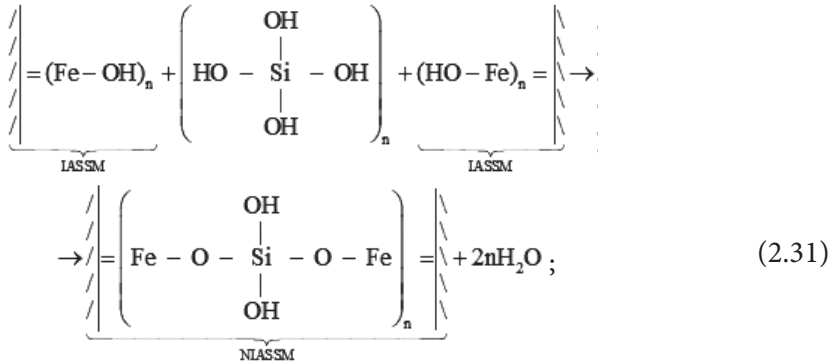
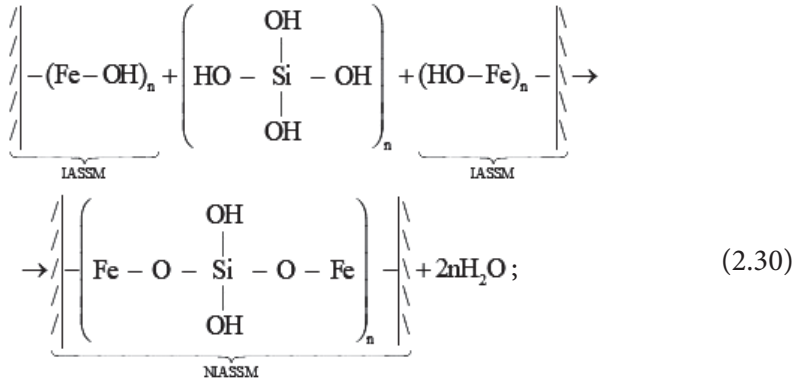
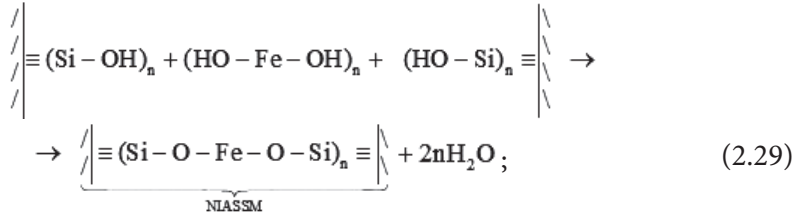
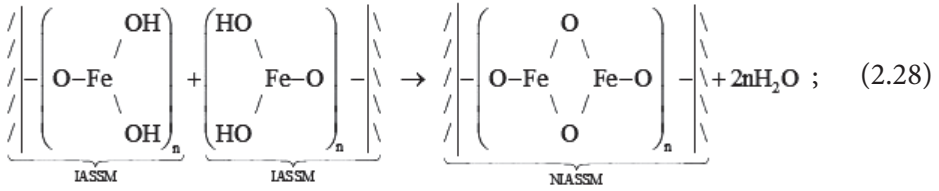


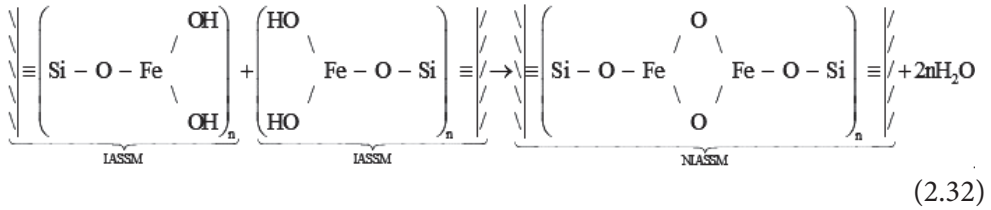
The formation of nanoclustered surface of iron-aluminosilicate structures is the result of biocolloidal chemical process (2.26). An alkaline medium appears also as the result of surface microbiological and chemical processes (Scheme 2.27). The products of reactions (2.8) and (2.27), nanoclusters and nanoparticles, are arranged in the surface contact zones (Fig. 2.11).

The ferrite, formed according to the scheme (2.8) reacts as follows:



Here with, nanoclusters of iron hydroxides, siderite, magnetite and goethite will be formed. $\text{Fe}(\text{OH})_3$, $\text{Fe}(\text{OH})_2$, Fe_3O_4 and FeOOH form phase contacts (Fig. 2.11) according to the schemes of reactions:





where (...)n — nanocluster or nanoparticle in phase contacts of NIASSMs; \equiv — surface of microparticles of iron-aluminosilicates (IASSMs).

It is evident from the models of reactions (2.8), (2.26)-(2.32) that interphase biocolloid interactions aided with surface-active products of microorganism metabolism are accompanied by formation of nanocluster coagulation-condensation or phase contacts between surfaces of similar or different disperse phases, and that leads to a secondary compaction of earlier dispersed iron-containing aluminosilicate materials. Such mechanisms of contact interactions testify that interphase interactions are stronger with participation of Fe^{3+} than with participation of Fe^{2+} , because in the latter case (typical for models of surface nanochemical reactions (2.29) and (2.30)), microbiological oxidation of Fe^{2+} into Fe^{3+} and breaking of interphase —O—Fe—O— connections with goethite formation according to the general model (2.27) are possible. Hence, the biocolloidal mechanism differs from the previously described inorganic mechanism [16] by intermediate microbiological formation of GR (Green Rust) which transforms (model scheme 2.26) into goethite, magnetite, and siderite. At that, the role of magnetite becomes clear from Fig. 2.14 (similar to Fig. 2.2). It can also be explained by the fact that the dependence of microbiological, physicochemical, and geomechanical features of a self-dispersion process and a process of further compacting of fractured or porous iron-aluminosilicate oolitic sediments and their derivative pelitic ones and clays, and their further structural compacting in certain conditions can be also found from analysis of data in [23, 321, 325]. According to the above, the contact compacting substantially depends on the microorganisms vital activity and products of their metabolism. Thus, according Figs 2.2 and 2.14, pelitic sediments after 45—60 days of microbiological treatment (accompanied by self-dispersion process and increasing η and P) have a $\text{Fe}^{2+} : \text{Fe}^{3+}$ ratio close to 1 : 2, which corresponds to magnetite structure with the strongest bonds among the known ironoxide compositions. Therefore, the further nanostructural sediment compaction is accompanied predominantly due to formation of magnetite clusters and nanoparticles in contact zones of larger microstructures (Fig. 2.11). It should be emphasized that magnetite formation occurs in the conditions of an anaerobic state (model in Fig. 2.6), whereas in the conditions of an aerobic process, goethite is formed.

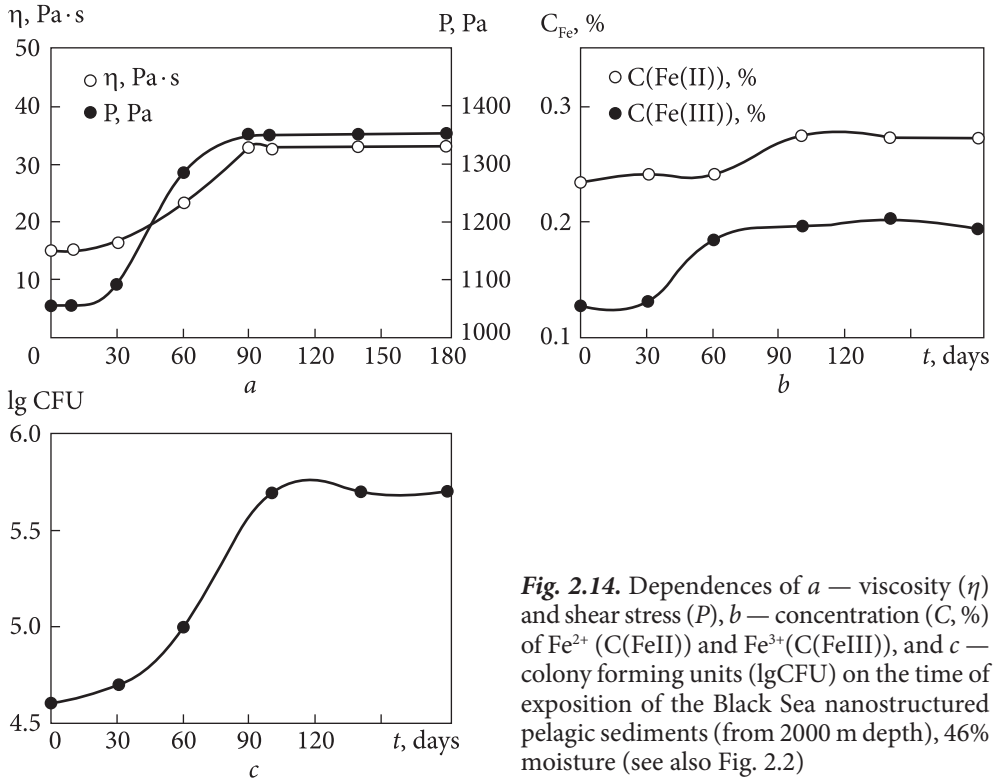
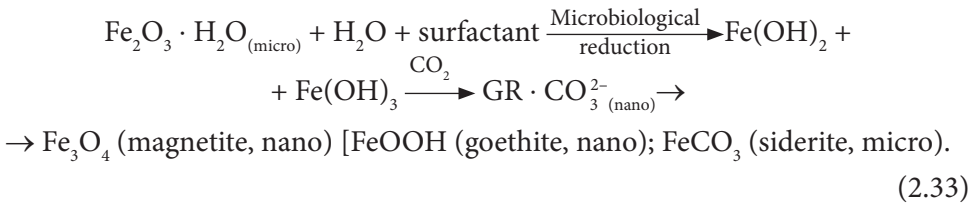
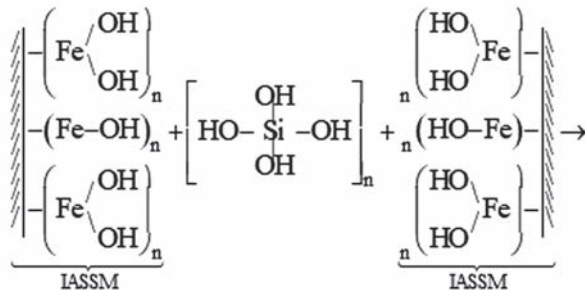


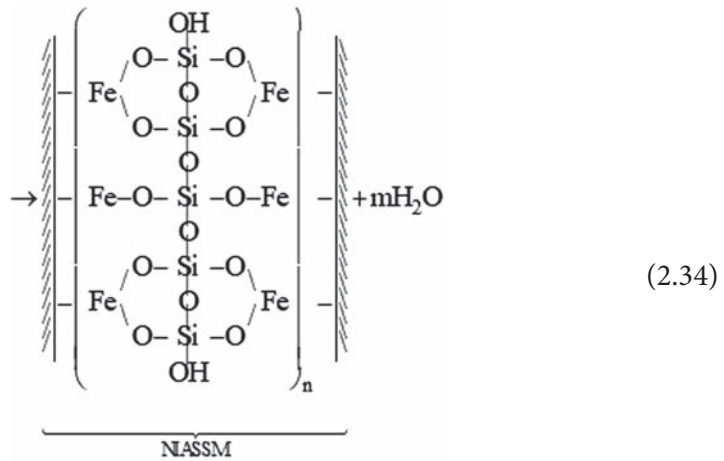
Fig. 2.14. Dependences of *a* — viscosity (η) and shear stress (*P*), *b* — concentration (*C*, %) of Fe²⁺ (C(FeII)) and Fe³⁺ (C(FeIII)), and *c* — colony forming units (lgCFU) on the time of exposition of the Black Sea nanostructured pelagic sediments (from 2000 m depth), 46% moisture (see also Fig. 2.2)

Data from Figs. 2.2—2.14 allow us to present the scheme (2.26) of the biocolloidal process in the adjusted way:



And reactions (2.30)-(2.32) can be transformed in such a way:





These data obtained for the Black Sea peloid taken from of 2000 m depth, are in good agreement with the data shown in Section 2.1.2 for the Black sea peloid taken from the 1800 m depth (Fig. 2.2).

Analysis of nanostructural phenomena in NIASSMs (Figs 2.13 and 2.14) with consideration of their general scheme of nanotransformations (Fig. 2.3) allows us also to estimate the role of the phenomena established with the help of complex rheological and other physicochemical researches partially published in [16]. It comes from them that, along with the well-known physicochemical and nanochemical processes in disperse iron-aluminosilicate sediments and clays, there are additional compaction processes and essential dispersion under the influence of surface-active substances (SAS), namely micro-organism metabolites, whose quantity may reach up to 3000 [12]. This also influences the formation of the new nanostructural disperse organoclay-carbonate products, enriching bottom pelitic sediments and clays with organic substances, iron oxides and calcite [325]. As a result, micro- and nanodispersed rocks of sediments transform into concentrated pasty watertight nanostructural compositions, located mainly on slopes and bottoms of seas and oceans. Such compositions are structured with nano- and microparticles of iron oxides, clays, carbonates, and organic substances and form strong coagulation-condensation contact nanophase bonds according to the schemes of nanochemical reactions (2.8)-(2.24) and (2.34). And that has an essential influence on the geomechanical properties of sediments.

So, nanostructuring processes of clay suspensions, nanochemical processes of nanoparticle formation in them, including biocolloidal ones, and also chemical composition of nanoparticles exert an important influence on the rheological behavior of NIASSM dispersions, and also significantly depend on the amorphous clay-carbonate iron part of pelitic sediments and peloids.

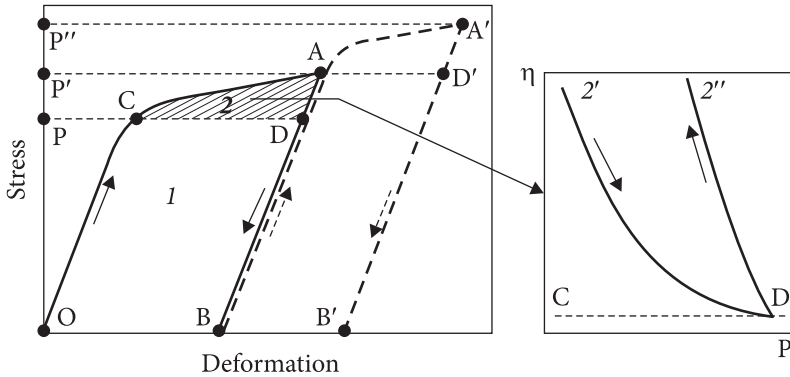


Fig. 2.15. Elastoplastic deformation of clay and pelitic sediments (NIASSMs) concentrated dispersions (theoretical ideas): 1 — elastic and 2 — plastic deformation; 2' — and 2'' — are rheological curves of ultraanomalous viscosity at increasing or decreasing of P in conditions of plastic flow; η is the structural viscosity

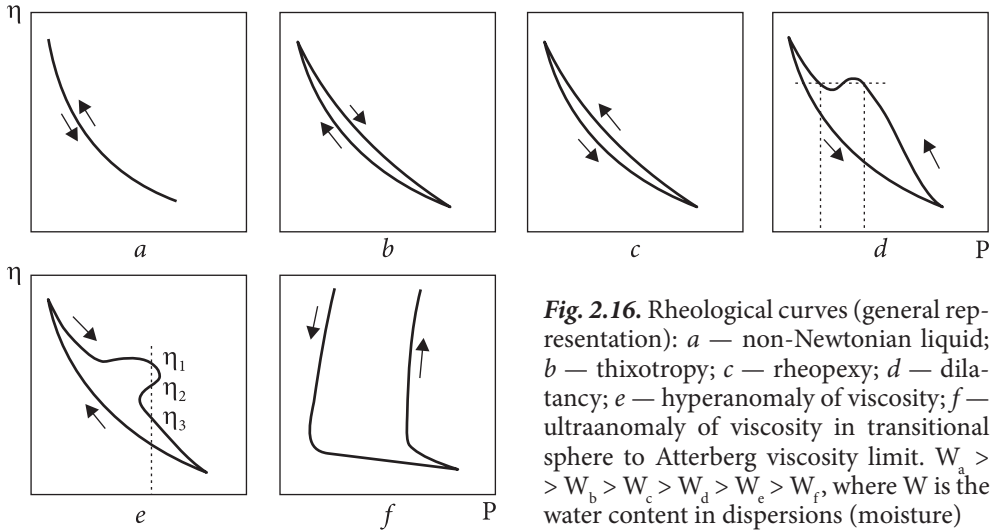


Fig. 2.16. Rheological curves (general representation): a — non-Newtonian liquid; b — thixotropy; c — rheopexy; d — dilatancy; e — hyperanomaly of viscosity; f — ultraanomaly of viscosity in transitional sphere to Atterberg viscosity limit. $W_a > W_b > W_c > W_d > W_e > W_f$, where W is the water content in dispersions (moisture)

Taking into account the above considerations, Figs 2.15 and 2.16 present the data concerning the influence of the disperse phase concentration on the rheological behavior of NIASSMs in the form of loading and unloading curves for elastoplastic materials like pelitic sediments of carbonate iron-aluminosilicate-type [11, 16, 55, 325, 329], where authors of [55] also include iron-containing bentonite suspensions in the conditions of hyperanomalous effect of viscosity there. As seen, the hyperanomaly of viscosity [55] is typical for larger moisture of NIASSMs dispersions than for its ultraanomaly, which was experimentally recorded in 2003 at first [329], but for the first time explained — in the present research (Fig. 2.17). In general, with increasing disperse phase concentration, the

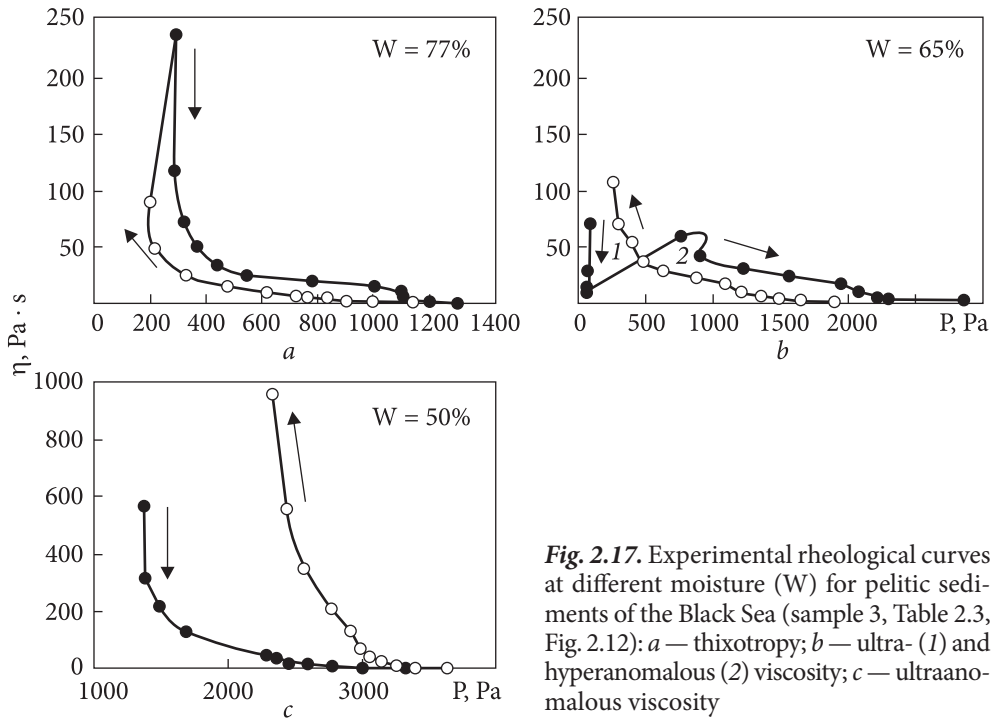


Fig. 2.17. Experimental rheological curves at different moisture (W) for pelitic sediments of the Black Sea (sample 3, Table 2.3, Fig. 2.12): a — thixotropy; b — ultra- (1) and hyperanomalous (2) viscosity; c — ultraanomalous viscosity

character of dispersion flow changes in the sequence: thixotropic — dilatant-rheopetic — hyperanomalous — ultraanomalous (Fig. 2.16).

The established laws of nanostructural phenomena in disperse NIASSMs of the Earth's crust and its surface allowed us also to develop and carry out a number of methods for direct control of sediments structure, based on the achievements of physicochemical geomechanics, biocolloid chemistry, and on the laws of nanoscale contact interphase interactions [10, 11, 16, 323, 325, 329]. For example, methods for control of physicochemical properties of barrier structures, soils, and rocks under the action of active natural and technogenic mediums have been substantiated according to conceptions of colloid chemical materials science and physicochemical geomechanics [8, 10, 16, 20, 319, 323].

The obtained data, generalized in Figs 2.13-2.18, provide the opportunity to consider the practical significance of the viscosity ultraanomaly effect for transformation of NIASSMs and denudation of continental slopes of seas and oceans by means of biogeo- and nanochanges in elastoplastic properties of underwater sediments, deposited on underwater slopes of reservoirs, as well as for the opportunity of stress phenomena prevention in them [8, 10, 11, 16, 17, 20, 23, 88, 89, 306, 308, 309, 319, 323-328]. Those results coincide with recent conclusions of other authors [17, 326], whose findings are also presented in Figs. 2.18 and 2.6, and

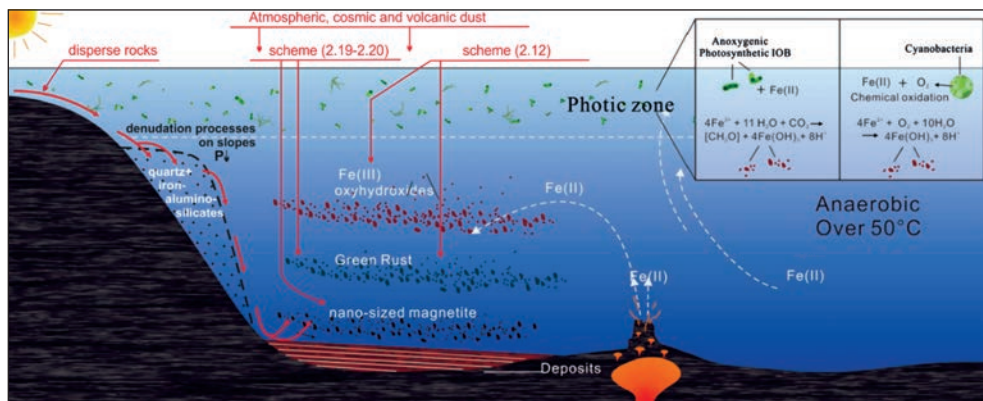


Fig. 2.18. Modified (as compared to Fig. 2.6) transformation models of iron compounds in oceans [17, 326] and the present geomechanical, nanochemical, and biocolloid processes with iron-aluminosilicates and silicates on slopes [323] and in different water basins [10]

also broadened by biocolloidal processes corresponding to the schemes (2.8), (2.24)-(2.33).

Conclusions. Theoretical and experimental ideas about transformation mechanisms of iron-aluminosilicate compounds of concentrated dispersions, sediments, and soils have been developed on the basis of complex physicochemical, microbiological, and geomechanical researches in conditions of stress processes (natural and technogenic catastrophes). The leading significance of nano- and microstructures in stress phenomena behavior was shown, the main factors of which are geomechanical and biocolloidal dispersion processes and following coagulation-condensation transformations in conditions of an elastoplastic dispersion flow. It was also shown that for iron-aluminosilicate dispersions with varying content of surface-active compounds, and hydrated iron and silicon oxides, with increasing disperse phase concentration and its flow, change in the dispersion viscosity depending on the shear stress occurs in the sequence: thixotropic → dilatant-rheopectic → hyperanomalous → ultraanomalous flow character. The effect of ultraanomalous viscosity in iron-aluminosilicate dispersions on stress phenomena (mud shifts of underwater and land sediments and soils) was reviewed. The previous recommendations for control overstress phenomena based on detected regularities were provided using fine-disperse technogenic sludges and waste piles of iron-silicate ore materials.

The performed analysis of studies concerning nanostructured phenomena in iron-aluminosilicate materials of the Earth's crust including stress ones, and the additional experimental findings for the influence of nanochemical and microbiological processes on the phenomena in rocks and disperse NIASSMs indicate a short-term possibility to create exact nanochemical and rheological mechanism

descriptions for most of physicommechanical stress and catastrophic processes running in the Earth's crust and on its surface, in reservoirs, seas, oceans and in technogenic conditions. The carried out studies allowed more detailed consideration of ideas about soil and NIASSM sediment creep mechanisms and transformation of mechanically strained areas of a disperse structure. The general concepts of physicommechanical, nanochemical, and biocolloid regulation of structural properties of NIASSMs and disperseporous sediments in natural and technogenic conditions were defined for prevention of stress and catastrophic phenomena in them. The effect of ultraanomalous viscosity on natural catastrophic processes in NIASSMs was revealed, and subsequent steps in developing indicated fundamental problems, as well as in giving general recommendations for their practical applications were underlined. The latter includes developing slope and dam creep regulators on the basis of modified metallurgical sludges and slags, and waste piles of iron-ore deposits [10, 323, 329].

CHAPTER **3**

**MECHANISMS
OF COLLOID-CHEMICAL,
NANOSTRUCTURAL-
NANOCHEMICAL,
AND BIOCOLLOIDAL
PROCESSES
IN PELAGIC SEDIMENTS
WITH PELOID
(THERAPEUTIC MUDS)
PROPERTIES**

Among most of IASSMs and NIASSMs, pelagic (pelitic) sediments (PS), especially of marine origin, recently have attracted the attention of researchers. The reason, as shown in the previous chapters, is that PS are easily activated in the biogeocenosis presence and exhibit specific properties of therapeutic muds (peloids). Whereas classic peloids have been investigated for a long time, however, marine pelagic sediments were disclosed recently [17]. They have peloid properties and almost inexhaustible deposits. Besides, they have unique properties as well. Most of them have not yet sufficiently investigated, in particular nanostructural nanochemical, colloid-chemical and biocolloidal interactions in them. Conceptions concerning mechanisms of colloid-chemical, nanostructural nanochemical and biocolloidal processes in PS are almost not developed. These processes in PS lead to formation of valuable for spa and medical application of peloids (the therapeutic muds) with unique characteristics. Thus, generalized studies of such IASSMs and NIASSMs with a developed nano- and microstructure are surely topical. First of all, this refers to biogeocenosis in transformation mechanisms of characteristics and properties of PS consisted of IASSMs and NIASSMs. Especially this concerns the realization of such mechanisms in conditions of nanostructural nanochemical processes in pelagic sediments and biocolloid-chemical interactions in clay-containing peloids.

3.1. Nanostructural nanochemical processes in peloid sediments aided with biogeocenosis

As shown above, partially nanostructured polymineral iron oxide-aluminosilicate systems and materials (NIASSMs) and pelagic sediments (PS) have important rank among natural dispersed mineral formations. Some of them possess therapeutic properties and are related to the so-called peloids. Such NIASSMs, PS, and peloids always have been of great importance in biomedical and colloid-chemical investigations. Over last decades peloids in NIASSMs have been studied more and more widely by physical chemists. The purpose of such studies is to establish the influence of peloids on biocolloidal interactions, which can be measured as interphase colloid-chemical transformations in peloids and similar disperse systems under the action of microorganism metabolic processes. However, determination of such effects on complex polymineral NIASSMs and PS in various specific cases has not yet completed. This is because of insufficient definiteness of multi-pronged physicochemical, colloid-chemical and biocolloid methods of their investigation [8, 16, 17, 18, 21, 326, 330, 331]. Today it is known in general that physicochemical, colloid-chemical, nanochemical transformations and contact interphase interactions in IASSMs, NIASSMs, and PS lead to the formation of new and in

many cases at least of the same complexity polymineral nanostructured materials with new properties [17, 326]. Such transformations and interactions are aided with microbiological processes. The formed materials consist of iron, aluminum and silicon oxides in general, often in the form of montmorillonite and glauconite clay minerals. There are many, but in fewer quantities, other inorganic and organic components in them as well [11, 16, 17, 23, 106, 326].

Such materials and disperse systems of the NIASSMs' type are widely used in practice. They include iron oxide-silicate sedimentary ores, iron-containing bentonitic and other clays, pelitic marine and lake sediments, coastal and shelf sands and other sedimentary and solid ore deposits and soils, the total capacity of which in the Earth's crust reaches 90%. During their geological history, many of them have been transformed under the action of microbiological and secondary tectonic processes. For example, this concerns solid iron quartzites (jaspellites), which are the basis of general iron ore deposits. It was recently established that they started forming two billion years ago as a result of the microorganism activity with further tectonic cementing of formed disperse formations [22]. Thus, microorganisms play a significant role in structural formation of different iron oxide-aluminosilicate materials and PS among them.

As far as practical importance of PS and other similar nanostructured materials is increasing constantly, the attention of scientists investigating fundamental microbiological and biocolloid processes increases as well. Thus, such investigations are actual one. At this point a problem of setting special studies of fair-investigated nanostructural-and-nanochemical processes is arisen and also a necessity to analyze the influence of such processes on the biomedical properties of peloid sediments and their main inorganic components, namely clay minerals and clays.

Experiment and discussion

The work relates to investigation of deep-water clay-carbonate pelitic sediments of a gigantic peloid deposit, taken in the west region of the Black Sea from 2 km depth layer. The Black Sea peloid properties, and the peloid sample were taken from the Kuyalnik Estuary (Odesa) for comparison and are described in [17, 326]. Bentonitic (montmorillonite) clay and glauconite were used as a model sample and hydromica as a comparative sample.

The chemical composition of studied bentonite was (wt%): 49.52 SiO₂; 21.06 Al₂O₃; 2.72 Fe₂O₃; 5.70 CaO; 1.61 MgO; 0.37 Na₂O; 0.28 K₂O; 0.02 C_{org}. Aqueous bentonite suspension with 57% of water had the following physicochemical indices: pH 7.3; Eh +370 mV; shear stress 821 Pa; stickness 1840 Pa. Clay fraction contained 19.1% of 1–10 μm particles and 2.9% of particles sizing under 1-10 μm.

The chemical composition of studied bentonite was (wt%): 57.46 SiO₂; 7.49 Al₂O₃; 17.50 Fe₂O₃; 0.36 FeO; 0.35 TiO₂; 3.06 CaO; 2.41 MgO; 0.07 Na₂O; 5.35

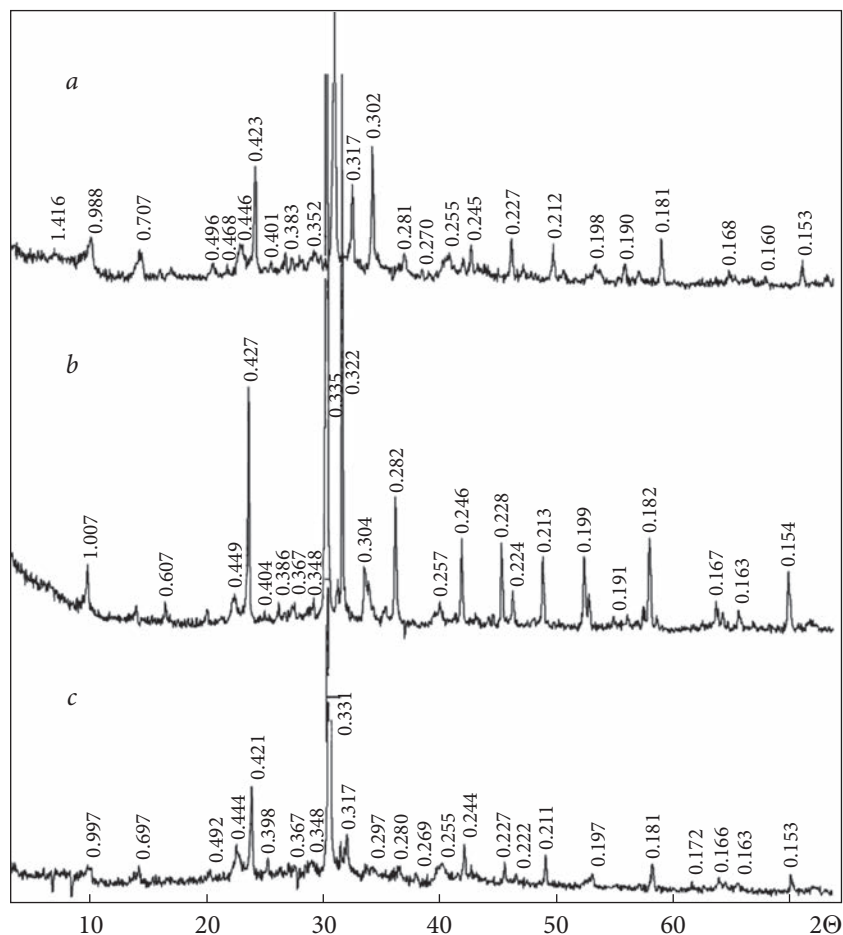


Fig. 3.1. XRD patterns of pelagic sediments of the Black Sea (a), the Kuyalnik estuary (b), and the Azov Sea (c)

K_2O . Aqueous glauconite suspension with 39.5% of water had the following physicochemical indices: pH 7.7; Eh +210 mV; shear stress 405 Pa; stickness 1250 Pa. Clay fraction contained 22.5% of 1–10 μm particles and 6.8% of particles under 1–10 μm .

The selected materials were studied using XRD, sorption, rheological, SEM, chemical and biomedical methods [16, 17, 21, 326, 330]. The results of investigation are partially shown in Figs 3.1 and 3.2 and in Table 3.1. Physicochemical and microbiological tests were conducted according to the procedures described in [47, 48].

According to the data shown in Fig. 3.3, the process of peloid sediment biocolloidal reduction proceeds with symbate change in its indices: lgCFU, peloid suspension viscosity and reduced iron content. The data of Table 3.1 confirm this

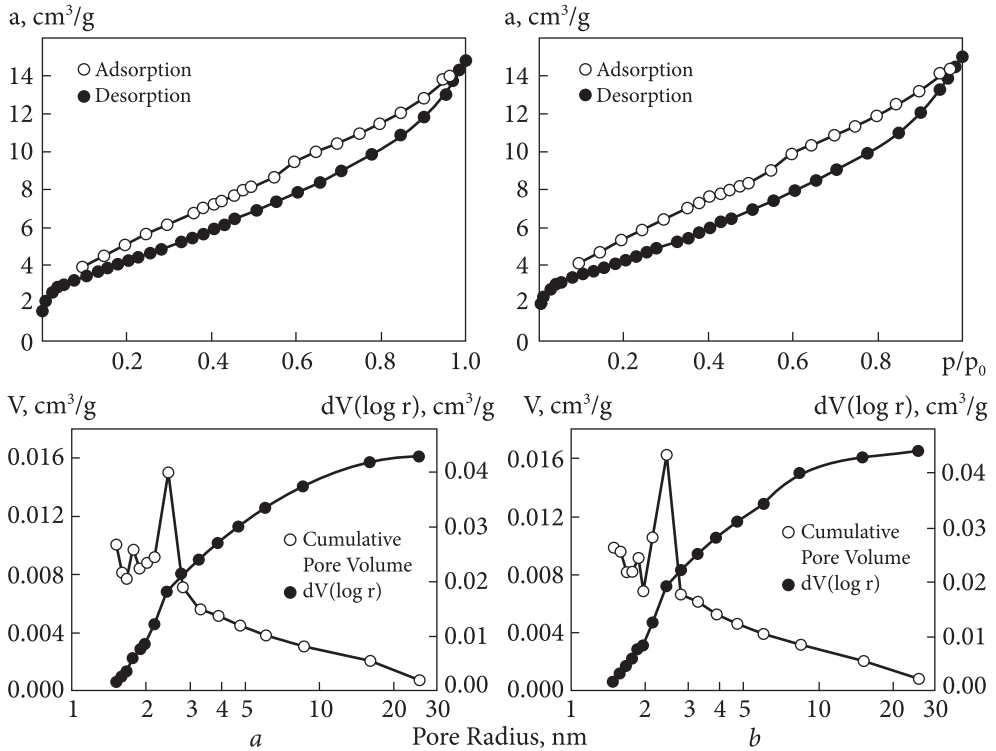


Fig. 3.2. Nitrogen sorption isotherms ($a - p/p_0$) and dependences of pore size ($V - r$, $dV(\log r) - r$) for two Black Sea pelagic sediment samples (a and b) taken from different distant points

conclusion. The correlation between biocolloidal reduction indexes points that the investigated process runs according to the general complex biocolloidal mechanism under the influence of organism metabolism. Its products affect the structural and nanochemical transformations of the peloid inorganic components [332], which, in turn, influences the rheological properties of suspensions-tested. This is also proved by preliminary investigations of the biocolloidal recovery of the pelagic sediments [102].

First of all, as for microbiological processes, the obtained data (Fig. 3.3, Table 3.2) clearly indicate their significant role in the formation of conditions for the biocolloidal reduction of iron contained in peloids. This is also pro-

Table 3.1. Minerals of pelagic sediments of (1) the Black Sea, (2) the Kuyalnik Estuary, (3) the Azov Sea

Pelagic sediment, No.	Minerals
1	Quartz, mica, glauconite, chlorite, kaolinite, field spar, montmorillonite
2	The same
3	» »

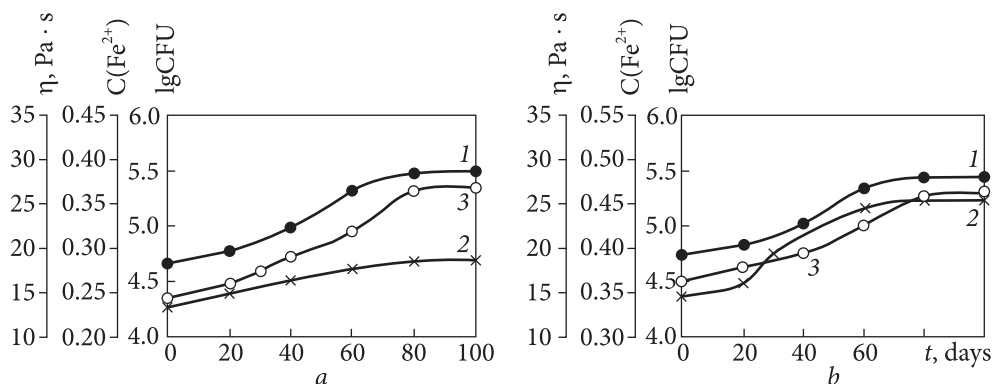


Fig. 3.3. Dependence of 1 — colony forming units (lgCFU); 2 — concentration of reduced iron $C(Fe^{2+})$; and 3 — viscosity (η , Pa · s) of the Black Sea (a) and the Kuyalnik Estuary (b) pelagic sediments on the time of their biocolloidal treatment

Table 3.2. Dynamics of average indices in biocolloidal reduction of the Kuyalnik Estuary sediments depending on the duration of exposure

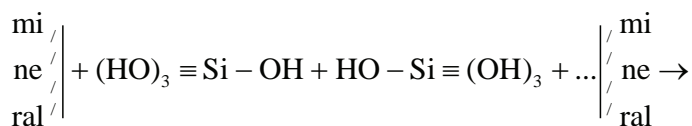
Exposure duration, days	Moisture, wt%	Shear stress, Pa	Concentration of reduced iron, C_{Fe}^{2+}	pH	Eh, mV
0	53	1211	0.35	6.9	-179
30	53	1164	0.39	6.7	-189
60	53	1149	0.44	6.8	-192
90	53	1128	0.51	6.9	-195
120	53	1187	0.50	6.9	-183
150	53	1196	0.49	6.8	-177

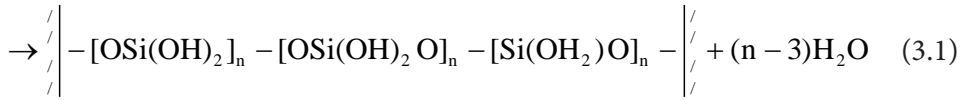
ved by the literature data, which show that bacterial reactions in nature lead to the formation of unstable nanostructures of the layered double hydroxides $Fe^{2+}-Fe^{3+}$ (LDX) type or Green Rust (GR). These nanostructures are easily transformed during oxidation into lepidocrocite, hematite and magnetite [90, 117, 119, 121, 122]. The process of chemical transformation of the GR of $GR(CO_3^{2-})$ and $GR(SO_4^{2-})$ types into $\gamma-FeOOH$ (lepidocrocite) is considered in [117]. In [90, 119, 121, 122], the processes of phase formation aided with microorganisms are described. Microorganism interaction with minerals and organic matter in natural ecosystems has been studied in [121]. It was also established that non-fermentative bacteria are adopted to the bacterial iron reducing mechanism and breath with help of iron, as well as fermentative bacteria of IRB, DIRB (dissimilation iron-reducing bacteria). A complex investigation of the processes of reduction, solution and iron extraction from the mentioned nanodispersed minerals has been completed. And the general role of IRB in the GR formation in natural con-

ditions was confirmed [92, 94, 96, 97]. Such a process mechanism comes to the reduction of Fe^{3+} and interaction of Fe^{2+} ions with mineral structure. The processes in sea water have their own features. Bacterial reactions in such conditions occur with aid of both iron-reducing bacteria *Clostridium* sp. uncultured, and sulfate-reducing bacteria *Desulfovibrio caledoniensis* (SRB). The vital activity of the latter is activated by the pyrite FeS_2 particles with the formation of $\text{GR}(\text{SO}_4^{2-})$ [92, 94, 97, 122]. DIRB slows down this process [96]. Works [94, 102] consider an interaction mechanism between SRB and DIRB. The finding in [102] have proved that in a presence of *Shewanella putrefaciens* (DIRB), the $\text{GR}(\text{CO}_3^{2-})$ and $\text{GR}(\text{SO}_4^{2-})$ are formed. Their proportion depends on the ratio between carbonate and sulfate concentration (C) in the solution. At $C \geq 0.17$ only $\text{GR}(\text{CO}_3^{2-})$ is formed, and at $C < 0.17$ there is a mixture of $\text{GR}(\text{SO}_4^{2-})$ and $\text{GR}(\text{CO}_3^{2-})$ [102]. As follows, in the case of solution-air contact, it is difficult to obtain pure $\text{GR}(\text{SO}_4^{2-})$ structures, which can accordingly influence the results of kinetic investigations of $\text{GR}(\text{SO}_4^{2-})$ formation in sulfate solutions due to uncontrollable migration of CO_2 from air into the solution, and also complicates unmistakable modeling of GR formation processes in the presence of some types of microorganisms, whose vital activity product is CO_2 .

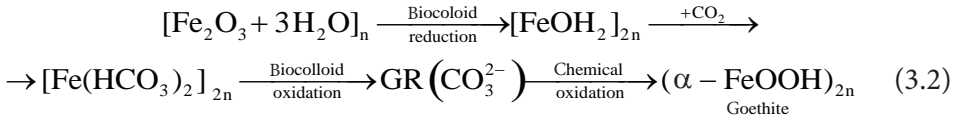
Thus, the analysis of literature data indicates that the GR formation in natural conditions at oxygen deficit (deep-water processes in sea water and in groundwater) is conditioned by the microorganism vital activity, iron-reducing ones foremost. As in natural conditions in most cases, concentration of SO_4^{2-} ions is low, $\text{Fe}^{2+} - \text{Fe}^{3+}$ LDX of $\text{GR}(\text{CO}_3^{2-})$ type forms mostly. The last ones are unstable substances and so they are active reductants. Their chemical activity increases as well since the GR particle sizes fall in the range of typical nanosizes (10-100 nm). It is quite possible that all aforesaid in specific conditions provokes some not studied yet nanochemical reactions both in IASSMs, NIASSMs and in PS with other iron oxide minerals, and metabolism is a prime mover here. That is why a disadvantage of the conducted investigations can be the lack of proper attention to colloid-chemical mechanisms of transformation processes and their role in the formation of more complex mineral and polymineral iron oxide-silicate systems and pelagic sediments.

Relating to completed study (Figs 3.1-3.10), some conclusions can be made, which add and specify already known or substantiate new conceptions concerning biocolloidal processes in pelagic sediments followed by nanochemical, nanostructural, and physicomachanical interphase contact interactions, conditioned by the following chemical and bacterial processes and reactions [7, 333]:

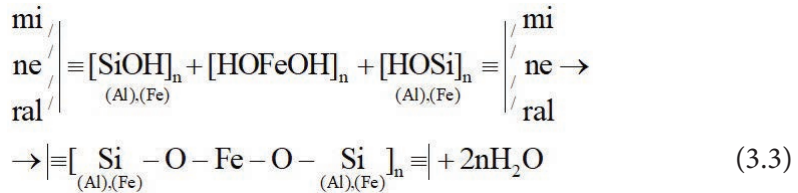




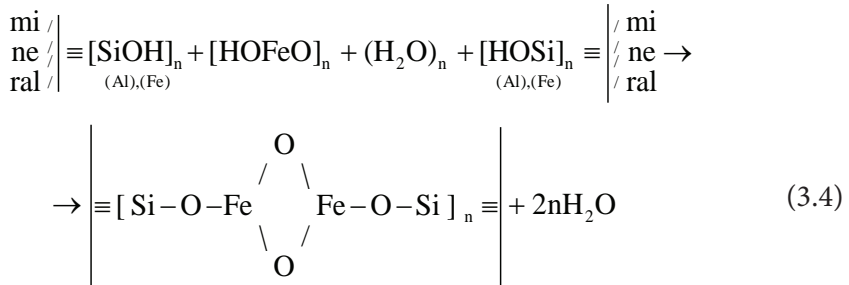
(interphase nanochemical structure polycondensation of silicate nanoclusters and nanoparticles);



(biocolloidal iron reduction-oxidation aided with biogeocenosis);



(interphase nanochemical interaction and structuration in NIASSMs aided with nanoclusters and nanoparticles of silicon hydroxide, bivalent iron, aluminosilicates or GR);



(interphase nanochemical contact interaction in IOHSSs aided with nanoclusters and nanoparticles of goethite formed as a result of partial microbiological oxidation of preliminary reduced bivalent iron hydroxide into GR and its further chemical oxidation).

As we can see from some shown processes and reaction schemes, there are chemically and microbiologically formed nanoclusters and nanoparticles of silicon and iron hydroxides, and aluminosilicates, involved in interphase nanochemical contact interactions [7, 333]. Iron compounds play the general role in the processes, which is confirmed by the data in Fig. 3.3 and Table 3.2. Herein, nanocluster structural interactions between separate microparticles according to scheme (3.3) are conditioned by the —O—Fe—O—Fe—O— bonds. This does not fully correspond to the character of the shear stress curve for peloid disper-

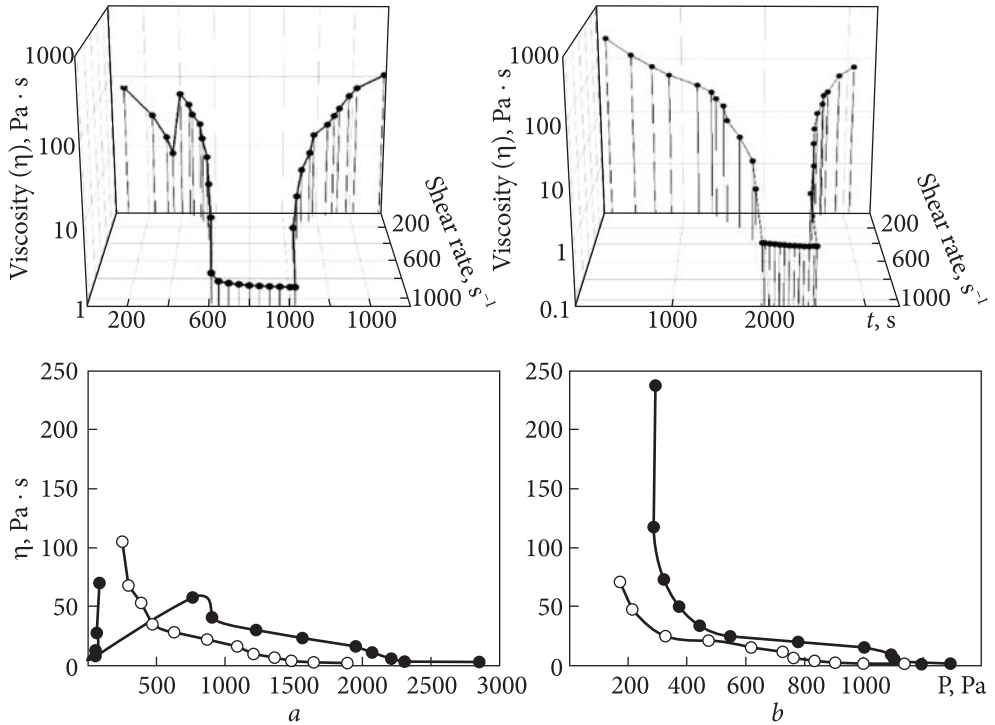


Fig. 3.4. Rheograms of the Black Sea pelagic sediments with moisture of *a* — 65% and *b* — 77%; ● — direct way; ○ — reverse way of curves

sion [333], which is also shown in Fig. 3.3. Thus, according to the data obtained, as the exposure time of dispersion to biogeocenosis presence increases, the quantity of reduced iron increases, and shear stress of dispersion increases as well, which indicates a formal dispersion nanostructurization by the scheme (3.3). However, the more detailed investigation [333] has shown that concurrently with the reduction processes of unstable $\text{Fe}(\text{OH})_2$ and GR nanostructure formation, simultaneous processes of their microbiological and chemical oxidation into nanogoethite occur. This happens due to the air oxygen action and following contact interactions by the scheme (3.4). According to this scheme, the quantity of iron–oxygen bonds increases by 1.5 times if compared to the scheme (3.3). This indicates a higher strength and stability of interphase contact nanostructured bonds in systems of the NIASSM type, which include Fe^{3+} compounds. At the same time, the bonds formed by the scheme (3.3) are intermediate and less strong. They are also less stable, since such structures are liable to transformation due to oxidation processes which weaken contact interactions, i.e. decrease shear stress. That is why only nanogoethite participates in contact nanostructured interphase processes between separate mineral colloidal and microparticles of PS at the final stage of

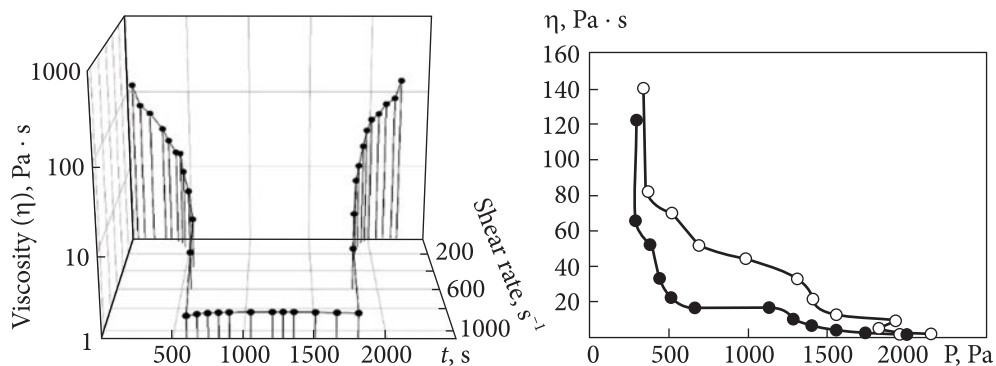


Fig. 3.5. Rheograms of the Kuyalnik pelagic sediments with 55 wt% moisture: ● — direct way; ○ — reverse way of curves

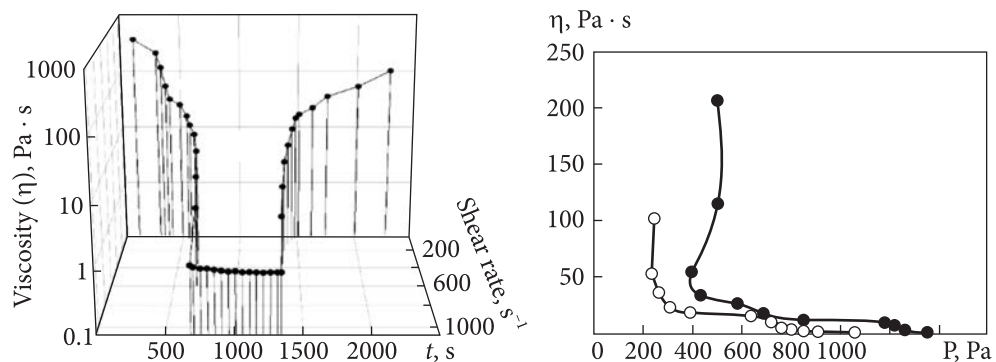


Fig. 3.6. Rheograms of the Azov Sea pelagic sediments with 77% of moisture: ● — direct way; ○ — reverse way of curves

biocolloidal interactions. This can be seen from the obtained data and their analysis. In addition to the biogeocenosis effect, physico-mechanical nanostructuring processes play an important role in complex biocolloidal processes in IASSMs, NIASSMs and peloid sediments. The last ones associate with the chemical-mineralogical composition of PS clay components (Fig. 3.1), their sorption (Fig. 3.2), and rheological properties (Figs 3.4-3.9), which are substantially dependent on the moisture of dispersion composition. Peloid sediment composition includes clay minerals like kaolinite, hydromica, montmorillonite as part of bentonite and glauconite (Figs 3.1 and 3.10). Montmorillonite is the most inclined to nanoparticle formation among them. Nanoparticles are located in contact zones between colloid particles (Fig. 3.10, *d*). Hydromica demonstrates the same character but with bigger nanoparticle sizes (Fig. 3.10, *f*). Small colloidal particles of glauconite compose aggregates of nanoparticles. The surface of bigger particles is usually partly covered with small nanoparticles (Fig. 3.10, *e*). A similar structuration aid-

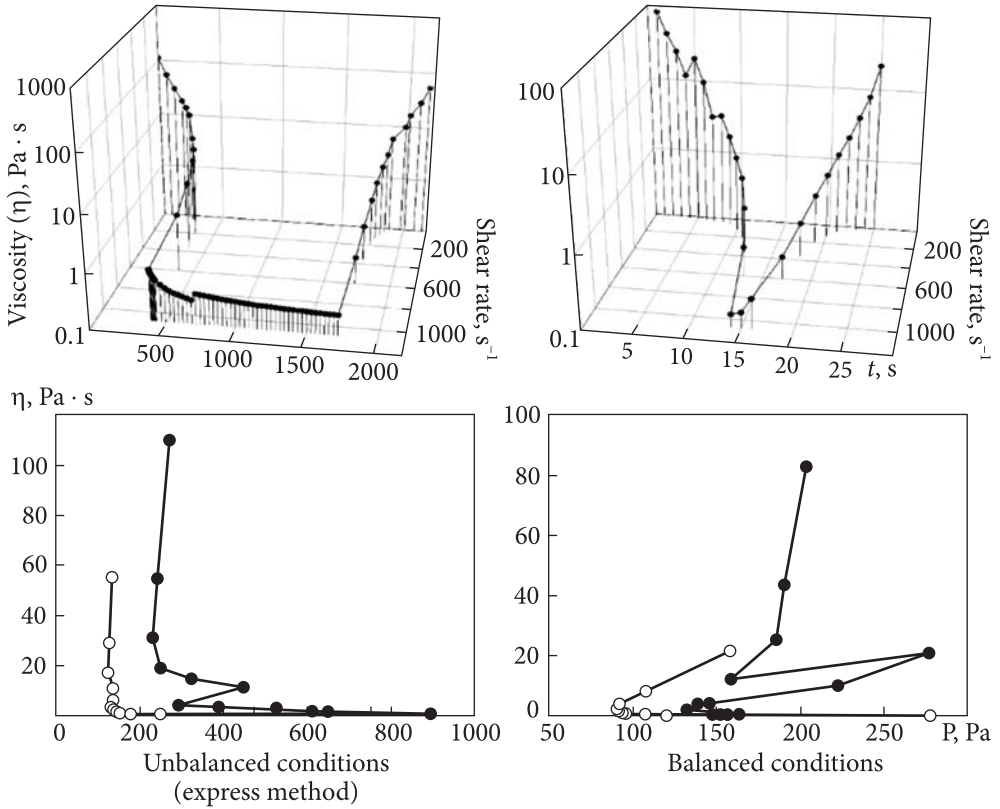


Fig. 3.7. Rheograms of bentonite (montmorillonite) clay suspension with 55% of moisture: ● — direct way; ○ — reverse way of curves

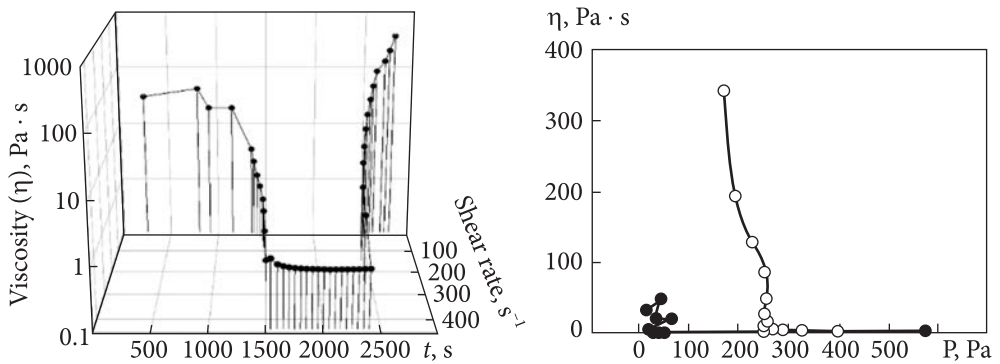


Fig. 3.8. Rheograms of glauconite suspension with 50% moisture: ● — direct way; ○ — reverse way of curve

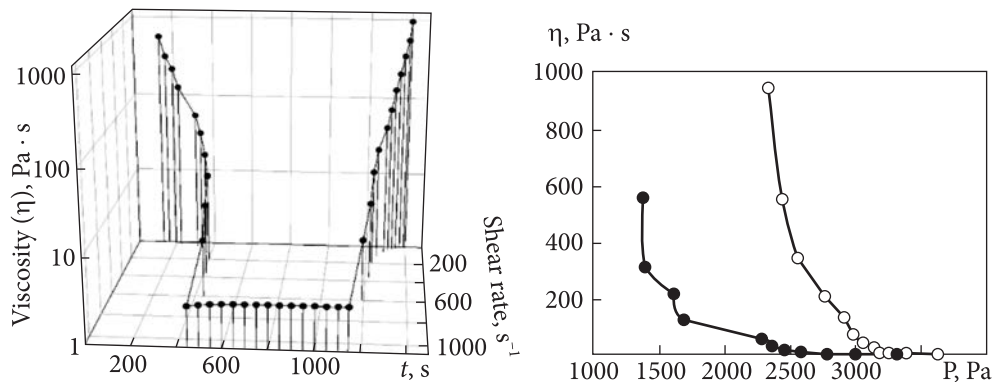


Fig. 3.9. Rheograms of hydromica suspension with 50% moisture: ● — direct way; ○ — reverse way of curve

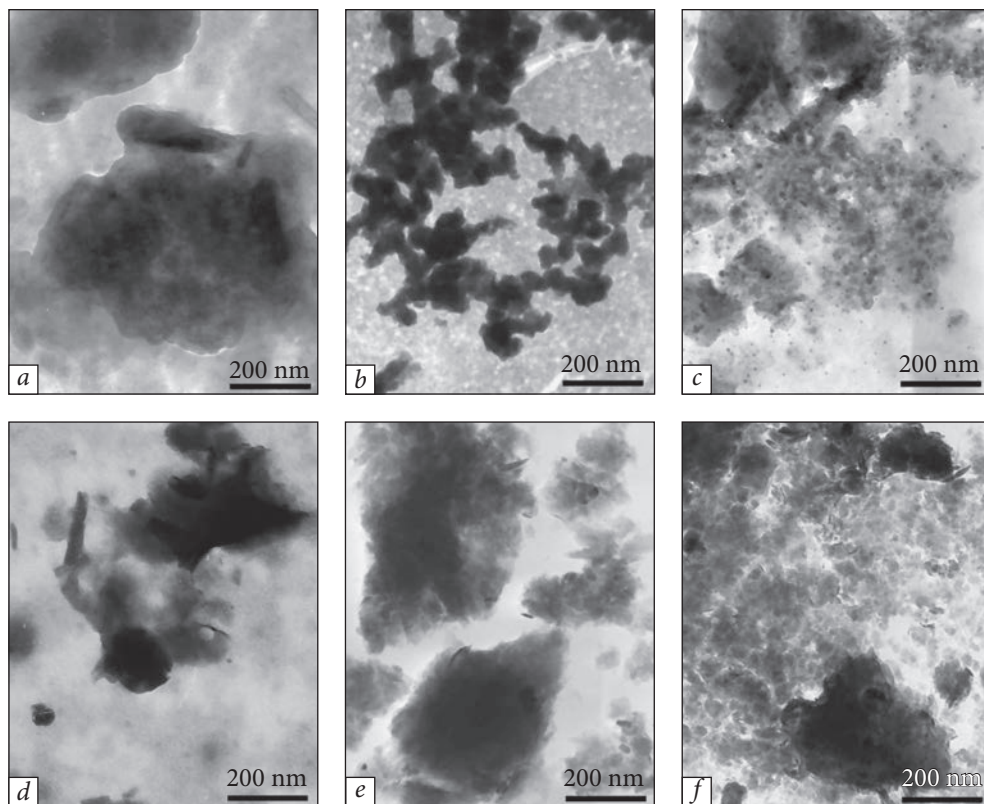


Fig. 3.10. SEM images of peloid sediments and clays: *a* — the Black Sea sediment, *b* — the Kuyalnik sediment, *c* — the Azov Sea sediment, *d* — bentonitic clay, *e* — glauconite, *f* — hydromica

ed with clay particles is observed in the Black Sea (Fig. 3.10, *a*) and the Azov Sea (Fig. 3.10, *c*) peloid sediments.

The Kuyalnik Estuary peloid sediment has aggregates of clay mineral nanoparticles (30-100 nm in size) firmly connected by the phase contacts (Fig. 3.10, *b*) [7]. The above findings are also confirmed by adsorption data (Fig. 3.2) where different samples of the Black Sea peloids exhibit relative structural-sorption properties. For example, their effective pore radius is close to 2.5 nm. By stoichiometric conceptions, this witnesses that minimal nanoparticle sizes approach 4 nm. It is therefore quite possible that they are connected with phase contacts as well. It has already been indicated for the Kuyalnik peloid (Fig. 3.10, *b*). Physico-mechanical properties of IASSMs, NIASSMs, and PS are mostly affected by moisture mass content in their composition. Thus, comparatively low-concentrated peloid suspensions from the Black Sea (35% and 23% of solid phase) are characterized by the thixotropic flow mode (Fig. 3.4). Abnormal rheopectic flow mode for the Kuyalnik peloid is observed at a solid phase mass fraction of 45% (Fig. 3.5). As it has been mentioned, this is explained by strong phase nanocontacts in aggregates of colloidal particles (Fig. 3.10, *b*). The Azov Sea pelagic sediment suspensions at 23% moisture mass fraction are characterized by the thixotropic flow mode, similar to low-concentrated the Black Sea peloid (Fig. 3.4, *b*). At the same time, flow curves for concentrated suspensions of bentonite clay (Fig. 3.7), glauconite (Fig. 3.8) and hydromica (Fig. 3.9) have an abnormal character. The same character was also detected for concentrated suspension of IOHSS from marine PS, the composition of which was 16% of clay components and 84% of goethite [333]. All four samples had concentrations close to the Atterberg plasticity limit, which separates plastic state from conditionally solid (semisolid). These results need additional description using conceptions of classic mechanics.

Fig. 3.11 shows theoretical loading and unloading curves typical for elasto-viscous state of tested material. While loading (OCA curve segment), solid material elastic state turns into viscous one (OA curve segment). While unloading (AD segment), plastic sample properties disappear. Along with that, elasticity usual for solid (semisolid) material returns in condition of irreversible process (point B). With the further sample loading (dashed curve BA'), its plastic properties appear in the AA' segment and disappear in the A'D' segment. The estimated viscosity curve for plastic flow in the CAD segment (Fig. 3.11, curves 1 and 2) shows that the change in the sample viscosity under loading is described by curve 1 at lower shear stress than under unloading (curve 2). Those curves (1 and 2) as compared with respective abnormal rheological curves in Figs 3.7-3.9 and in [333], first of all show that the curves have similar curve way as a result of identical plastic flow mechanism based on an effect of system transition from solid-like to plastic state in conditions of phase contacts formation [7]. Interaction of mi-

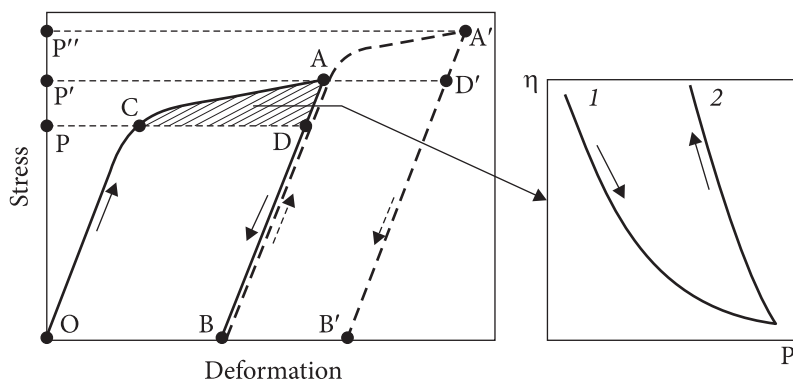


Fig. 3.11. Loading (OCA) and unloading (ADB) curves for an elastoviscous material: CAD — plastic flow area; OC and DB — elastic deformation; BAA'B' — repeated loading and unloading; CA, AA', 1 and 2 — loading and unloading curves in conditions of plastic flow; η — viscosity

cro- and colloidal particles in the phase contacts, according to Rebinder is conditioned by short-range forces of cohesion or adhesion. The last ones are realized on a surface much larger than the surface of elementary lattice. Adhesion of solid-like structures in such conditions is formed from not less than 10^2 - 10^3 atomic bonds, i.e. at the nano- or colloidal level with the formation of a structural-mechanical barrier according to Rebinder. Such bonds can be seen in Fig. 3.10. They are formed with nanoparticle participation. As distinct from the coagulation ones, they dissociate irreversibly, as shown by the experimental curves in Figs. 3.7-3.9 and theoretical curves in Fig. 3.11. Thus, it can be considered as proven that the abnormal rheological curve trend for concentrated suspensions of clay minerals, IOHSS, PS, and peloids is conditioned by irreversible dissociation of interface solid-like contacts built from nanoparticle blocks of silicates, aluminosilicates, and iron oxide-silicates. The latter, as mentioned above, play the general role in those processes [reactions (3.1), (3.3), and (3.4)] and are intensified by metabolism of microorganisms as part of biogeocenosis (scheme (3.2)).

The results obtained are of not only fundamental, but also of practical importance for scientific reasoning the use of peloid sediments and their compounds as materials for treatment of burnt surfaces, injuries and articulations, in cosmetology, in ecotechnologies for environment protection and other purposes. It seems interesting to use general mineral compounds of peloid sediments in a pure form: clay minerals after their processing with biogeocenosis. Montmorillonite (as a compound of bentonites) and glauconite are the most promising among such minerals. The tested bentonite for applications had a total bacterial count (CFU/g) of $1.1 \cdot 10^5$. Pathogenic staphylococcus, intestinal enterococcus and blue pus bacillus were absent. Bentonite proved to be compliant to sanitary needs. The samples had no bactericide effect, but they can be used as protection of ecological

bacteria from UV-radiation or from toxic substances due to inorganic nutrients (microelements) and ability for ion exchange. They also can be used as a minimal vivifying substrate for bacteria breeding. Bentonite was determined to give a therapeutic and prophylactic effect in case of gastric ulcer and hepatitis treatment. Those effects originate due to adsorption and ion exchanging organism detoxification with simultaneous anti-inflammatory and positive immunodeficiency action, and due to the action of iron oxide-aluminosilicate nanoparticles.

Glauconite exhibits a moderate bactericide action. Its sample was determined to contain:

- saprophytic bacteria which produce catalase;
- microorganisms that assimilate nitrogen;
- microorganisms that assimilate carbon;
- heterotrophic bacteria, which produce surface-active amino acids;
- manganese and iron redox bacteria.

There were determined no mico- and spore-forming bacteria, yeasts, actinomycetes and streptomycetes. Glauconite was the most effective for treatment of dexamethasone arthrosis and endogenic intoxication.

In addition to the advantages stated, it was proven that tested clays and peloids with their content are effective for state correction of hemophilic genic-broken blood coagulation due to their chemical composition (presence of iron and microelements) and extremely high adsorption ability [52].

Also, bentonite and glauconite were studied in modeling conditions of their biogeocenosis impacted influence on the properties of more complex materials, namely peloids and pelagic sediments. The conducted investigations allowed concluding that the change of physicochemical properties of such materials correlate with nanostructural nanochemical clay mineral transformations with oxide and silicate compounds of iron — the schemes (3.1)-(3.4). In turn, the latter ones are connected with changing of therapeutic properties of peloids and clays in the peloid composition.

Thus, nanostructural nanochemical processes aided with biogeocenosis in the iron oxide-aluminosilicate systems and materials (IASSM)) with formation of nano- and microstructural NIASSMs were studied by physicochemical, colloid-chemical and biocolloidal methods using theoretical concepts of physicochemical and classic mechanics, and geomechanics. Since general properties of such systems closely match the properties of peloid sediments (PS), the Black Sea and the Azov Sea clay-containing PS and other peloids, as well as general iron-containing clays were selected as main research materials. The experimental findings show that nanostructural and nanochemical processes in IASSMs, NIASSMs and sediments based on them are controlled by appropriate metabolic processes in microorganisms. Microorganisms are the part of studied systems and sediments and

were shown to consist generally of iron-reducing and autotrophic bacteria. They produce surface-active substances (surfactants), namely amino acids and other organic compounds, which take part in physicochemical hydration self-dispersing processes of micro- and macroparticles in IASSMs and PS up to colloids and nanoparticles. At the same time, due to bacterial reactions, Fe^{3+} from micro- and macroparticles turns into Fe^{2+} in the emerging nanoclusters and nanoparticles of iron-containing minerals (hydroxides and silicates), which then transform, chemically or microbiologically, into unstable layered double hydroxides Fe^{2+} and Fe^{3+} (Green Rust) under the action of CO_2 and O_2 from air, mainly of the $\text{GR}(\text{CO}_3^{2-})$ type. Respectively, chemical processes between O_2 of air and Green Rust lead to their sequential transformation into such nanostructures: $\text{Fe}_3\text{O}_4 \rightarrow \gamma\text{-FeOOH}$ (lepidocrocite) $\rightarrow \alpha\text{-FeOOH}$ (goethite). The last in the contact zones of colloidal, micro- and macroparticles takes part in the nanochemical processes of creating coagulation-condensation structural bonds in NIASSMs. The bonds affect their rheological and other physicochemical characteristics. It is shown that with increasing concentration of solid phase in NIASSMs of the peloids type, contact bonds change as follows: coagulation \rightarrow interphase \rightarrow solid-state \rightarrow crystallization. Thus, the flow of NIASSM dispersions with increasing concentration of solid phase and the content of nanoparticles changes in the following sequence: thixotropy \rightarrow dilatancy \rightarrow rheopexy \rightarrow hyperanomaly of viscosity \rightarrow ultraanomalous plastic flow of solid structures. With the help of theoretical ideas of physicochemical and classical mechanics and geomechanics, an abnormal plastic flow mechanism is established. There are provided examples of peloids and individual clays (bentonites and glauconites) application in spa and medical practice as antibacterial compositions and for the correction of the genetically damaged blood coagulation system in hemophilia.

Conclusions. Processes of nanochemical structuration in iron oxide-aluminosilicate systems and materials (IASSMs) aided with biogeocenosis have been investigated using physicochemical, colloid-chemical, and biological methods as well as theoretical concepts of physicochemical and classic geomechanics. Peloid sediments, peloids, and contained in them bentonitic and glauconitic clays were used as examples of such systems and materials. It was shown that nanochemical structuration of such systems and sediments is limited by metabolic processes of microorganisms, first of all, iron reducing ones and autotrophic bacteria producing surface-active substances. At that, bacterial reactions induce transformation of Fe^{3+} micro- and macroparticles of iron-containing minerals into nanoparticles and nanoclusters of Fe^{2+} hydroxides, which chemically or microbiologically transform under the action of CO_2 and O_2 from air into unstable nanostructured layered double hydroxides (LDX) of $\text{Fe}^{2+} \cdot \text{Fe}^{3+}$ (Green Rust) of the $\text{GR}(\text{CO}_3^{2-})$ type. Chemical LDX transformation during further interaction with O_2 from air results in forming of nanogoethite ($\alpha\text{-FeOOH}$), which disperse minerals by the general

scheme (3.4) in contact zones of micro- and colloidal particles of silicate or aluminosilicate minerals by interactions (3.1)-(3.3). Herein, there are formed new iron oxide-hydroxide-aluminosilicate systems with new properties. Along with the general process, clay minerals contained in iron oxide-aluminosilicate systems, peloid sediments and peloids, also take part in structure transformations. On examples of bentonite and glauconite, processes of their structuration in peloid sediment composition were modelled according to concepts of physico-chemical and classical mechanics and geomechanics. It is shown that rheological processes in concentrated clay and clay-peloid suspensions are characterized by abnormal flowing and viscoplastic properties close to the Atterberg plasticity limit. Mechanism of such processes has been determined. Clay minerals were shown not only to influence the properties important for practical use of peloids, but they can also be the basis for creation of antibactericide clay compositions with special properties and of antifiltration membranes for designing different ecotechnologies, which needs separate studies.

3.2. Colloid-chemical and nanochemical processes in peloids based on carbonate- and iron-containing clays

Clay-containing peloids (therapeutical muds) whose role in medical and spa practice is permanently growing are recent or geologically young organo-mineral fine-dispersed sediments of basins. They are formed as a result of biocolloidal decomposition of flora and fauna by microorganisms and simultaneous micro- and nanostructured reconstruction of inorganic peloid basis via complex biocolloidal (colloid-chemical and biochemical) processes [19, 21, 309, 334]. Peloids contain fine- and nanodispersed clay minerals, carbonates, feldspars, quartz, opal, diatomite, microorganisms and microalgae, bioactive organic substances, sulfur and other compounds [21, 309, 335-337]. Medical muds have different properties, and different chemical, mineralogical and microbiological composition. Nevertheless they exert almost the same multifunctional physiological and therapeutic effect on living organism and are used all over the world as ingredients of therapeutic and cosmetic compositions. However, increasing practical use of peloids results in their reserve depletion and decreasing quality. This problem can be solved by both finding new deposits of medical muds and carrying-out systematic physicochemical, colloid-chemical, biocolloidal and medical investigations of peloids from already known and new deposits. Latter should be done for the development of scientific basis of making new high effective peloid compositions and its rational use in balneological and medical areas.

One of the promising ways to solve this global problem is doping with nano-disperse inorganic additives of clays, sorbents and salts into peloids along with complex investigations of their influence on peloids [21, 309, 335-341]. These researches involve long-developed Ukrainian peloids (widespread in the Black Sea and the Azov Sea health-resort zones), as well as recently explored deep-sea (over 2 km) bottom sediments of the Black Sea. It was deduced that bottom sediments of the Black Sea, definitely contained in other seas and oceans (owing to common mechanism of pelagic sediment forming), exhibit unique medical properties [309]. However, the study of influence of nanosized additives on the running in peloids colloid-chemical and nanochemical processes was almost absent. And this was the reason for conducting the studies presented.

3.2.1. Colloid-chemical characteristics of peloids and peloid compositions

A sample of the Black Sea deep-water peloid was taken as an object of our colloid-chemical and biomedical researches. It was prepared according to the recommendations of [19, 21]. Analysis of microscopic images of peloid samples (Fig. 3.12) showed that their particle sizes are from 0.1 to 5-10 μm . Mineral component of peloids is presented by clay minerals, carbonate decomposition of microorganisms products (Fig. 3.12, *a*), sulfide formations (central part of Fig. 3.12, *b*) and rests of protozoa crustaceans (Fig. 3.12, *c*). Fig. 3.12, *d* demonstrates a micrograph of peloid composition added with chemically precipitated nano- and microparticles of calcium carbonate. And in Fig. 3.12, *e*, peloid composition containing nano- and microparticles of calcium carbonate obtained by power-dispersion of initial composition is shown.

Spectral investigation of the chemical composition of different parts of peloid shown on microscopic images revealed the presence of carbonates, aluminum oxides, silicon, iron and sulfides in a broad concentration interval (Table 3.3). The microelemental composition is as follows, wt%: 0.015 Mn; 0.003 Ni; 0.0003 Co; 0.03 Ti; 0.008 V; 0.006 Cr; 0.0003 Mo; 0.0006 Nb; 0.02 Zr; 0.005 Cu; 0.002 Pb; 0.0001 Ag; 0.0001 Bi; 0.006 Zn; 0.0004 Sn; 0.0008 Ga; 0.0003 Be; 0.002 Sc; 0.02 Ce; 0.01 La; 0.003 Y; 0.08 P; 0.005 Li; 0.02 Ba.

The average chemical composition of the peloid used, wt%: 54.57 SiO_2 ; 11.35 Al_2O_3 ; 5.54 Fe_2O_3 ; 8.87 CaO; 1.80 MgO; 0.04 MnO; 1.19 Na_2O ; 1.86 K_2O ; 14.71 LOI (loss on ignition).

On the whole, the investigation of peloids by physicochemical methods [309] showed their full compliance with the medical and spa standards and requirements for their colloid-chemical properties and composition.

Natural iron-containing bentonite clay (Dashukovka section of the Cherkasy deposit) and iron-containing saponite were used as nanoadditives to peloid. They

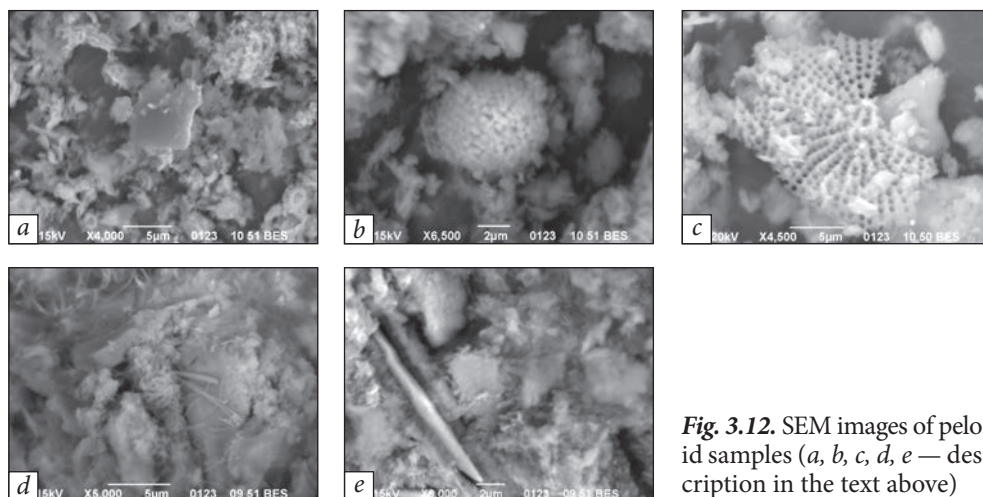


Fig. 3.12. SEM images of peloid samples (*a, b, c, d, e* — description in the text above)

Table 3.3. Energy-dispersive analysis of peloid sample in different spots of microscopic image

Element	Element concentration in different spots of microscopic image, wt%										
	1	2	3	4	5	6	7	8	9	10	11
C	19.95	3.95	12.26	21.15	48.80	4.99	17.13	7.60	12.21	12.19	9.23
O	15.04	60.29	61.23	40.66	37.87	60.00	57.71	45.96	57.00	58.76	60.36
Na	—	0.29	2.15	0.36	0.17	1.95	0.65	0.30	0.43	1.29	6.25
Mg	—	0.35	—	0.85	0.29	0.55	0.63	0.23	1.37	1.38	—
Al	—	12.76	4.36	8.37	3.31	8.11	4.26	2.88	6.72	6.27	5.81
Si	0.86	15.29	14.88	15.82	4.68	17.00	15.46	39.13	13.21	13.30	17.51
S	34.82	—	—	—	0.13	—	—	0.39	—	—	—
Cl	—	—	0.24	—	—	—	0.35	—	0.55	0.43	—
K	—	4.52	1.93	5.86	1.33	0.28	0.95	0.99	1.29	2.04	—
Ca	1.36	1.87	2.39	5.36	2.94	5.93	1.48	1.77	2.92	2.38	0.83
Fe	27.01	0.68	0.57	1.58	0.49	1.19	1.37	0.74	4.28	1.96	—
Br	0.95	—	—	—	—	—	—	—	—	—	—
Total	100	100	100	100	100	100	100	100	100	100	100

were preliminarily ultrasound-treated to obtain micro- and nanoparticles (Fig. 3.13). The chemical composition of bentonite, wt%: 53.61 SiO₂; 14.02 Al₂O₃; 7.63 Fe₂O₃; 0.96 CaO; 4.43 MgO; 0.39 Na₂O; 0.31 K₂O; 18.61 LOI. The chemical composition of saponite, wt%: 46.73 SiO₂; 5.12 Al₂O₃; 2.76 Fe₂O₃; 23.21 FeO; 3.87 CaO; 11.43 MgO; 0.24 Na₂O; 0.26 K₂O; 13.67 LOI. Bentonite was exposed to thermodestruction at 600 °C (Fig. 3.14) by the procedure [341]. Nanosized calcium

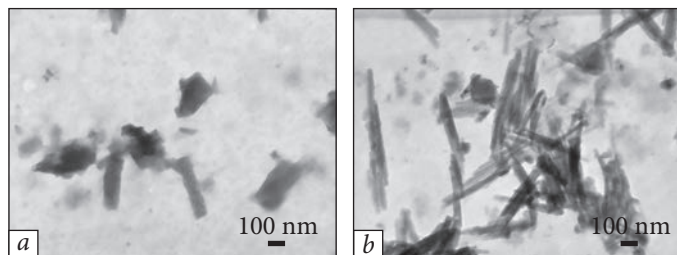


Fig. 3.13. Micrographs of Cherkasy bentonite (Ukraine) components: *a* — montmorillonite, *b* — attapulgite

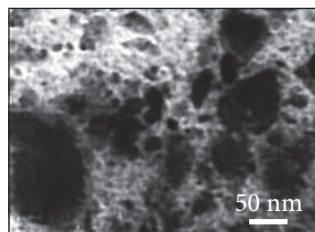


Fig. 3.14. Micrograph of nanoparticles of burnt at 600 °C bentonite with organic precursor

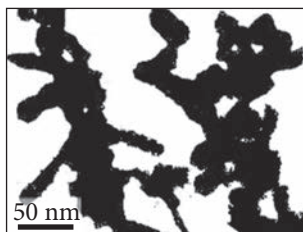


Fig. 3.15. Micrograph of calcium carbonate nanoparticles

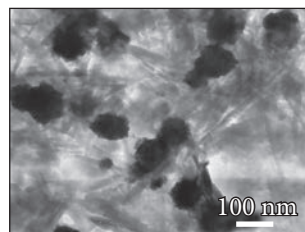


Fig. 3.16. Micrograph of polymineral clay with calcium carbonate additive

carbonate as an additive to peloids was prepared by chemical precipitation according to the method [342]. The obtained particle size was within 20-100 nm (Figs 3.14-3.16). Physiological tests of peloid compositions with nanomaterials (Fig. 3.12) were conducted according to the recommendations [343]: testing of composition influence on different systems of healthy animal (white Wistar rats) organism. Hereat, peloid and peloid composition influence on central nervous system (CNS) and liver were tested by a thiopental probe (0.75 mg of sodium thiopental per 100 g of body mass). The falling asleep time (minutes after barbiturate injection) was taken in account. It characterizes the influence of compositions on CNS. On the other hand, medication sleep duration characterizes antitoxic ability of the liver. Urine formation (uropoiesis) indexes were determined as well.

Composition components were transported into animal organism on a special stand by immersion of rat tails into tested suspensions for 2 h at 40 ± 1 °C.

3.2.2. Biomedical investigation of activity of NIASSMs and PSs based on carbonate-containing peloids

Data given in Fig. 3.17 show a skin-resorptive effect of natural bentonites on the functional liver state of lab animals. Addition of 5 or 10% of bentonite into peloid almost does not influence medication sleep after metabolic probe with barbiturates. This assumes [343] that such compositions have no neg-

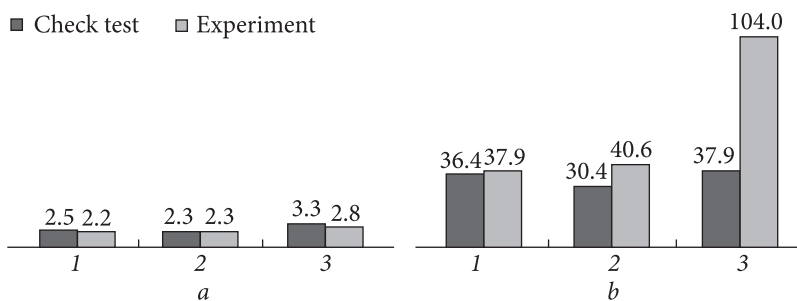


Fig. 3.17. Duration (in min) of *a* — falling asleep and *b* — sleep of laboratory animals after addition of 1 — 5%, 2 — 10%, and 3 — 15% of natural clay into peloid

ative influence on the central nervous system (CNS) and liver. An increase in the bentonite concentration up to 15% or addition of 5% of saponite clay into peloid composition decelerate metabolic processes in liver, which manifests itself by prolongation of animal metabolic sleep during thiopental test. At the same time, the functional state of CNS remains at almost the same level.

Testing of functional state of conventional animal kidneys under the skin-resorptive effect of peloids with nanoadditives showed that functions of kidneys remain almost the same after addition of 5% of bentonite clay. Increase in the clay additive up to 10% leads to negative effects, which manifest themselves in decreasing primary urine filtration in nephron glomerulus. This causes decrease in diurnal diuresis by 1.5 times, in diurnal urine excretion by 1.2 times and in creatinine by 1.6 times.

Addition of 5% of saponite clay into peloids stimulates mutually exclusive processes of uropoiesis (urine formation): primary urine filtration and urine reabsorption. At the same time, we can see no changes in diurnal diuresis, increase in creatinine excretion by 1.5 times and chlorides by 1.3 times. Daily chloride excretion and reaction of daily urine remains unchanged.

The investigation of the influence of thermodeconstructed at 600 °C bentonitic clay on the biological activity of peloids showed (Fig. 3.18) that addition of 5% and 10% into peloid changes this index notably. But its influence on CNS remains without changes, and antitoxic liver ability increases. The latter is confirmed by decreasing medication sleep by 3 times for 5% of bentonite and by 1.9 times for 10% of bentonite.

Rat uropoiesis improves (Fig. 3.19) with addition of 10% of burnt bentonite into peloid. Increase in daily diuresis is determined by growth of the primary urine rate and fixed reabsorption of water in the tubular kidney structure.

Addition of 5, 10, and 15% of chemically precipitated calcium carbonate (Fig. 9) showed that the functional state of CNS is stable but the antitoxic liver ability increases by 2-3 times. Addition of 5 and 10% of calcium carbonate does not change the kidney functional state while skin-resorptive using. Addition of 15% CaCO_3

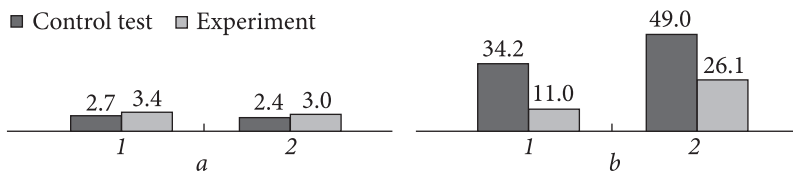


Fig. 3.18. The influence of addition of bentonite burnt at 600 °C on the duration (min) of *a* — falling asleep time and *b* — medication sleep of lab animals. 1 — 5% and 2 — 10% of bentonite

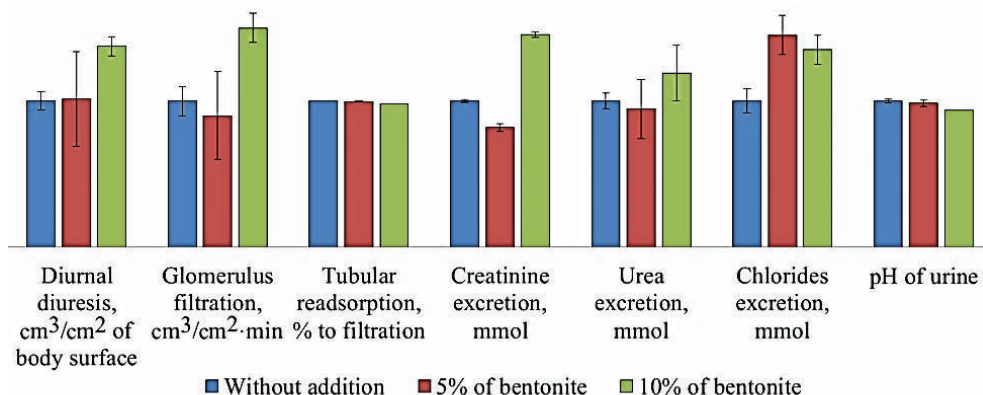
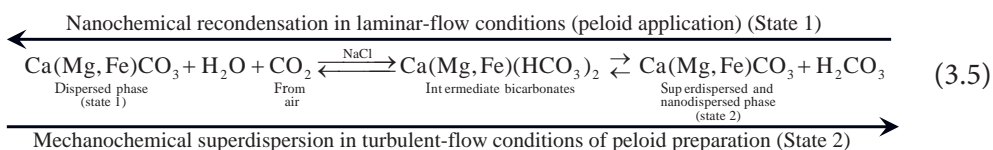


Fig. 3.19. Skin-resorptive effect of peloids with 1 — 5% and 2 — 10% of bentonite additive (burnt at 600 °C) on the kidney functional state of Wistar white rats

leads to increasing the primary urine rate in nephron glomerulus by 1.5 times with decreasing volume of reabsorbed water in the tubular kidney structure. Besides, the excrete kidney function is intensified. This is evident thanks to increase in creatinine excretion by 1.5 times and urea by 1.12 times. Chlorides are excreted from rat organism more actively as well.

However, the mentioned results were obtained for peloid compositions with artificially added calcium carbonate suspension with nanoparticles. According to [347], their role decreases with time owing to aging of clay-carbonate compositions in the quiescent state due to isothermal distillation process. On the other hand, the same paper [347] shows that in open dissipative systems (mixing conditions), nanochemical dispersion of carbonate microparticles with formation of nanoparticles in condition of availability of dissolved NaCl and air CO₂ occurs, which can be demonstrated by the scheme:



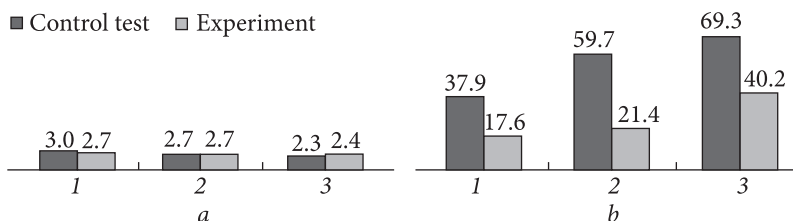


Fig. 3.20. Influence of calcite nanoparticles on the duration (min) of *a* — falling asleep, and *b* — medication sleep of tested animals: 1, 2, 3 stand for 5, 10, 15% of calcite, respectively

According to the scheme (3.5), it is possible to disperse carbonate microparticles from native salt peloids up to nanoparticles using intensive mixing with a nanochemical dispersion mechanism and subsequent recondensation described in [347]. Indeed, rheological investigation of the model composition (90% montmorillonite clay and 10% microsized calcium carbonate) prepared according to the recommendations [347] showed change in peloid suspension indexes after intensive mixing. Thus, according to Table 3.4, the effective viscosity of 50% clay-carbonate aqueous suspension increases in the conditions of long-term mixing and decreases in a quiescent state. This indicates that the process runs according to the scheme (3.5).

Testing of real peloid suspensions after their mixing for 10 h showed that their biological activity (within mistake limits) corresponds to the data for artificially prepared peloid compositions (Fig. 3.20).

Thus, the results undoubtedly indicate that mixing leads to realization of nanochemical dispersion mechanism for carbonate microparticles, which takes place under the action of mechanochemical processes [19, 348]. That, in turn, influences colloid-chemical properties and biomedical activity of peloids.

Additional investigations of biological activity and anti-inflammatory action of peloids with nanoadditives on intact animals in the conditions of ovalbumin

Table 3.4. The dependence of effective viscosity on the mixing duration for clay-carbonate suspension

Duration of mixing (1) or quiescent state (2)	Viscosity of 50% peloid suspension, Pa · s		Duration of mixing (1) or quiescent state (2)	Viscosity of 50% peloid suspension, Pa · s	
	Intensive mixing state (1)	Quiescent state after intensive mixing (2)		Intensive mixing state (1)	Quiescent state after intensive mixing (2)
0 min	0.83	15.50	10 h	15.70	8.90
10 min	5.30	14.30	3 months	—	2.30
1 h	10.20	10.10			

arthritis modeling showed that preventive way of medical mud application leads to a significant effect including improvement of metabolic and immunity indexes under inflammation and increase of glucocorticoid background in organism.

Thus, studies of influence of colloid-chemical and nanochemical processes aided with nanoparticles of montmorillonite and calcium carbonate contained in bentonites, compositions from ferrous clays and deep-water marine clay-containing peloids (used as medical muds) have been carried-out. They showed that natural bentonite which consists of 90% of montmorillonite, 4% of CaCO_3 and 6% of quartz sand, almost does not influence their biomedical properties. Otherwise, addition up to 15% of burnt at 600 °C bentonite increases the biomedical activity of peloid compositions by 2-3 times. It occurs due to the formation of nano- and microparticles during rehydration processes. A similar effect on the peloid composition balneological properties is shown for nanoparticles of calcium carbonate. On the other hand, carbonate and montmorillonite macro- and microparticles, included in the bentonite composition almost does not influence the biomedical indexes of peloids.

Conclusions. Analysis of the experimental results indicates that addition of natural bentonites and saponites into peloids has almost no effect on biological activity of medical mud. Also, it is stated that peloid bioactivity increases with increasing up to 15% of burnt bentonites and calcite addition.

These results show that increase in the concentration of bentonite or calcium carbonate nanoparticles increases biological activity of peloids. This evidently occurs due to raised sorption and ion-exchange ability of calcite and burnt (and rehydrated while making suspensions) clay minerals in bentonite [309, 341, 344, 345]. At the same time, nanoparticle formation process is suppressed in natural bentonite, unlike burnt one, in peloids with admixtures of calcite and sodium chloride via the mechanism described in [347], which does not improve biological activity.

The completed investigations and literature data about colloid-chemical and nanochemical transformations of clay-carbonate structures [19, 347] allow the following conclusion to be drawn: the presence of nanoparticles in clay-carbonate peloids (which contain salt media (brine) and have a contact with CO_2 of the air) can lead to considerable effect on the colloid-chemical properties of peloid compositions and their biological activity. The connection between nanochemical transformations, colloid-chemical properties and biological activity of peloid compositions in terms of the mixing state (application on skin or mixing, that is, thermodynamically isolated or open dissipative system, respectively) has been established. That confirms the conclusions made before [19, 347] for other clay-carbonate colloid systems. However, this connection is fair complex and the role of clay minerals in the biocolloidal properties changing has not yet properly clarified. Hence, all that needs further investigations.

3.3. Modeling of biocolloid-chemical modification of disperse marine pelitic sediments and peloids with mineral nano- and microparticles

As mentioned before, fine-disperse clay-carbonate ferrous pelitic sediments and peloids, having a large constant practical importance in medicine, balneology and cosmetology, attract the researchers' attention for many years [335, 338, 339, 349-356]. In particular, such sediments and peloids involve enormous bottom deposits of seas and oceans, for example, the Black Sea deposit of clay-carbonate sapropelic sediments. Their colloid-chemical properties have been studied insufficiently [53, 357] or on model compositions [352, 353].

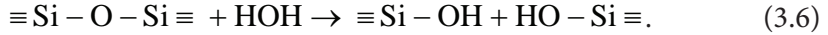
Clay-carbonate ooze sea sediments, similar to peloids from estuaries, are poly-disperse polymineral compositions of biocolloidal origin. They are formed following perennial geomechanical, biocolloidal, geochemical and nanochemical transformations aided with microorganisms and microalgae, salt aqueous and air media, under the influence of complex physicochemical, colloid-chemical and biochemical processes. Depending on combination of exposure to external factors, such processes can be accompanied with micro- and nanostructured transformation of the mineral and organic peloid base. For example, it was supposed that during intensive mixing of peloids, the number of nanoparticles increases and decreases during the rest state in accordance with established [358] occurrence of nanochemical dispersion of model suspensions. These suspensions include nanostructures and microparticles of clay mineral and calcium carbonate opposite to the isothermal distillation effect. Processes in clay minerals [359, 360] and hydration dispersion processes of heat-treated clays up to nanoparticles [345] can considerably influence bioactivity of peloids. At the same time, mechanisms of peloid formation, in particular the influence of geomechanical, physicochemical and microbiological transformations on them, have not properly investigated yet [53, 357, 361].

Therefore, the aim of the current studies of geomechanical and microbiologic processes aided with nano- and microparticles and nanostructures in clay-carbonate pelitic sediments and peloids is to specify (theoretically and experimentally) colloid-chemical mechanisms and features of these processes and to establish connection of biocolloidal and colloid-chemical transformations with changes in the properties and biological activity of bottom sediments, including model systems.

3.3.1. Influence of principles of physicochemical geomechanics on mechanisms of nano- and microparticle formation in iron oxide-alumino silicate clay-carbonate rocks and peloids

Disperse geological transformations of rocks with nano- and microparticle formation are preceded with peloid generation in natural conditions, ac-

accompanied by formation, along with macroparticles, of structure-forming nano- and microparticles. According to [362], such transformations are studied exactly by physicochemical geomechanics (FCGM). As far as water is usually included in polydisperse rocks subjected to mechanical stresses and liquid media, so rocks and peloids are dispersed mostly according to the mechanism of siloxane bonds hydrolytic fracture [315]:



The reaction (3.6) is accelerated by influence of mechanical stresses, which by-turn leads to relieving of dispersion nanocracks formation even in the presence of water traces [23, 315, 362]. Frequency of bond breaking on top of the crack and its growth rate (V) depends on the applied mechanical stress (P):

$$V = V_0 \exp\left[-(U_0 - \gamma P) / RT\right]; \quad V_0 \approx H_0, \quad (3.7)$$

where v is the Debye resonance frequency; γ is the activation volume including over-strain factor $(c/b)^{1/2}$; c is the crack size; b is the crystal lattice parameter; U_0 is the process activation energy at $P = 0$; R is the gas constant; T is the temperature.

At initial stages, the process of follow-up mechanical dispersion starts from reaction (3.6) and formation of at least nanocracks in accordance with equation (3.7). Then, in accordance with the Gibbs-Smith condition [315], grain boundary between crystals A and B is replaced by liquid C:

$$\sigma_{\text{GG}} > \sigma_{\text{AC}} + \sigma_{\text{BC}}, \quad (3.8)$$

where σ is the surface tension at the gas-grain (σ_{GG}), AC boundary (σ_{AC}) and BC (σ_{BC}) boundaries.

The dispersion process runs continuously and may be described by the linear-parabolic equation:

$$AL + BL^2 = t, \quad (3.9)$$

where A and B are coefficients, t is the time for the edge of liquid layer intrusion into crack tip to move at distance L from the liquid source.

The linear part of equation (3.9) is described by the kinetics of crystallization pressure (PCR) growth:

$$A = \delta RT / D_{\text{SL}} c_0 P_{\text{CR}} w, \quad (3.10)$$

where δ is the average grain size; R is the gas constant; T is the temperature; D_{SL} is the coefficient of grain matter diffusion in liquid; c_0 is the mole fraction; w is the molar volume.

The parabolic part of equation (3.9) is determined by the process limiting liquid by viscous flow in the (10-100 nm) gap between grains. The use of the

Poiseuille equation for coefficient B in (3.9) results in [315]:

$$B = 12\eta / \delta P_{CR} \quad (3.11)$$

where η is the liquid viscosity.

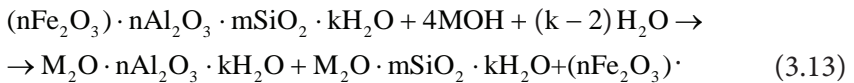
The value $1/B$ is considered as an effective (conditional) diffusion coefficient. It is many orders of magnitude larger than solid body diffusion coefficient. Hence, it follows that such hydrolytic splitting processes run rather rapidly. It was experimentally revealed that in porous bodies that include clays, the realization of such processes takes only 10-20 h [23]. The polycrystalline type of porous structures supposes particle formation of different sizes, including nano- and microparticles. Similar processes run in marine peloid sediments at high pressure conditions in large depths and in zones of natural gas and organic-clay sediments bedding.

Apart of examined silicate system fracture process, the process of spontaneous (chemical) dispersion under the action of water and aqueous solutions can be possible [315]. The kinetics of geological processes herewith also obey the equations (3.6)-(3.11). Recent experimental and theoretical analysis of the mechanism in terms of chemical dispersion and physicochemical geomechanics has shown [23] that the dispersion process may be over within few hours for porous silicate rock under the applied external mechanical action. An alkalescent medium of aqueous solutions enables that, and the dispersion kinetics submits to the equation:

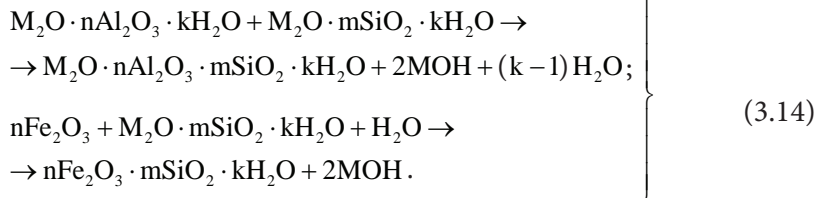
$$(S - S_0)^2 = kt, \quad (3.12)$$

where S_0 is the initial specific surface area of dispersed material.

Chemical processes in an alkalescent medium, which is typical for the most peloids, may run on the surface of particles and in cracks along with the reaction (3.6) according to the scheme:



Then the products (3.13) react by the following schemes:



Crystalline hydrate formed in a nano-crack by the reaction (3.14) has a bigger volume than that of the initial product in the reaction (3.13). Therefore, the formed crystallization pressure promotes rupture (chemical wedging) of the crack, and external mechanical force accelerates the process. Water, entering the

extended crack mouth up to microsized, also provides for adsorption reduction of strength (Rehbinder effect) and partial dispersion of initial iron-aluminosilicate (clay) material up to structure-forming nano- and microparticles. The aqueous alkaline solution formed by the scheme (3.14) participates again in remained solid matter chemical wedging by the scheme (3.13). This process runs similar to the case of liquid phases penetration through intergranular boundaries, but more rapidly. Laboratory studies showed that few hours is enough for its completion in case of porous or disperse materials, or few weeks for dense rocks [23].

Naturally, described physicochemical processes may take place in rocks and disperse clay-carbonate peloid compositions not only in the natural conditions, but also in the technogenic conditions of their practical application.

Along with physicochemical processes, microorganism-aided biocolloidal, biological, and biochemical processes are activated in disperse mineral systems (peloids). The latter provides formation of organic clay-carbonate structures, which enrich peloids with carbonate material while dying of living organisms, mostly in the form of calcite [361]. The dispersion of carbonates up to nano- and microparticles is aided by carbon dioxide from air through intermediate formation of calcium bicarbonate [23, 361].

Thus, most peloids are concentrated pasty aqueous dispersions including small amounts (2-4%) of structural nano- and microparticles of clays, carbonates and organic matter formed by the biocolloidal vital activity of microorganism-sand physical-geomechanical or geological processes. It is quite obvious that superfine clays, carbonates, and microorganisms form a complex of specific therapeutic peloid properties during physical-geomechanical and geological processes [53, 338, 349, 350, 352, 354, 357, 1, 2, 4, 7, 8, 12, 13, 361]. Thus, the mechanisms of such processes should be studied better, especially concerning nano- and microparticles of clays and carbonates.

3.3.2. Special methods for preparation of samples

Poorly studied deep-water clay-carbonate oozes of supergiant deposit taken from 2020 m depth in the western part of the Black Sea were used for the study. Oozes from six sampling points were mixed to homogenize their composition and kept in closed glass jars. Well studied peloids from the Kuyalnik Estuary (near Odesa, Ukraine) were taken as comparison samples. Bentonite from the Cherkasy deposit (Dashukivka, Ukraine) was enriched by elutriation in distilled water for separation of layered structure montmorillonite mineral which was able to disperse up to 30-40 nm particles. It was used to prepare model systems. Montmorillonite aqueous suspension was also stored in closed glass jars. Part of montmorillonite was dried and burned in air atmosphere at 500-600 °C.

The rest was milled up to 0-63 μm particle sizes, mixed with precursor (lignin) and burned without air access until the formation of a nanoporous sorbent by method described in [363]. The burned samples were milled in a porcelain ball mill at the material : balls : water ratio of 1 : 1,5 : 0,45 in the presence of chemical additives which form nanoclusters and nanoparticles [23].

Chemically pure soda and calcium chloride were used to obtain artificial calcite nanoparticles [358].

Sampling from jars for investigation of the influence of micro- and nanoparticles on the variation in colloid-chemical and medicobiological (biomedical) properties was made by "cutting ring" method using a sterile glass tube with 10 mm inner diameter. Peloid samples were mixed with sterile mineralized water (25 g/dm^3 NaCl).

Investigations of the materials were made by XRD, EMI, thermogravimetric, rheological, chemical and sedimentometric methods, as well as with medicobiological methods described in [361].

3.3.3. Physicochemical indexes, chemical and mineralogical composition of the Black Sea peloids

The main results of definition of physicochemical indexes of marine deep-water bottom oozes are presented in Table 3.5. There are also indicated comparative data for oozes of shallow-water Kuyalnik coastal estuary. Deep-sea oozes are dark-gray and black plastic well-spreading muds with hydrogen sulfide smell. They have alkaline reaction of medium. Negative values of Eh redox potential indicate dominance of reduction processes in them. Water concentration is within the limits acceptable for ooze peloids (25-75%). They are also characterized by high shear stress and plasticity providing for better peloid bonding with human skin. Pollution of deep-sea bottom sediments with particles bigger than 250 μm is negligible. Nano- and microparticle content is small as well, and the organic carbon C_{org} content is typical for ooze peloids (1-5%).

The subsequent investigation of physicochemical, mineralogical, and chemical peloid characteristics revealed that the mass of soluble salts is basically presented by chloride ions (0.92%) and the sum of potassium and sodium cations (0.53%). The basic components of calcium-magnesia structures are calcium carbonate (9.19%) and phosphate (0.39%). The solid base of the structures of coarse-dispersion complex includes also particles above 1 μm containing crystals of salts, gypsum cuts, remains of plants and living substance microcosm, in particular, carbonate remains of Foraminifera (Fig. 3.21, *b*), as well as live microorganisms [361]. The increased carbonate concentration in sediments depends on the content of Foraminifera remains and, to a lesser extent, on carbonate precipitation from mud solution during the diagenesis process.

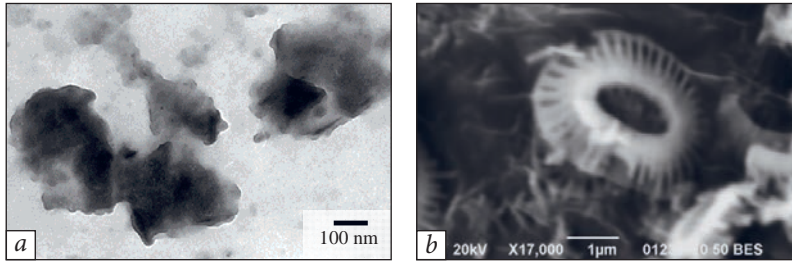


Fig. 3.21. SEM images of different Black Sea peloid fractions: *a* — nano- and microstructures; *b* — microorganism (Foraminifera) carbonate rests

Analysis of data in Table 3.5 indicates a correlation between shear stress values. The fine-dispersed part of peloids, or their colloidal complex, containing nano- and microparticles of under 1 μm , consists of decayed organic matter and mineral substances including iron sulfides, silicic acid, layered smectite clay minerals, etc. The composition of hydrophilic colloid complex consists generally of mineral substances. Among them, nanodisperse and colloid-dispersed clay minerals, hydrates of iron sulfides, hydrotroilite and iron oxides are the most influential upon the viscosity.

According to the XRD and chemical analysis and data in Fig. 3.21 and in [361], marine peloids contain quartz (7.3—14.9%), calcium and magnesium carbonates (15.2—26.5%), clay minerals, including hydromica, kaolinite, glauconite, montmo-

Table 3.5. Main physicochemical indexes of the Black Sea bottom sediments

Index	Black Sea deepwater sampling points				Kuyalnik Estuary
	1	2	3	4	
pH of liquid phase	7.35	7.52	7.40	7.05	7.20
Redox potential	-165	-175	-150	-105	-227
Moisture, wt%	64.21	51.19	71.25	77.04	58.1
Volume weight, g/cm^3	1.30	1.50	1.23	1.20	1.47
Adhesiveness, Pa	833	971	944	555	833
Shear stress limit, Pa	490	552	674	484	491
Specific heat capacity, $\text{kJ}/\text{kg} \cdot \text{K}$	2.99	2.55	3.23	3.43	0.59
Concentration of H_2S , %	0.023	0.024	0.016	0.030	0.17
Concentration of C_{org} , %	2.02	0.96	3.34	3.26	2.06
Concentration of particles $\geq 250 \mu\text{m}$, %	0.067	0.036	0.042	0.013	0.61
Concentration of particles $\geq 1 \mu\text{m}$, %	2.28	2.47	2.31	2.48	2.65
Concentration of particles $\leq 100 \text{nm}$, %	0.36	0.39	0.41	0.25	0.34

rillonite (40-70%) and amorphous silica (0.1-4.0%). Spectral analysis of selected spots during peloid SEM imaging showed the presence of carbonates, oxides of silicon, aluminum, iron and also sulfides in broad concentration ranges.

3.3.4. Microbiological investigation of marine pelitic sediments and peloids

Along with other components, peloids contain microorganisms (Figs 3.21, *b* and 3.22) contacting to micro- and nanoparticles [361]. As a result of the metabolism processes, they form deep decay products of organic and inorganic substrates. The latter substantially determines biocolloidal properties of peloids. The natural process of peloid formation goes on from few years to many centuries at big depth in strict selective conditions of aerobic-and-microaerophilic mediums with high content of salts. Microbiocenosis, consisting of different microorganism group representatives formed in such conditions, adapts to a common existence as an autonomic object controlling the following processes, basic for all types of natural mediums:

- decay of organic matter with saprophytic and other microorganisms resulting in the formation of carbon dioxide or methane, hydrogen sulfide, and ammonia in anaerobic conditions;
- sulfatereduction with the formation of hydrogen sulfide in anaerobic conditions;
- transformation of nitrogen compounds by ammonification (protein hydrolysis with formation of ammonia);

Table 3.6. Concentration of microorganisms in marine peloids (CFU/cm³)

Type of microorganism (bacteria)	CFU/cm ³ in peloids		
	Initial	Used	After activation
Cellulose-fermenting			
aerobic	$1 \cdot 10^3$	$1 \cdot 10^4$	$1 \cdot 10^3$
anaerobic	$1 \cdot 10^1$	$1 \cdot 10^1$	$1 \cdot 10^1$
Butyric-acid	$1 \cdot 10^4$	$1 \cdot 10^2$	$1 \cdot 10^4$
Denitrifying	$1 \cdot 10^2$	$1 \cdot 10^2$	$1 \cdot 10^2$
Sulfate-reducing	$1 \cdot 10^4$	$1 \cdot 10^2$	$1 \cdot 10^4$
Nitrifying	$1 \cdot 10^6$	$1 \cdot 10^5$	$1 \cdot 10^6$
Methane-producing	$1 \cdot 10^7$	$1 \cdot 10^6$	$1 \cdot 10^7$
Iron-oxidizing	$3 \cdot 10^6$	$1 \cdot 10^6$	$3 \cdot 10^6$
Ammonificating			
aerobic	10^6	10^2	10^6
anaerobic	10^2	10^2	10^2
Fat-decomposing	10^2	10^2	10^2
Sulphur-oxidizing	10^4	10^4	10^4

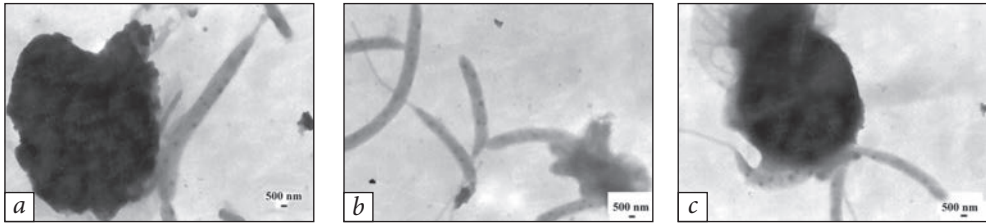


Fig. 3.22. SEM images (*a, b, c* — different parts of the same sample) of microorganisms in clay-carbonate peloid composition

- denitrification by anaerobic process of nitrogen compound reduction up to oxide/protoxide and free nitrogen;
- nitrification following ammonia oxidation to nitrites and then to nitrates in aerobic conditions;
- reduction or oxidation of iron and manganese compounds by various aerobic and anaerobic microorganisms.

Different concentrations of ecotrophic group microorganisms in averaged mixtures of peloids of Kuyalnik Estuary (initial, used (after therapeutic mud application) and after their microbiological activation) are presented in Table 3.6. Opportunistic microorganisms (colibacterias and staphylococcus) have not been revealed in samples. The pH values of the initial sample (7.4), used sample (6.8), and after regeneration (7.3) testify of peloid ability to recover its physicochemical properties after microbiological activation.

The dynamics of changing saprophytic microorganism concentration in peloids during their regeneration under 20 cm of brine is shown in Fig. 3.23. The above data display that saprophyte count increases up to the values in the initial peloids during incubation. Regeneration process is completed after 100 days of exposure. *E.coli* bacteria die within 9 days of incubation after their addition in peloids.

Tested peloids relate to high-bactericide ones. They preserve this property after regeneration. Thus, the lost peloid properties can be restored by microbiological activation to use the peloid again in therapeutic practice. The self-purification of peloids takes place owing to pathogenic and opportunistic microflora intruded into them during their application and storage. Other peloid properties (organic matter content, catalase activity, concentration of hydrogen sulfide, sulfate and hydrocarbonate ions, and medium activity) restore during activation as well.

3.3.5. Influence of nanodisperse inorganic additives on balneological peloid activity

The results obtained show that the Black Sea bottom sediments, which undoubtedly exist in other seas and oceans, have unique therapeutic properties according to common mechanism of pelagic sediment formation [151]. However, the

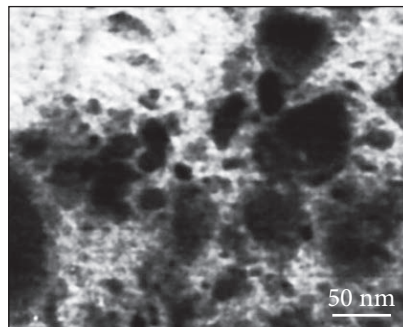
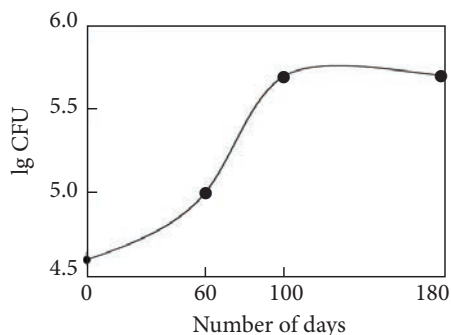


Fig. 3.23. Dynamics of microbiological composition changing during the regeneration process of preliminarily used peloids

Fig. 3.24. SEM image of burnt at 600 °C bentonite nanoparticles

effects of external factors, including their modification with bioactive clays and calcium carbonate, has not yet studied well enough [53, 357, 361].

Natural bentonitic clay from the Dashukivka deposit (Ukraine) was used as clay nano- and microadditives. It was thermally treated for hydrophobization at 600 °C before its addition to peloid samples. This was required in order to obtain nano- and microparticles after the further contact of thermo-treated bentonite with aqueous medium [363]. Sizes of formed nanoparticles were within 20-100 nm (Fig. 3.24). Physiologic investigations of peloid compositions with nanomaterials were carried out by estimation of the response of different healthy animal (white Wistar rat) organism systems to the biological activity of these compositions. Peloid and peloid composition influence on the central nervous system (CNS) and liver were tested via injection of sodium thiopental solution into abdominal cavity of animals with a dosage of 0.75 mg of dry substance per 100 g of body mass. Falling asleep time (in min) after barbiturate injection was measured for influence on CNS characterization. Medication sleep period characterizes anti-toxic liver ability. The compositions were used on animals by inserting of their tails into tested suspensions at 40 ± 1 °C for 2 h.

Fig. 3.25 shows a skin-resorptive effect of montmorillonite, extracted from natural bentonite (Fig. 3.25, *a*) in marine peloid composition, on the intact animal CNS and liver functional state. As seen, 5%, 10% and 15% of montmorillonite addition into peloids almost does not influence the falling asleep time and sleep duration during metabolic test with barbiturates. Also, there is no negative influence of the studied composition on CNS and liver. Increase in the natural bentonite concentration up to 15% (or 5% addition of saponite clay into peloid composition) decreases metabolic liver processes, which is confirmed by increasing animal metabolic sleep time during the thiopental test (Fig. 3.25, *b*). The CNS functional state remains almost the same.

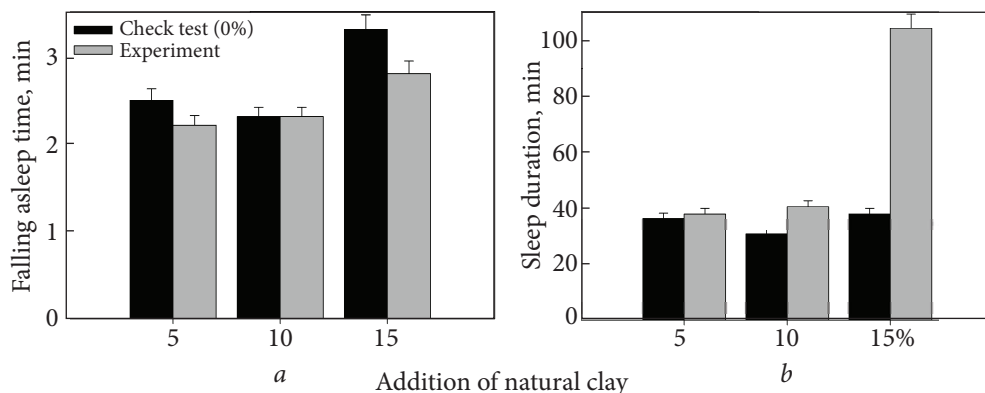


Fig. 3.25. Falling asleep time (*a*, min) and sleep duration (*b*, min) of intact animals for 5, 10 and 15% additions of montmorillonite taken from natural bentonite clay into peloids of the Black Sea

Thus, the investigation gives reasons to believe that colloid-chemical properties of up to 10 % additions of montmorillonite, taken from natural bentonite clays, into peloids exert almost no influence on biomedical characteristics of peloid compositions. Therefore, the effect of hydrophilic nanoparticles of bentonite clay is weak as well.

Investigation of the influence of thermally treated (at 600 °C) hydrophobized montmorillonite, taken from bentonite clay on the peloid biologic activity (Fig. 3.26) showed that its 5-15% addition substantially changes biomedical characteristics of the composition. Influence on CNS remains almost the same, but antitoxic liver ability increases which can be seen by medication sleep duration decrease down by 3 times for 5% of bentonite or montmorillonite and by 1.9 times for 10 and 15% of bentonite or montmorillonite. Medication sleep duration decreases down by 3.7 times for 5% of bentonite or montmorillonite and by 2.2 times for 10% of bentonite in case of preliminary mechanochemical grinding of burnt bentonite in a ball mill for 1 h.

Addition of 5, 10 and 15 wt% of chemically precipitated calcium carbonate (Fig. 3.27) into peloids shows that the CNS functional state is unchanged, but antitoxic liver ability increases by 2-3 times.

However, such results were obtained for model peloid compositions with addition of prepared suspension of calcium carbonate containing nanoparticles. According to [358], their role is diminished as far as clay-carbonate compositions are aged in the quiescent state due to the isothermal distillation process in them. At the same time, in open dissipative systems (mixing conditions), the effect of nanochemical dispersion of microparticles up to nanoparticles can be observed in the presence of dissolved NaCl in the disperse medium and carbon dioxide in the air medium. The latter can be described by the following generalized scheme (Fig. 3.28).

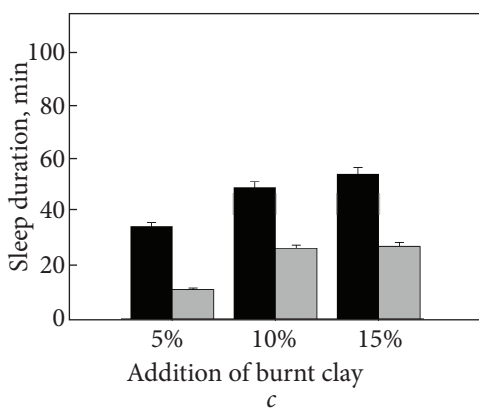
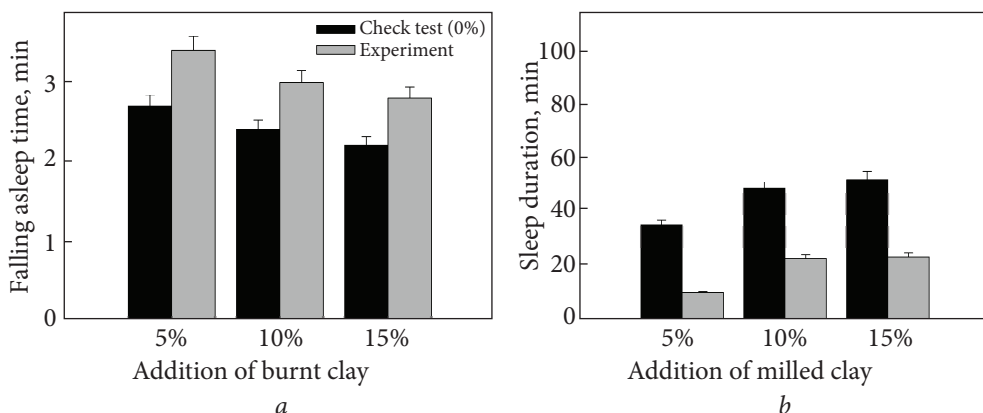


Fig. 3.26. Influence of *a*, *c* — burnt at 600 °C montmorillonite taken from bentonite and *b* — dispersed in a ball mill montmorillonite processed by lignin at 600 °C on *a* — falling asleep time and *b*, *c* — medication sleep duration of intact animals

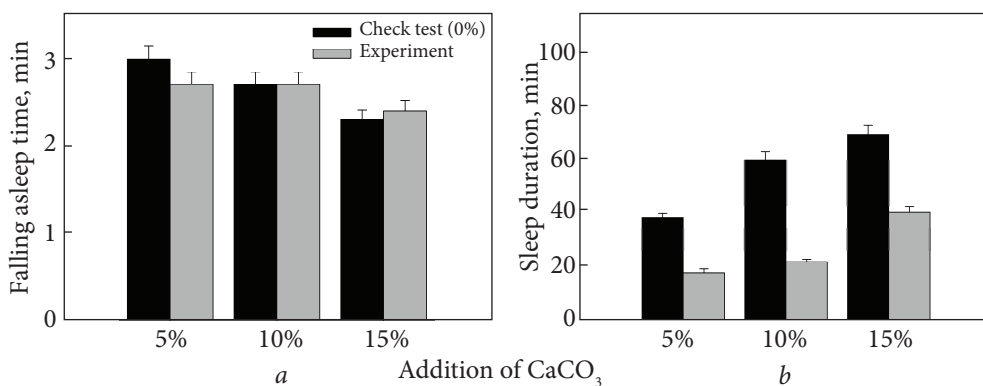


Fig. 3.27. Calcium carbonate nanoparticle influence on *a* — falling asleep time and *b* — medication sleep duration of intact animals

It follows from the scheme (Fig. 3.28) that while intensive mixing, one can disperse carbonate microparticles contained in natural salt peloids up to nanoparticles. This can be done in accordance with the mechanism of nanochemical

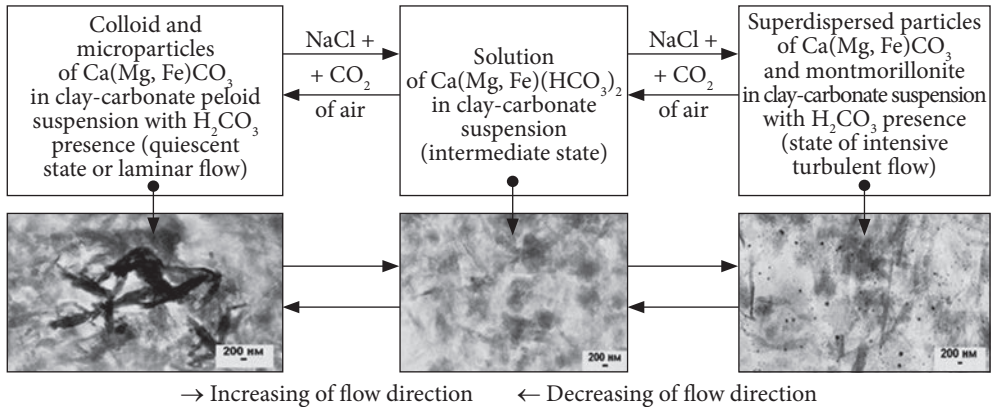


Fig. 3.28. Scheme of nanochemical dispersion of clay-carbonate suspensions and inverse isothermal distillation process

dispersion in intensive mixing conditions followed by delayed recondensation in the quiescent state [358]. Really, rheological investigations on the model composition containing 90% of montmorillonite clay and 10% of microdisperse calcium carbonate display a substantial change in peloid suspension parameters after its intensive mixing (Figs. 3.27 and 3.29).

Testing of real peloid suspensions after their mixing for 10 h showed that their biological activity, within measurement error limits, corresponds to the data obtained for the model peloid composition (Fig. 3.27).

The aforesaid results prove that, while mixing, the mechanism of carbonate microparticle nanochemical dispersion is affected by mechanochemical processes promoting its realization, which affects the colloid-chemical properties and therapeutic activity of peloids.

Additional investigations of bioactivity and anti-inflammatory action of peloids with nanoadditives on intact animals and in the ovalbumin arthritis modeling conditions, as well as in spa-resort practice showed that the application of composition in the prophylactic way is accompanied with significant therapeutic effect conditioned by improvement of inflammatory metabolic and immune rates, as well as by increasing glucocorticoid background in an organism.

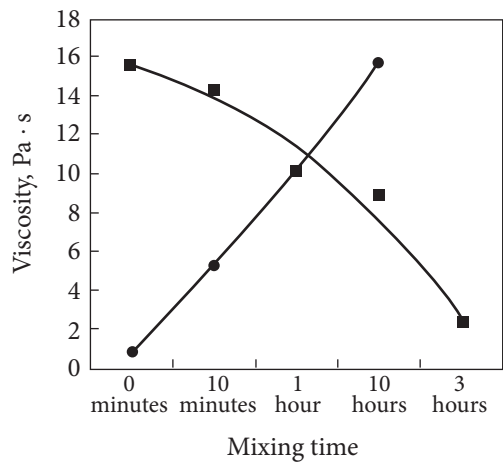


Fig. 3.29. Dependence of the effective viscosity of 50% clay-carbonate brine suspension on the mixing time: ● in mixing conditions, ■ in a quiescent state

Conclusions. Investigations of physicochemical and microbiological properties and analysis of obtained laboratory and practical data prove that peloid microbiocenosis of the Black Sea deep bottom sediments is a formation having the ability for self-purification and regeneration of its composition. The high content of nitrifying and iron-oxidizing aerobic bacteria in tested peloids indicates the fact of quite active oxidation processes enriching environment with proteases, catalases, other ferments and bioactive substances. Estimation of the peloid antimicrobial effect for *E. Coli* (added directly into peloid suspension with infective dose of 10^6 CFU/cm³) showed that tested bottom sediments are high-bactericidal and therefore can be recommended as a remedy for series of diseases.

Furthermore, it was determined that additives of natural hydrophilic bentonites into peloids do not practically influence the biological activity and hence they do not worsen medicine-therapeutic characteristics of peloid compositions. At the same time, up to 15% concentrations of burnt bentonites and calcite substantially improve peloid balneal activity.

These results testify that increasing quantity of nanoparticle aggregates in peloids following introduction of burnt nanoporous bentonite or nanostructured calcium carbonate additives there shall potentiate the peloids balneological activity, probably at the expense of increased sorption and ion-exchange ability of calcite nanoparticles and burnt dehydrated clay minerals in the bentonite composition. At the same time, formation of calcite nanoparticles in natural bentonite is inhibited, which does not improve the biological activity of the system.

Following the completed investigation and analysis of collected data on colloid-chemical and nanochemical transformations of clay-carbonate structures [357, 358, 361], it was shown that the presence of nanoparticle in clay-carbonate peloids containing saline water (brine) and CO₂ from the air can substantially affect the colloid-chemical properties and balneological activity of peloid compositions, containing calcite. Correlation has been determined between nanochemical transformations, colloid-chemical properties and balneal activity depending on the fact that such compositions are in the quiescent state, for example, when applied on animal skin, (thermodynamically isolated system) or in intensive mixing conditions.

CHAPTER **4**

**NANO-
AND MICROSTRUCTURAL
TRANSFORMATIONS OF
DISPERSE ROCKS, SOILS
AND OOZES IN PROTECTIVE
BARRIERS, MEDICINE
AND BALNEOLOGY**

Natural micro- and nanostructured disperse rocks, are widely distributed in the Earth's crust and are used for different purposes. Iron oxide-aluminosilicate disperse rocks, usually containing admixtures of carbonates, the products of micro-organism metabolism, take a special place among them. Their physical, physico-chemical and chemical transformations in the Earth's crust lead to formation of disperse nano- and microstructural polymineral compositions, which consist of iron oxides, silicon and aluminum, as well as other inorganic and organic compounds. First of all sea pelitic sediments, peloids (therapeutical (medical) muds), iron clays, soils, sedimentary iron-aluminosilicate carbonate ores and microcrystalline iron quartzite (jaspilites) are the main types of such compositions [11, 16-18, 20, 21, 23, 326, 364, 365]. However, the model representations of transformation processes in such materials taking into account the laws of physicochemical geomechanics and microbiological processes of their nanochemical, mechanochemical and structural transformations from dense rocks into the sedimentary materials have not yet particularly developed. The problems of suspensions stability (including in stressed conditions) of disperse rocks in the presence of surface nanoclusters and nanoparticles of iron oxide-hydroxide and silicon compounds have not been discussed. The influence of microorganisms and their mixing intensity on the physicochemical suspension state, which is important for their effective application for practical purposes, have not been discussed either. As follows, study of the interrelation of dense rock transformation into nanostructural disperse rocks with their chemical, geochemical, microbiological, nanochemical and structural changes is urgent. The researches of further transformation processes for rational use of their water suspensions in biogeotechnologies of water body barrier protection, balneology and medicine are urgent too.

4.1. Analysis of experimental and theoretical findings

Methods of electron microscopy, thermogravimetric, X-ray, rheological, mechanochemical, chemical and special biomedical testing have been used in the studies [11, 18, 20, 326]. SEM images of samples were studied using a "Selmi" electron microscope in the light field mode. Sample morphology was ex-

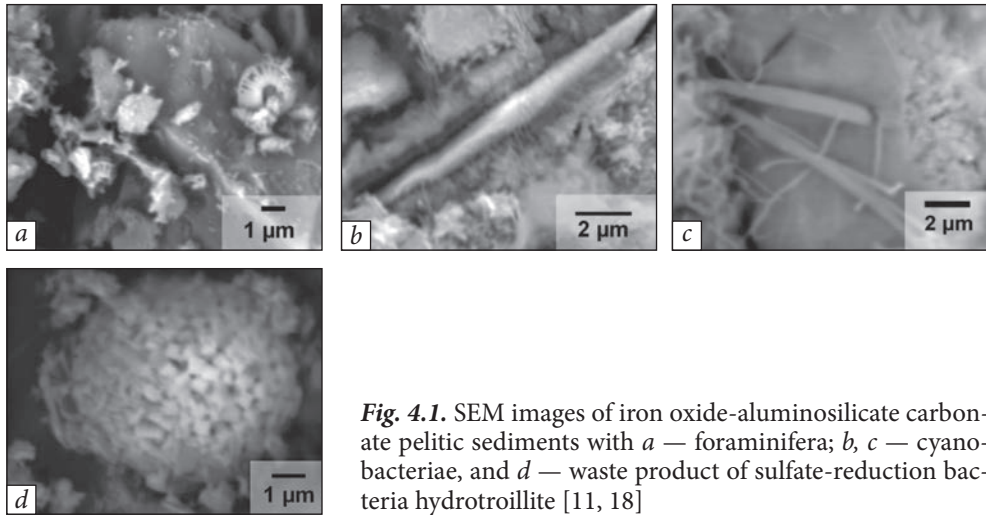


Fig. 4.1. SEM images of iron oxide-aluminosilicate carbonate pelitic sediments with *a* — foraminifera; *b*, *c* — cyanobacteria, and *d* — waste product of sulfate-reduction bacteria hydrotroillite [11, 18]

amed on a scanning electron microscope JSM6490LV of JEOL Company (Japan). Sample thermograms were obtained in inert atmosphere on an automatic Differential Thermal Analyzer. XRD were recorded on DRON-UM1 with two Soller slits under CuK α filtered emission. Rheological investigations were performed with a Rheotest 2 (Germany) connected to PC for data processing. Chemical composition of the samples was determined with the help of chemical X-ray fluorescence method. Geomechanical and nanochemical transformation processes in iron disperse rocks were modelled using well known physicochemical geomechanics methods [23]. Microbiological suspension testing was performed according to the methods [326]. Peloids of giant field pelitic sediments of the Black Sea and disperse goethite-saponite iron-aluminosilicate carbonate sediments (Figs 4.1 and 4.2) located in the south of the Azov Sea [11, 18], as well as samples of dense iron oxide-aluminosilicate rocks and soils were used as the basic samples for research [18].

In accordance with the theoretical concepts of colloid chemistry, particularly physicochemical mechanics and geomechanics [23], the formation of sedimentary materials is preceded by interrelated with them geological rock transformations, accompanied by mechanochemical and nanochemical processes of nano- and microparticles formation [11, 18], as well as subsequent nano- and microstructural contact interactions [8, 16, 21, 20, 22]. Mostly, methods and laws of physicochemical geomechanics, taking into account the important role of water in the mechanochemical processes of rocks dispersion [11, 23], are used for the analysis of similar geological and further colloidal and biocolloidal transformations. The latter contain nanocracks and are subjected to combined mechanical influence of the Earth's crust mass and chemically active and surface-active liquid

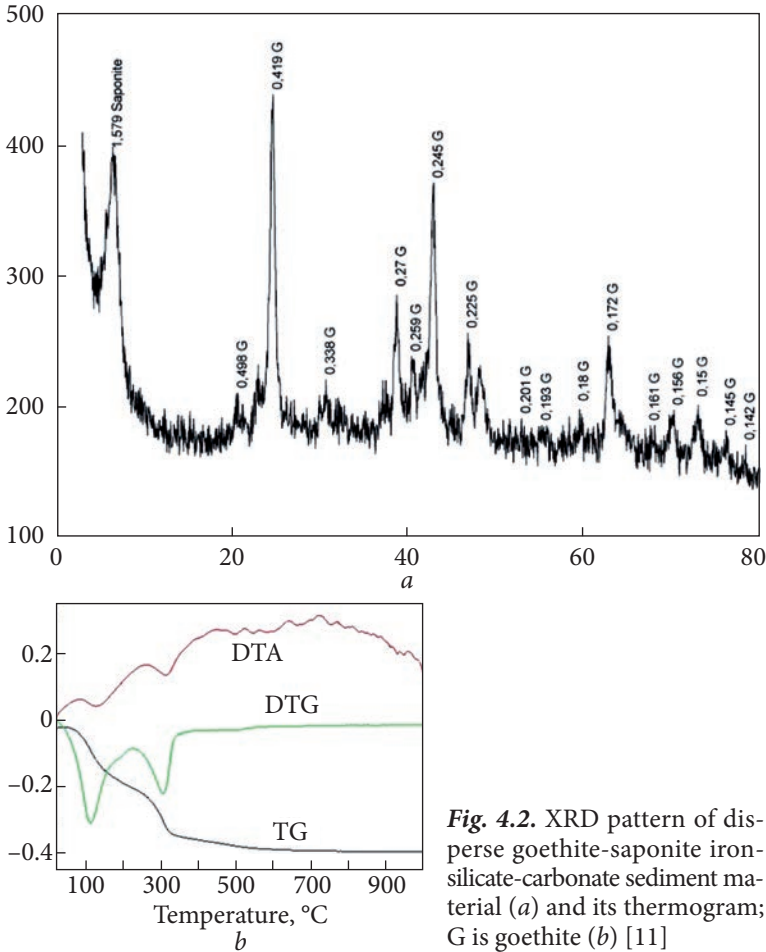
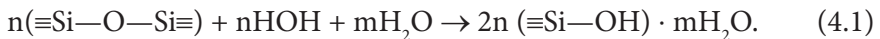


Fig. 4.2. XRD pattern of disperse goethite-saponite iron-silicate-carbonate sediment material (a) and its thermogram; G is goethite (b) [11]

medium [23]. As a rule, rocks and their transformation products, including weathering ones [16, 21], are dispersed by nanocracks through mechanism of hydrolytic breaking of siloxane bonds in silicate structures:



Nanochemical reaction (4.1) fastens under the influence of mechanical strain due to water penetration into nanocracks and increasing hydrated silicate structure volume. This leads to breaking of cracks and rock dispersion even in the presence of only traces of water, and especially in the presence of surfactants [11, 20, 23]. Such hydrolytic splitting processes of dense rocks run relatively rapidly (tens of thousands of years) [23]. Experimentally it has been also shown that in porous and predispersed by the above mechanism materials, which include iron oxide-aluminosilicate carbonate sediment mineral formations, a few tens of hours

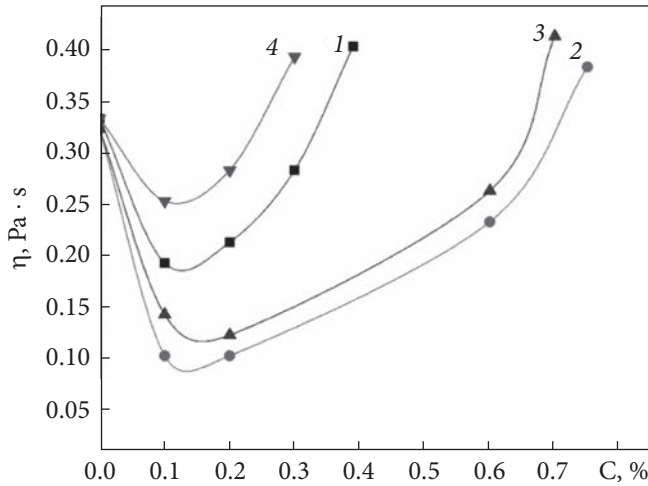


Fig. 4.3. Influence of silicate nanostructural chemical structure on the viscosity (η) of 50% suspension (precrushed iron oxide-aluminosilicate rock, Kryvyi Rih iron ore deposit) depending on the concentration (C) of nanoclusters of the following chemical structure: 1 — $(\text{Si}_2\text{O}_7^{2-})_n$; 2 — $(\text{Si}_2\text{O}_5^{2-})_n$; 3 — $(\text{SiO}_3^{2-})_n$; 4 — $(\text{SiO}_4^4)_n$

would be sufficient for implementation of such processes [20]. Besides, a polycrystalline nature of porous structures supposes particle formation of various sizes during dispersion, including microparticles and nanoparticles. In the same paper [20], it was also shown via using concepts of nanoscience that small amounts (0.05-0.1%) of alkaline silicate surface-active nanoclusters may additionally increase water dispersing ability for rock materials of different nature, including iron-oxide-silicate-carbonate materials. It happens due to simultaneous effects of mechanical external loads and internal stresses of self-dispersion as a result of the chemical processes of $\equiv\text{SiOH}$ group polycondensation. Such stresses are connected with mechano- and nanochemical phenomena [8, 20], particularly with the nanochemical process flowing (4.1) and other complex reactions [20]. The result of the discussed complex effects of mechanical forces, chemical and nanochemical reactions, as well as organic and inorganic natural surfactants is aduration of dispersion process insolid rocks shorteningfrom a few years to a few hours [20]. Data obtained through using model inorganic silicate surfactants as dispersing activators, experimentally confirming the conclusion, are presented in Figs. 4.3 and 4.4.

Fig. 4.3 presents experimental results for the dependence of viscosity of iron oxide-aluminosilicate rock crushed to a particle size less than 63 microns, on the chemical structure of different surfactant silicate nanoclusters.

The obtained data show that only 0.1-0.2% of silicate surfactants is sufficient for suspension viscosity to substantially reduce; herein the maximum dispersion rate is reached. Fig. 4.4 represents data on dispersion kinetics in water for iron-oxide-silicate rock fraction with an original particle size under 1 mm to the final particle size under 0.063 mm in a porcelain ball mill. Degree of size reduction was determined (in %) as a ratio of particle mass with a size less than 0.063 mm to the total mass of the crushed material particles.

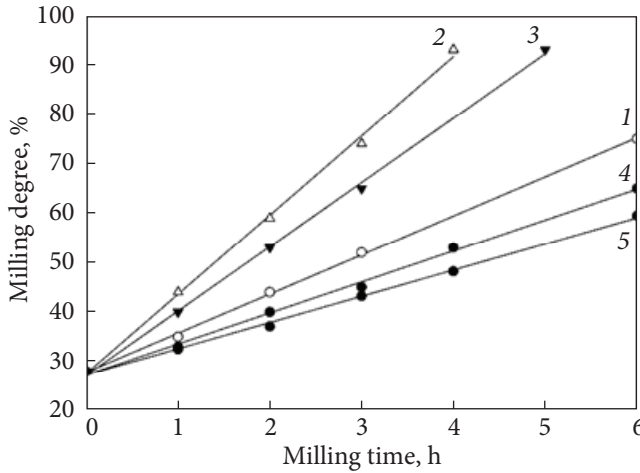


Fig. 4.4. Kinetics of dispersion in water for iron oxide-aluminosilicate rock with the components ratio 1 : 1, precrushed to particle size ≤ 1 mm, at content of silicate nanoclusters different by structure of 0.2% in water. Chemical composition of nanoclusters: 1 — $(\text{Si}_2\text{O}_7^{2-})_n$; 2 — $(\text{Si}_2\text{O}_5^{2-})_n$; 3 — $(\text{SiO}_3^{2-})_n$; 4 — $(\text{SiO}_4^{4-})_n$; 5 — without nanoclusters [11]

The data presented in Fig. 4.4 allow making a conclusion that silicate nanocluster chemical structure markedly influences the rate and, probably, the mechanism of mechano- and nanochemical dispersion of precrushed iron-oxide-silicate rock. Thus, the maximum dispersion rate is achieved for the disilicate $(\text{Si}_2\text{O}_5^{2-})_n$ and metasilicate $(\text{SiO}_3^{2-})_n$ nanoclusters. The mechanism of their influence on the iron-oxide-silicate clay dispersion was partially discussed in [20], allowing the possibility of its further clarification in a special study. Thus, analysis of the kinetic dependences (Fig. 4.4) makes it possible to draw some additional conclusions concerning the process character. For example, it was established [11, 20] that studied dispersion processes obey the equation:

$$(S - S_0)^2 = kt \quad (4.2)$$

where S and S_0 are the current and original external surface area of disperse material; k is the conditional rate constant of a heterophase process; t is the process time duration.

However, since specific surface area (S) is proportional to the average particle diameter (d_{av}) of crushed material, the equation (4.2) can be rewritten as

$$(d_{0av} - d_{av})^2 = k't, \quad (4.3)$$

where d_{0av} and d_{av} are the average particle diameter before and after crushing; k' is the conditional rate constant for a heterophase process.

It is evident that equation (4.2) is suitable to analyze the physical dispersion processes not only of dense, but also of porous particles of material being milled, because the internal surface area, depending on porosity, in this case almost does not influence the dispersion rate. In the case of porous particles dispersion, under the influence of mechano- and nanochemical processes running in cracks and

pores of milling material, the total dispersion rate will be higher than that of analogous dense material by a value, proportional to the mechanochemical dispersion rate in internal pores. Hence, it appears that having a porous and a similar to it by composition dense material, we can estimate, with using equations (4.2) and (4.3), the contribution of nanochemical reactions, accompanying the mechanochemical dispersion, to the general dispersion degree. Therefore, such approach allows verifying and validating experimentally the theoretical laws of physicochemical geomechanics presented in [23], which summarize the perennial researches results.

Owing to the reviewed processes and laws, the concepts (actual in geological science as well) concerning the fact that the colloid state is typical for many mineral substances and systems, especially in the hypergenesis zone, were confirmed in [21, 364, 365]. And, as a result of similar rock dispersion processes [22], sedimentary nano- and microstructured formations of disperse materials are concentrated in salt lake, sea and ocean beds, whereas gravel ones — at the bottom of rivers and sea coasts, and weathering deposits on continent surfaces [21, 22], predominantly in the forms of soils.

Naturally, the aforesaid physicochemical geomechanics transformations of solid, granular and porous sedimentary rocks followed with nano- and microparticle formation can run not only in natural, but also in technogenic conditions, effecting noticeably the behavior of the related ecosystems. Their existence is substantially determined by geomechanical rock dispersion processes as well as by various microorganism vital functions [17, 326, 364]. At that, under the influence of removed by microorganisms mass of biologically active matter and surfactants, the biocolloid interactions are additionally activated, stipulated by combined colloid, biological and biochemical transformations in living and nonliving material biogeocenosis [22].

The data also point on the dependence of such processes out of sediment formation conditions, which usually run in river deltas, salt lakes, estuaries, seas and oceans [16, 21, 364]. According to [22, 326], the processes also substantially depend on biocolloid (microbiological and colloid) processes in pelitic sediment dispersions of mineral substances. Biogeocenosis and bioosteal aggregates are formed according to the biogeochemistry laws as a result of selective interaction of microorganisms with mineral particles. They transform into oolites, which are the basis of sedimentary iron-oxide-silicates and other ore deposits [21, 22]. The inorganic structure of bioosteal aggregates or oolites of sedimentary deposits also contains organic matter, namely microorganism waste products along with living organisms (Fig. 4.1). These metabolism processes are accompanied by formation of various organic substances including bioactive and nanostructured surfactants [11, 17, 22, 326, 365].

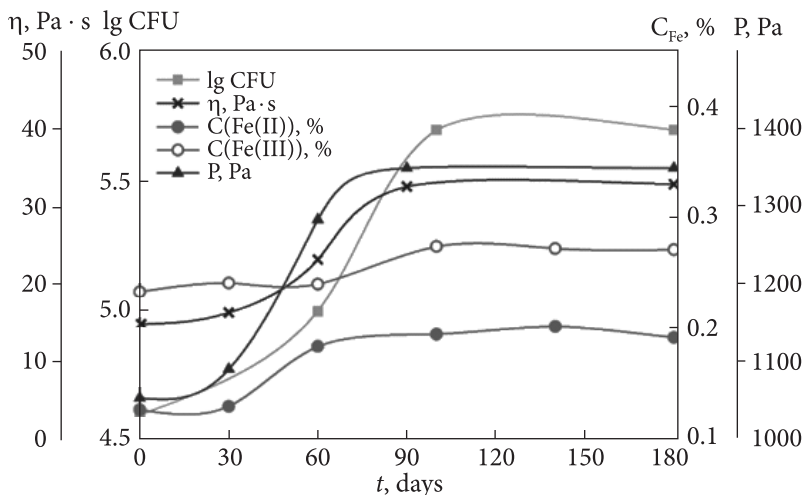


Fig. 4.5. Dependences of viscosity (η), yield stress (P) and microbiological composition ($\lg\text{CFU}$) of partly deactivated suspensions of iron-containing pelitic sediments on kinetics of their activity restoration and also on the ratio between Fe(II) and Fe(III) in disperse medium

However, the role of living microorganisms in dispersion and transformation processes of mineral sediments in aqueous medium at ambient temperature below 38°C is still not quite clear [22, 326]. Fig. 4.1 demonstrates some SEM images of mineral substances contained in pelitic sediments of the Black Sea with microorganisms and their metabolic products, in particular, with Foraminifera (Fig. 4.1, *a*), cyanobacteriae (Figs 4.1, *b* and 4.1, *c*) and waste product of sulfate-reduction bacteria — hydrotroillite (Fig. 4.1, *d*).

The presented structures contain mineral nano- and microparticles partially formed as a result of microorganism vital activity (Figs. 4.1 and 4.5). Besides, excreted surfactants promote activation of hydrolytic mechanism of fracturing dispersion effect of bigger mineral particles [23]. Therefore, the products are formed as a result of metabolic processes, and they substantially define biocolloid properties of pelitic sediments (Fig. 4.5).

Studying the role of different ecotrophic group microorganisms [11] in samples of pelitic sediments testifies their ability to restore the physicochemical properties. The change in viscosity and yield stress during sample maturation for 90-100 days confirms the realization of dispersion hydrolytic mechanism [23] under the action of surfactant-like products excreted by microorganisms during Fe^{3+} into Fe^{2+} reduction processes followed by Fe^{2+} oxidation (Fig. 4.5).

It follows from Fig. 4.5 that the Fe(II) amount in disperse medium increases by 0.07% within maturation processes period (30-100 days). Here in the Fe(III) content increases synchronously by 0.035% at the expense of partial iron oxida-

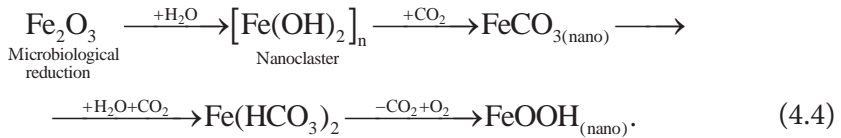
tion by air oxygen with transformation into goethite, and it gives 0.105% of Fe in sum. Therefore, at the total Fe content in sediment material 2.7% in terms of elementary iron, part of surface mineral fracturing, which is proportional to the reduced iron content mainly in the form of nanoparticles [317], reaches 4% for 90–100 days. This markedly affects the growth of yield stress and suspension viscosity owing to the increasing amount of iron-oxide-hydroxide nano- and micro particles during dispersion, which indicates the intensification of contact interactions between mineral particles and compaction of pelitic sediment in the absence of its mixing, i.e., in common conditions for natural processes.

Moreover, natural sediment deposition processes in result of combined chemical and geomechanical transformations and accompanied by nano- and microparticle formation compacting the sediment, last from several years to centuries under the layer of mineralized sodium chloride water in the conditions of anaerobic microaerophilic medium. The specific microbiocenosis formed in such conditions, additionally compacting the sediment, and consisting of different microorganism groups [11] adapts to the common existence as an independent object. It controls various processes such as the decomposition of organic matter by saprophytic and other microorganisms with formation of carbon dioxide, methane, hydrogen sulfide and ammonia in the anaerobic conditions; sulfate reduction with formation of hydrogen sulfide or hydrotroillite in the anaerobic conditions; transformation of nitrogen compounds by ammonification (proteins hydrolysis with ammonia formation); denitrification due to anaerobic reduction of nitrogen compounds to oxide or protoxide and free nitrogen; nitrification as a result of ammonia oxidation to nitrites and then to nitrates in the aerobic conditions; reduction or oxidation of iron and manganese compounds by various aerobic and anaerobic microorganisms [11].

The considered physicochemical geomechanical dispersion processes of iron-oxide-silicate polymineral structure sediments and their biocolloidal transformations under the influence of the formed biogeocenosis [8, 11, 17, 20-23, 326] allow to make a conclusion that carbonates obtained due to microorganism vital activity [11, 364] take part in formation of iron oxide-aluminosilicate carbonate sediments, which as shown in [18], change their rheological properties depending on the intensity of their mixing in the laminar or turbulent mode due to the influence of not only of the nature of nanochemical transformations of $\equiv\text{Si}-\text{O}-\text{Si}\equiv$ and $\equiv\text{Fe}-\text{O}-\text{Fe}\equiv$ structures, but also of carbonates. At the same time, the influence of sodium chloride solutions, similar in composition to the marine ones, has not practically studied yet [19, 317]. There are no research results for similar processes for iron oxide and silica-containing formations [12]. The effect of iron and silica oxides on the rheological behavior of iron-containing quartz sand suspensions, practically included in all sedimentary iron oxide-silicate dis-

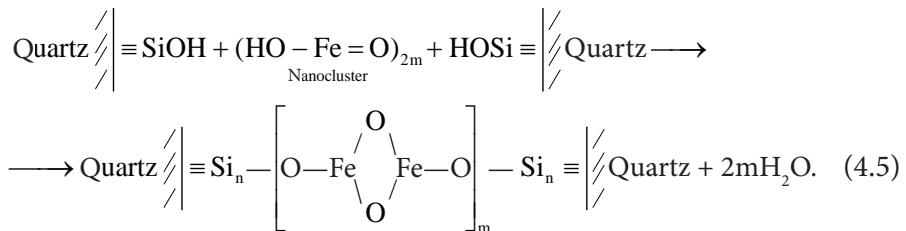
perse rocks and products of their metamorphism aided with natural biocenosis was examined. Iron-containing river sand was chosen as a model sample, which was exposed to dry grinding to a particle size under 0.1 mm. As preliminary studies had shown, the sand contained Fe^{2+} hydroxides and carbonates, located in contact zones of quartz particles and formed by natural microbiological processes (Fig. 4.5). The obtained results are shown in Fig. 4.6 for suspensions, premixed for 24 h at the maximum shear rate (γ) 1074 s^{-1} with its subsequent gradual decrease down to $\gamma = 1 \text{ s}^{-1}$ and recording of shear stress (P) and viscosity (η) at different values of parameters.

The obtained anomalous curves for suspensions (Fig. 4.6, a) coincide with the data [12, 18], which indicates that change in shear stress with changing shear rate passes through a minimum, corresponding to B point, and then through a maximum (Fig. 4.6, c). This effect is explained by nanochemical transformations of iron hydroxides-oxides in contact zones of quartz (Fig. 4.6) or other silicate particles (Fig. 4.5) with participation of CO_2 as well as formed under microbiological processes, according to the irreversible scheme:



The scheme (4.4) demonstrates that microbiologically reduced Fe_2O_3 transforms into $\text{Fe}(\text{OH})_2$ nanoclusters, and then into nanogoethite through the intermediate formation of nanostructured FeCO_3 and soluble $\text{Fe}(\text{HCO}_3)_2$.

Nanogoethite formation in contact zones of quartz particles leads to increasing suspension viscosity with increasing shear rate (γ) from 1 s^{-1} to 1074 s^{-1} (Fig. 4.6, b), which is due to the process (4.4) acceleration and subsequent coagulation-condensation interaction of $\equiv\text{SiOH}$ groups on the surfaces of neighboring quartz particles with intermediate goethite nanostructures by a bridge mechanism:



where $m \gg n$.

This mechanism is confirmed by the results, shown in Fig 4.6, c, from which it is evident that processes (4.4) and (4.5) take place in the case of quartz suspen-

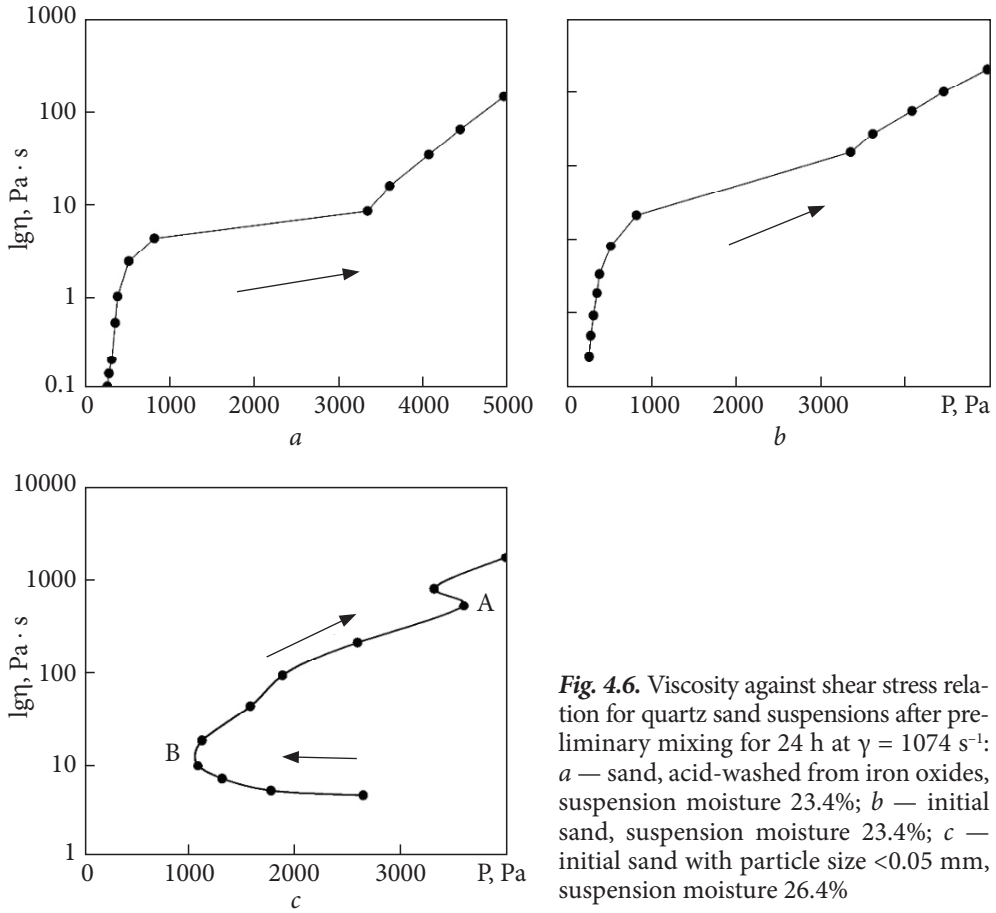
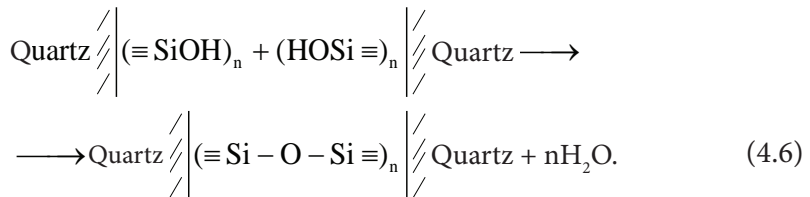


Fig. 4.6. Viscosity against shear stress relation for quartz sand suspensions after preliminary mixing for 24 h at $\gamma = 1074 \text{ s}^{-1}$: *a* — sand, acid-washed from iron oxides, suspension moisture 23.4%; *b* — initial sand, suspension moisture 23.4%; *c* — initial sand with particle size $<0.05 \text{ mm}$, suspension moisture 26.4%

sion preliminary grinding for 24 h at high shear rate (1074 s^{-1}). Therefore, B point in Figs 4.6, *a* and 4.6, *b* is absent, because there are no ferrous compounds in suspension — they completely have transformed into goethite.

Fig. 4.6, *a* data show the influence of surface iron compounds removal into contact zones of quartz particles: like in the case shown in Fig. 4.6, *b*, B point in Fig. 4.6, *a* is absent, which is connected with inability of mechanisms (4.4) and (4.5) to realize. In this case, transition to another type of interaction in contact zones is realized (Fig. 4.6, *a*), which is accompanied by decreasing η :



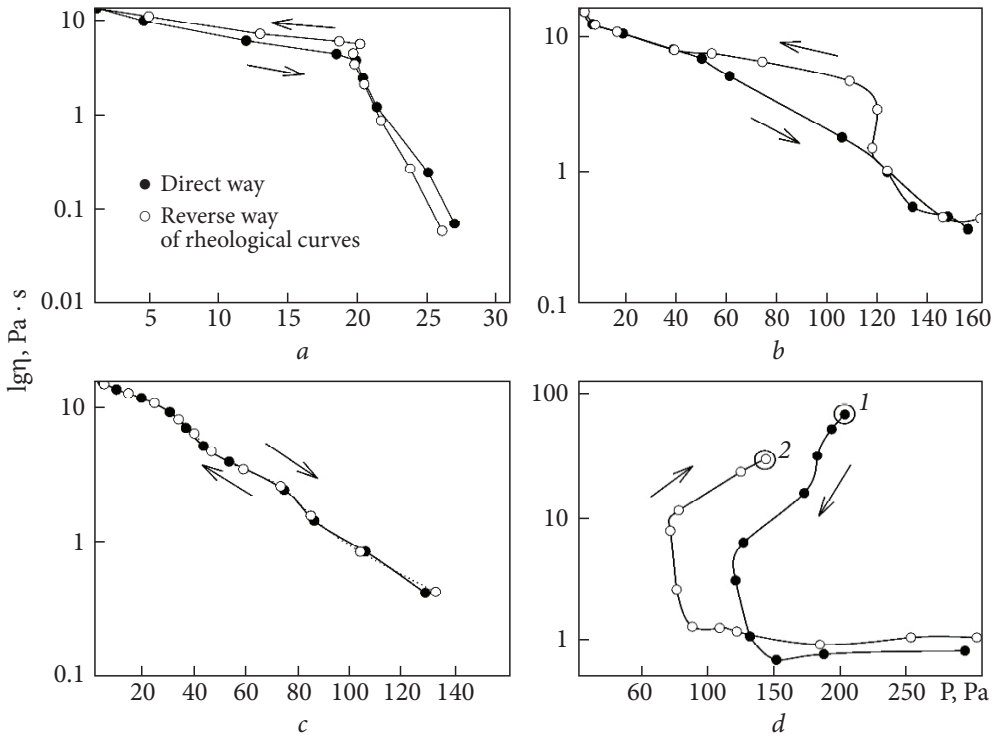
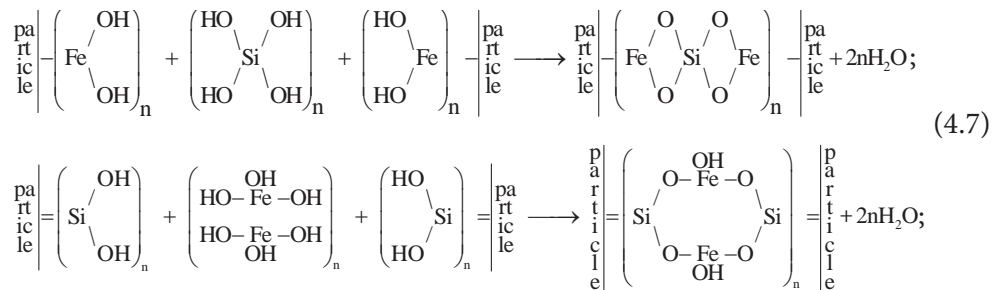


Fig. 4.7. Viscosity against shear stress for *a* — 25% suspension of bentonite clay; *b* — oversanded suspensions of hydromica clay; *c* — the Black Sea bottom sediments; *d* — goethite-saponite sedimentary ore material with high iron content (59.1% of Fe_2O_3). Suspension moisture: *a* — 70%; *b* — 67%; *c* — 66%; *d* — 46%

The results of rheological researches of sodium chloride ($18 \text{ g/dm}^3 \text{ NaCl}$) suspensions of natural fine-grained nanostructured iron-containing bentonite and hydromica clays and coarse-grained pelitic Black Sea oversanded sediment, taken in the Danube mouth area, are shown in Fig. 4.7. The content of Fe_2O_3 in them was at the level of 3-5%. As seen from the presented curves (Fig. 4.7, *a*, *b*, *c*), the dominant influence on the character of rheological curves is exerted by fine-disperse nanostructured clay-silicate components [12, 18, 333], while the influence of processes running in the quartz particles contact zones with goethite participation is leveled and appears to be of secondary importance. At the same time, sediment suspension with high content of goethite (Fig. 4.7, *d*) exhibits anomalous viscous properties, similar to those of quartz sand suspensions (Fig. 4.6). It testifies of determining influence on the suspension viscosity of the contact interactions mechanism according to schemes (4.4) and (4.5). Nevertheless, the mentioned findings do not give the opportunity to make a complete consideration of the multiparametric influence of separate mechanical, biocolloid, nanochemical,

rheological and other factors on the complex mechanism of processes discussed. Such mechanism can be clarified by data in publications [12, 333] and modern concepts of colloid-chemical science in the field of physicochemical mechanics and rheology [366]. By comparing data given in [333] and in this research, one can see that the rheological curve in Fig. 4.7, *d* for goethite-saponite ore suspension, the composition of which is similar to that of the ore used in [12, 333], is almost identical to the analogous curve presented in [333]. That indicates the reliability of obtained results. At that, the inflection points on the curve Fig. 4.7, *d* are related to the appearance of an unusual anomaly (hyperanomaly or ultraanomaly) of viscosity, caused by formation of nanoscale iron oxide-silicate structures (phase contacts [366]) in the contact zones of disperse particles as a result of microbiological ([326] and Fig. 4.5), and subsequent nanochemical and mechanochemical processes. From the viewpoint of physicochemical mechanics [366], the inflection points are explained by the transition from a viscous-elastic to an elastic-plastic flow of suspensions (the reverse way of the curves) or from an elastoplastic to a viscous-plastic flow (the direct way of the curves). Upper points 1 and 2 of the curves in Fig. 4.7, *d* correspond to the minimum shear rate of 1 s^{-1} , and indicate that under those conditions the suspension is already an elastic body. The inner cylinder of the rheoviscometer “slips” on its internal surface, which was also confirmed by visual observations.

According to the representations of modern physicochemical mechanics [366], such a process is conditioned, for example, for curve 2 in Fig. 4.7, *d*, by transition from weak coagulation interactions to stronger coagulation-condensation interactions, to increasing suspension viscosity and the appearance of an unusual anomaly (hyperanomaly or ultraanomaly) of viscosity as a result of the nanochemical reactions:



This scheme explains the inflection points on the curves in Fig. 4.7, *d*.

4.2. Scientific basis of environmentally acceptable biogeotechnologies for anti-stress protection of reservoir barriers using IASSM and NIASSM compositions

The obtained data, as well as results presented in Figs 4.7 and 4.8, make it possible to control biotechnological reservoir protection processes at the expense of additional compaction of antifiltration protective screens made of pelitic iron oxide-aluminosilicate carbonate sediments containing microorganisms. As tests showed, water filtration rate through such a screen decreases by 6-7 times. It permits to increase the volume of water, entering the reservoir at preset filtration rate by 6-7 times.

The main rheological and physicochemical characteristics of different soils, which are a part of compositions of materials for barrier shields and bottom screens, are presented below. Thus, the samples of soils (Table 4.1) were used at optimal moisture values (Atterberg yield strength [7]) during study of rheological parameters. It was taken into account that the Atterberg limits of consistency are:

- 1) the yield strength point which separates the liquid state from plastic state;
- 2) the yield strength point which separates the plastic state from semi-solid (elastic) state.

The yield strength here is signified in percentages of water content to the mass of dry sample. The optimal water content of sample suspensions was determined

Table 4.1. Rheological parameters of soils and gels

Sample No., cylindrical system	Sample	Average particle size, mm	Moisture, W, %	Dynamic yield strength, P_{k2} , Pa	Lowest plastic (Bingham) viscosity, η , Pa · s	Interparticle interaction, F, N
1 z/z	Sand	0.05	18	946.7	5.7	$1.0 \cdot 10^{-7}$
2 h/h	»	0.05	26	186.5	14.2	$8.8 \cdot 10^{-7}$
3 z/z	Gel AA-AA (poly-acrylic acid)	0.2	90	449.5	60.9	$2.7 \cdot 10^{-5}$
4 z/z	Gel AA-AA saturated with metals	0.2	81	109	8.525	$3.78 \cdot 10^{-7}$
5 z/z	Gel + 10% sand	0.185	88	2090.6	8.3	$3.6 \cdot 10^{-4}$
6 s/s2	Chernozem (humus)	0.063	35.4	18.0	6.4	$7.54 \cdot 10^{-8}$
7 n/n	Gray forest soil	0.063	33.6	74.0	8.7	$2.78 \cdot 10^{-7}$
8 n/n	Cespistoze podzolic soil	0.063	33.2	63.6	6.8	$2.9 \cdot 10^{-7}$

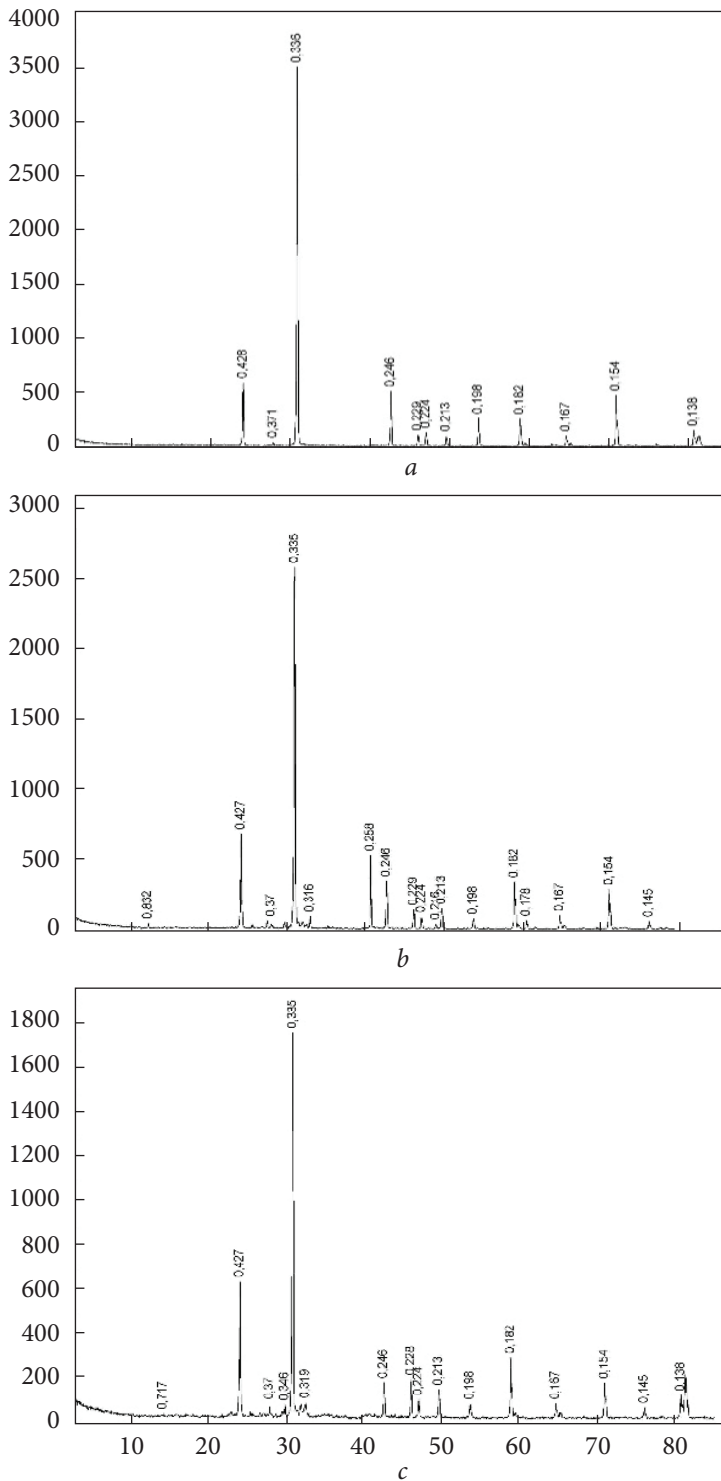


Fig. 4.8. XRD patterns of *a* — river sand; *b* — grey forest soil; *c* — humus

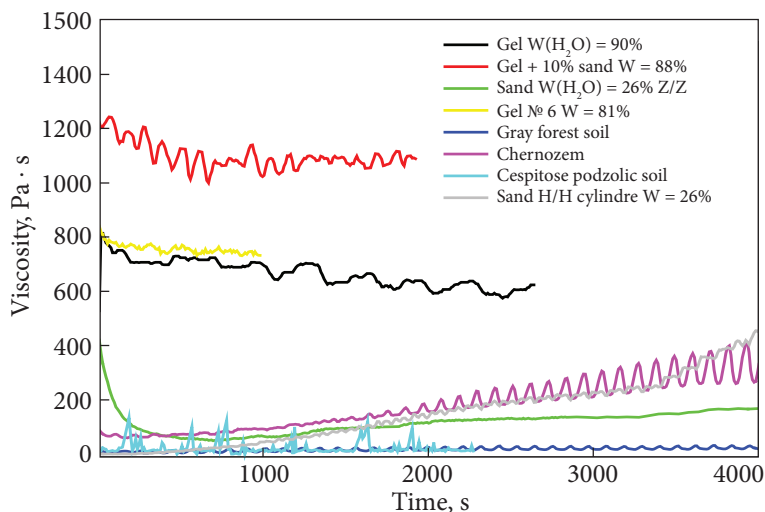


Fig. 4.9. Rheological dependence of viscosity on time at minimum cylinder speed (s^{-1})

by the method of capillary wetting (swelling measurement), since a sample picks up the maximum amount of water (above which the system is unstable) by this method.

Analysis of XRD patterns (Fig. 4.9) showed that silica is the basic mineral for all tested soils, so river sand was additionally taken for making gel soil compositions in barrier screens. Ad mixtures of amphiboles and sylvan were found in gray forest soil. Traces of kaolinite and sylvan were found in humus.

The samples (Table 4.1) were analyzed by Shvedov-Bingam's model. Interparticle (interaggregate) interaction was determined by Casson model:

$$\bar{F} = \frac{6d^2 P_0 (\ln v_r)^2}{[\ln(1-\varphi)(v_r^{1/2} - 1)]^2}, \quad (4.8)$$

where φ is the volume content of disperse phase, $\eta_r = \eta_{\text{plastic}}/\eta_0$ is the relative viscosity, d is the particle size.

The following rheological dependences were obtained:

Structural mechanical characteristics of soil composition dispersion were studied by the method of tangential shifting of corrugated plate in the system volume at constant shear stress, which was increased for each research up to the system destruction. The deformation-time curves $\varepsilon = f(t)$ were plotted for different constant shear stresses ($P_1, P_2, \dots, P_n = \text{const}$) with a help of differential transformer installed in Weiler-Rehbinder device [307] and connected to DS1-03 recorder. Structural mechanical properties were evaluated using a quasi instantaneous shear modulus G_1 , which corresponds to elastic deformation, which arises at the moment of the system loading and decreases after unloading (shear stress)

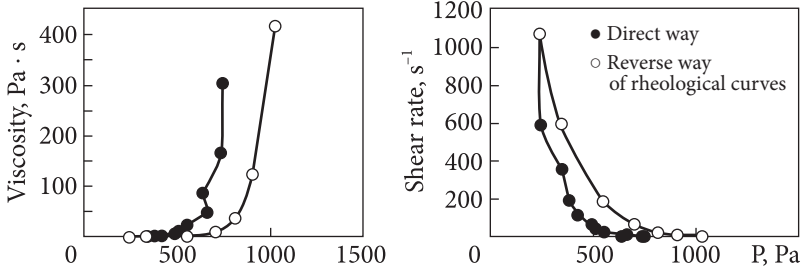


Fig. 4.10. River sand, fraction 0-0.05 mm, moisture ~18% (sample 1)

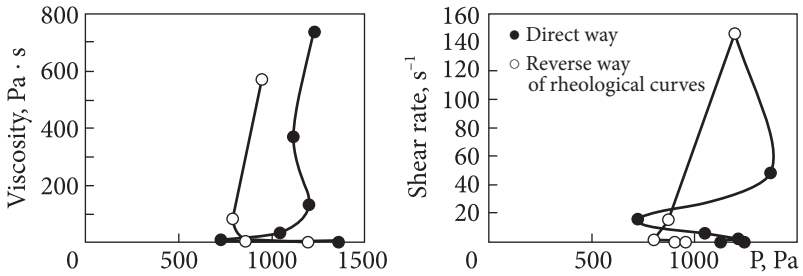


Fig. 4.11. River sand, fraction 0-0.05 mm, moisture 26% (sample 2)

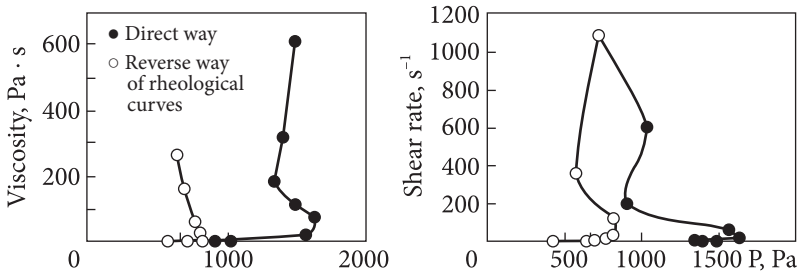


Fig. 4.12. Polyacrylate gel, moisture 90% (sample 3)

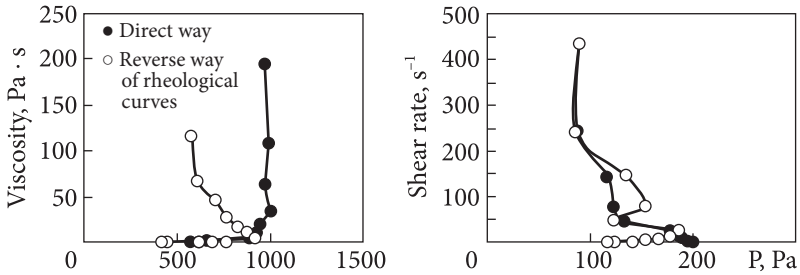


Fig. 4.13. Acrylate gel saturated with metals, moisture 90% (sample 4)

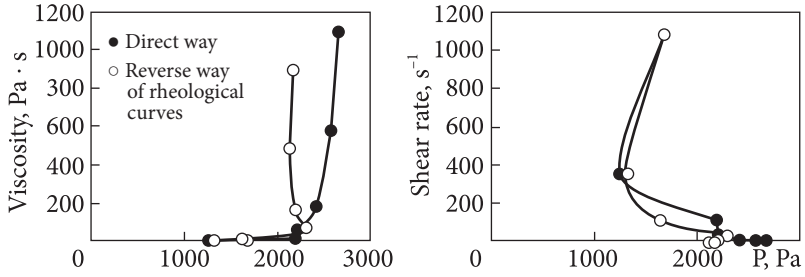


Fig. 4.14. Polyacrylate gel +10% sand, moisture 88% (sample 5)

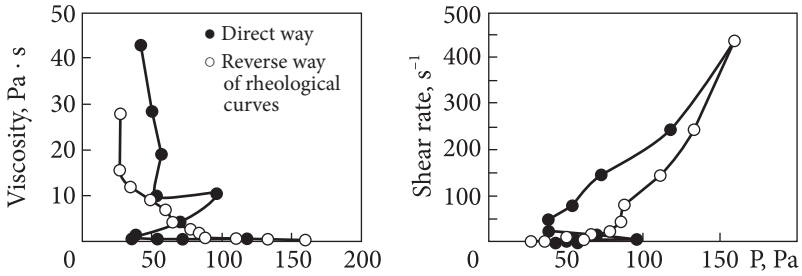


Fig. 4.15. Chernozem soil, moisture 48% (sample 6)

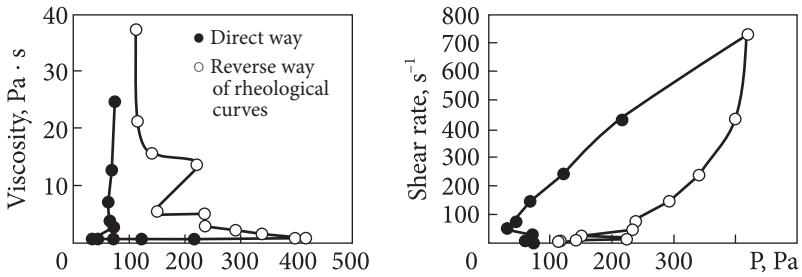


Fig. 4.16. Gray forest soil, moisture 44% (sample 7)

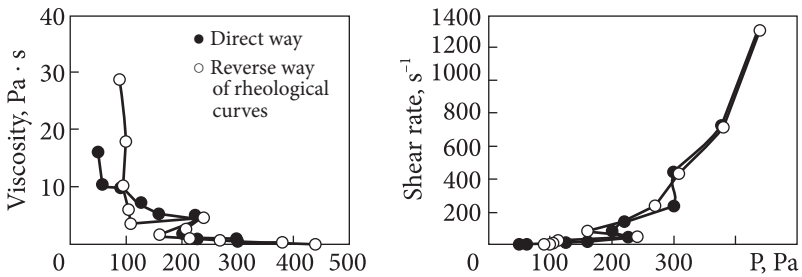


Fig. 4.17. Cespitose podzolic soil, moisture 46% (sample 8)

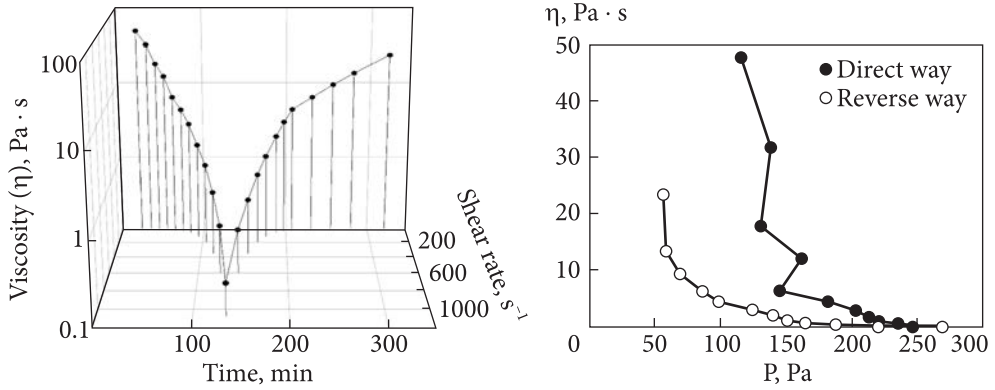


Fig. 4.18. Rheograms of sapropel-containing composition of the bottom sediment (moisture 92%, fraction 0-0.63 mm)

with the sound velocity. Elastic module G_2 corresponds to slow elastic deformation development. The Maxwell-Shvedov-Kelvin model was used to estimate shear deformation under the action of constant shear stress. According to this model ($P = \text{const}$) shear deformation ($\dot{\epsilon} = \epsilon/a$) is described by the equation:

$$\dot{\epsilon} = \frac{P}{G_1} + \frac{(P - P_{K1}) \cdot t}{v_1} + P \frac{1 - \exp\left(-t \frac{G_2}{v_2}\right)}{G_2} \quad (4.9)$$

where a is the distance from the plate to the cuvette wall; P is the shear stress; P_{K1} is the relative static yield strength, or plastic strength; η_1 and η_2 are the highest plastic viscosity and viscosity of slow elastic deformation, respectively; G_1 and G_2 are the shear modulus of rapid and slow elastic deformation, respectively.

This method better shows the real situation, as the samples were taken in the initial state, i.e., were not grinded. The sample and plate were placed into a cuvette and exposed in desiccator with water for 1h. In some cases, it was left for a whole night.

The obtained data are presented in the Table 4.2.

Observations of the reservoir over a number of years revealed that the continuing microbiological and biocolloidal processes at the reservoir bottom contribute to the further compaction of bottom protective screen and decreasing of filtration rate.

Obtained results have also found their application in balneology for activation of exchange processes with application of therapeutic muds [18] and in medicine for hemophilia prevention and treatment, gunshot wounds, joint injuries, etc. [12].

The obtained experimental data and their generalizations allow optimizing many technological processes using science-grounded recommendations and

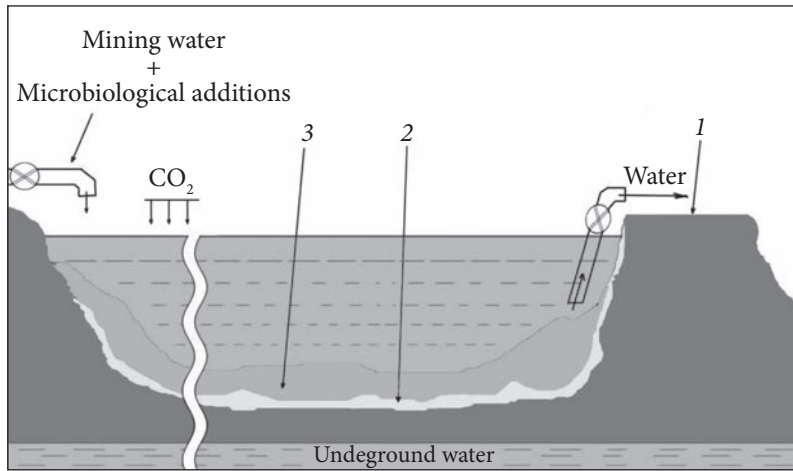


Fig. 4.19. Scheme of barrier protection of a reservoir with mineralized water using bigeo- and nanotechnologies: 1 — dam body, 2 — clay barrier shield (screen), 3 — microbially active nanostructured iron oxide-aluminosilicate-carbonate material

Table 4.2. The data obtained using a Weiler-Rehbinder device (in static conditions)

Sample No.	Sample	Moisture, W, %	Module of fast elastic deformation, G_1 , kPa	Module of slow elastic deformation, G_2 , kPa	Equilibrium module of deformation, G, kPa	Static yield strength, P_{K1} , kPa	Largest plastic viscosity, η , MPa · s
1	Sand	18	897	194	160	83	67.8
2	Sand	24	288	108	78	44	64.6
3	Sand + 4% gel AA-AA	39	141	111	62	49	49.1
4	Sand + 8% gel AA-AA	52	176	227	99	55	44.4
5	Gel AA-AA	68	41	62	25	25	16.0
6	Gel saturated with metals	68	82	42	28	29	5.5
7	Humus	36	49	9	8	16	1.2
8	Grey forest soil	36	20	20	10	6	0.4

practical developments, for example, in balneology, as well as through control of the biotechnology of basin (reservoir) barrier protection (Fig. 4.19). The cutaway of real dam body (1) is shown in the figure to be in Kryvyi Rig (Ukraine), which acts as the main barrier shield containing polymineral clay materials. The main characteristics of such materials are represented in Addition. An additional bar-

rier shield, containing generally bentonite-hydromica clays with additives of binding alkaline silicate materials (Fig. 4.19, layer 2), protects the basin bottom and the dam enclosure. Iron oxide-silicate materials (iron ore or argillites from iron ore or coal facilities) precipitated in general while filling the basin with mine water and microbiological additives, also form a microbiologically active layer 3 (Fig. 4.19). Layer 3 in contact with layer 2 forms specific for each layer biocenosis (biogeocenosis) of microorganisms. They participate in microbiological, nanochemical and physicochemical processes considered while interpreting Figs 4.3-4.7. Due to such complex impacts on the barrier shield, it is compacted in the absence of macromechanical effects. The shield resistance to the mechanical stress shifts increases by 2-3 times, and the filtration rate of mine water into ground water decreases additionally by 50-60% due to biocolloidal processes. Furthermore, microbiological purification of mine water takes place, leading also to decrease in its negative impact on the environment. Such a science-ground regulated biogeotechnology for reservoir barrier protection guarantees the highest antistress characteristics of the barrier and effective protection of the environment. At the same time, continuous filling and draining the reservoir with water is possible, providing a 6-7-fold decrease in the filtration rate of mine water through the barrier shield. An alternative version relates to seasonal filling of the basin with water after its emptying in spring and mixing of mine water with meltwater. In summer and partly in winter, biological water purification from harmful organic substances and heavy metals takes place with the participation of parallel microbiological, nanochemical and physicochemical processes, which increase the efficiency of the reservoir barrier protection, and were considered while analysis of Figs 4.3-4.7 data. In this case, it becomes possible to increase the volume of stored water in the reservoir by 6-7 times and to prolong the guaranteed barrier stability from 3-5 to 10-15 years. In spring, biologically purified water, containing only such minerals as alkaline chlorides and alkaline earth metals, is discharged with meltwater. The developed biogeotechnology allowed increasing the volume of iron ore mine waters stored in the industrial reservoir in Kryvyi Rig (Ukraine) from 2 to 12 million cubic meters with an eco-safety guarantee for 10-15 years.

As a result of the study, models of physicochemical, nanochemical, colloidal and biocolloidal metamorphism processes in iron-oxide-silicate rocks were offered. They are accompanied by formation of nano- and microdisperse pelitic sediments, peloids (therapeutic muds), clays, sedimentary iron-silicate-carbonate ore materials. The role of microorganisms in these processes and the surface-active products of their vital activity is discussed. There are expanded ideas of the role of chemical formation of iron and silicon nanoclusters in the strength changes in the contact zones of microparticles of polymineral dispersion systems. It is shown that in the presence of sodium chloride (seawater, lake brine), for low-iron

clay-sand systems, a dilatant-thixotropic nature of the flow is observed, where as at high iron content in the form of nanostructured goethite a hypernomalous growth of iron-silicate suspension viscosity and enhancement of contact interactions are observed. Taking into account the established phenomena, the use of iron-oxide-silicate peloid compositions in the construction of protective barriers, in medicine and balneology (treatment of injured joints, wounds, leukemia, etc.) is considered. The mechanism of these phenomena is implemented also in balneology for activation of metabolic processes, which can be explained by the data presented in Fig. 4.5, according to which, metabolic processes are activated while storing peloids for 30-60 days (growth of lgCFU). Dispersion processes and sediment compaction (increase in viscosity η and shear stress P) are activated within the same period. That increases the efficiency of barrier protection, as it has been discussed. In the case of balneological use of peloids, an empirical manual application of the suspension to the patient skin, while rheological parameters are unknown, frequently occurs. Otherwise, it could be done on the basis of the data in Figs 4.5 and 4.7, i.e., suspension should be preliminarily mechanically mixed (in a mixer) up to precisely defined parameters, determined as a result of evaluation of the rheological curves (Fig. 4.7). Thus, it follows that curves of suspension viscosity against shear stress are to be noticeably changed in conditions of maximum manifestation of dilatancy, rheopexy, hyperanomaly or ultraanomaly of viscosity. According to [12, 333, 366], such phenomena lead to restructuring of micro- and nanostructures with formation of "loose" aggregates in mixing conditions. It facilitates substrate diffusion transport through layers of free dispersion medium for microorganism metabolism activation. As a result, subsequent better transport of metabolic products to contact zones of peloid-patient skin occurs during balneological treatment. Experimental verification of such balneological procedures in conditions of the Ukrainian Scientific-Research Institute of Medical Rehabilitation and Balneology has fully confirmed the efficiency of the scientifically substantiated method for patient treatment considered here.

Conclusions. On the basis of the findings of electron microscopy, thermogravimetric, X-ray, rheological, mechanochemical, and biomedical research methods models of physicochemical, nanochemical, colloidal and biocolloid transformation processes in iron oxide-aluminosilicate rocks are proposed. They are accompanied by formation of nano- and microdisperse pelitic sediments, peloids (therapeutic muds), clays, soils, sedimentary iron silicate carbonate ore materials. The role of microorganisms and surface-active products of their vital activity in these processes is shown. It was noted that a stable existence of ecosystems which contain polymineral disperse iron oxide-hydroxide aluminosilicate compositions, is largely determined by preliminary processes of geomechanical dispersion of rocks and by subsequent deeper dispersible processes resulted from vital activ-

ity of biogeocenosis of various microorganisms. The surface active amphiphilic metabolic products of such microorganisms (their quantity can reach 3000) activate biocolloid interactions due to cooperative colloidal, biological, biochemical and nanochemical transformations of biogeocenosis of living and non-living matter. There have been developed conceptions for the role and meaning of various chemical processes and biocolloidal processes of iron and silicon interface nanocluster formation in the strength changes in the contact zones of microparticles in polymineral disperse systems. Respectively, such changes influence their rheological properties and the choice of rational technologies for creation of stress resistant compositions of IASSM and NIASSM. It is shown that in the presence of sodium chloride (seawater, lake brine) even for low-iron clay-sand systems, a dilatant-thixotropic nature of the flow is observed. And at high iron content, especially in the form of nanostructured goethite, a hypernomalous growth of concentrated iron-aluminosilicate suspension viscosity and shear stress occurs. It is also shown that contact interactions in the suspensions are intensified by microorganisms' vital activity. Taking into account the established phenomena, the application of iron oxide-aluminosilicate peloid compositions in the stress resistant construction of protective barriers, in medicine and balneology (treatment of injured joints, wounds, leukemia, etc.) is considered. The leading role of nano- and microstructures in processes of geomechanical and biocolloidal dispersion of iron oxide silicate rocks of IASSM and NIASSM, pelitic sediments, peloids and soils types is also shown. It has been established that in biocolloidal dispersion processes, biogeocenosis of living and not living matter take part. The metabolism processes in them proceed with releasing a huge amount of biologically and surface active matter, which accelerate transformations of microcolloidal and nanostructural iron oxide-aluminosilicate materials. Models of nanochemical contact interactions of disperse mineral particles with the participation of iron hydroxides are proposed.

CHAPTER **5**

**NANO-
AND MICRODISPERSE
STRUCTURES IN PROCESSES
OF TRANSFORMATION,
REDUCTION SINTERING,
AND COMPONENT SEPARATION
OF IRON OXIDE-
ALUMINO SILICATE MATERIALS**

Biocolloidal iron oxide-aluminosilicate ore materials (IASOM) and their technogenic processing products, widespread in the Earth's crust, including processed in reductive conditions at high temperatures, belong to natural nanostructured materials (of IASSM and NIASSM types) with great practical importance. As a rule, IASOMs contain polydisperse and polymineral formations based on iron, silicon and aluminum oxides and containing admixtures of other inorganic and organic components [11, 17-20, 23, 367, 368]. Basic IASOM types include nanostructured sedimentary iron ores, highly ferrous clays, which contain quartz sand and feldspars as main admixtures and raw material admixtures-impurities, in particular compounds of sulfur, phosphorus, arsenic, etc.

Practical importance of IASOMs increases constantly in connection with the development of high-quality ore deposits, and fields of their application are broadened respectively. This fact attracts and will attract attention of many researchers to high-temperature processes in them [11, 17, 19, 20, 23, 106, 108, 367-371]. At the same time, conceptions of physicochemical geomechanics and microbiological role in processes of nanochemical, mechanochemical and structural IASOM transformations have not yet properly developed. And many problems of IASOM transformation and metamorphism with further nanodisperse structure formation, high-temperature separation, concentration, purification, and practical appliance have not been discussed at all. The role of silicates, sulfur, phosphorus, arsenic compounds and other admixtures in nanochemical IASOM transformations are also studied insufficiently. No doubt, further investigation of the aforesaid transformations will give new opportunities for their science-grounded controlling.

These reasons point on the relevance of investigations of IASOMs metamorphism and transformation along with their chemical, physical-geomechanical, microbiological and nanochemical transformations and processes of their reduction at high temperatures and purification from admixtures of nano- and microparticles of silica, arsenic and phosphorus. This is the basis for the current study.

5.1. Discussion of experimental and analytic findings

Electron-microscopic IASOM sample images were obtained on an SELMI electron microscope in a light field mode, and the morphology of samples were studied on a JEOL scanning electron microscope JSM6490LV. Thermograms of samples were obtained in an inert atmosphere. XRD patterns were recorded using a DRON-UM1 unit with two Soller slits under CuK α filtered emission. Rheological investigations were performed using a Rheotest 2 (Germany) connected to PC for data recording. The chemical composition of samples was analyzed by X-ray fluorescence method. Physical-geomechanical and nanochemical IASOMs transformation processes in natural and technogenic conditions were modelled using physicochemical geomechanical methods [20] and their reduction up to magnetite or metallized product in conditions described in [369-371]. Microbiological IASOM suspension were tested according to methods [21]. Fine-disperse pelitic iron-oxide-silicate material (Azov region) of sedimentary biocolloid origin which contained 39.87% Fe; 8.71% Mn; 0.95% Ca; 0.28% Mg; 3.89% Al; 7.81% Si; 0.45% Ti; 0.05% V; 0.98% P; 0.21% S and 0.12% As was used as a main sample for study and other iron-containing materials were used as well [17, 106, 108, 369-371].

Rheological study of typical ore iron oxide silicate material [17] (Fig. 5.1) showed that its concentrated suspension flow is characterized by nonstandard hyperanomaly (ultraanomaly) of viscosity attributed to the influence of micro- and nanoparticles contained in zones of mechanochemically and nanochemically transforming coagulation-condensation contacts on the IASOM rheological processes [23]. The XRD pattern of a sample in Fig. 5.2 points on an amorphous fine-disperse IASOM structure. Its composition included goethite, saponite, quartz, sulfides, nanodisperse admixtures of phosphates and arsenates of aluminum and iron of microbiological origin [17, 22].

According to the obtained thermograms (one of which is shown in Fig. 5.3) as well as XRD investigation in [370], the processes of IASOM reduction begin at

above 450 °C and run by the summary reaction $3\text{Fe}_2\text{O}_3 + \text{C} = 2\text{Fe}_2\text{O}_{4(\text{nano, micro})} + \text{CO}$ up to 990-1000 °C [108, 367].

Above this temperature, magnetite is reduced up to wustite (FeO). Then active metallization process is

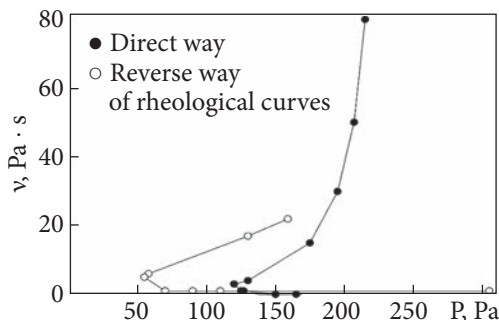


Fig. 5.1. Viscosity presupposes (η) against shear stress (P) for sedimentary IASOM with 46% suspension moisture

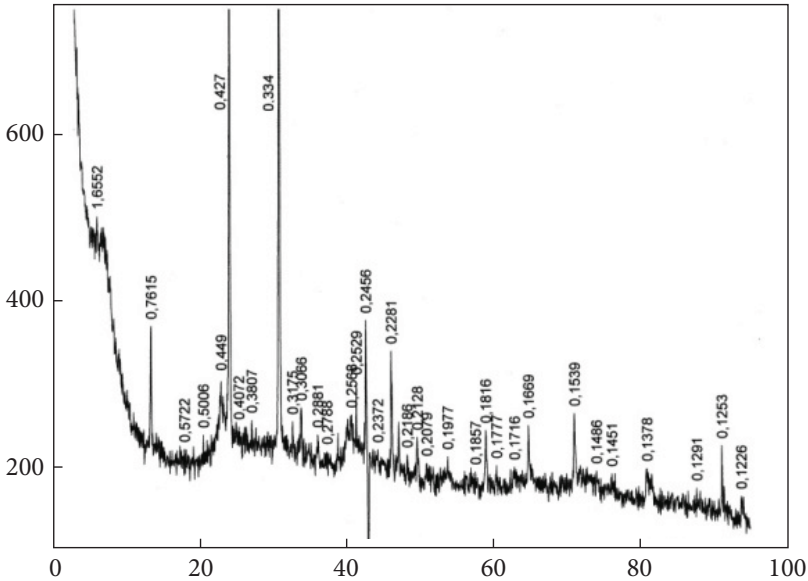
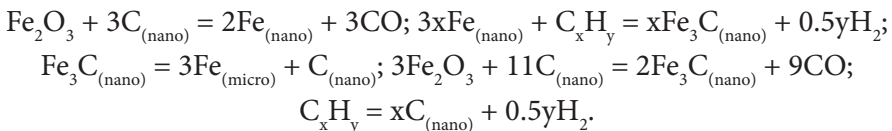


Fig. 5.2. XRD of sedimentary IASOM

held in the interval of 1050-1150 °C by the reaction $\text{FeO} + \text{C} = \text{Fe} + \text{CO}$. Once metallization process with formation of nanoparticles of metallic iron on magnetite surface begins yet at 500-700 °C, this iron takes part in formation of amorphous carbon reducer ($\text{C}_{\text{nano}} + \text{Fe}_3\text{C}_{\text{nano}}$) from volatile hydrocarbons yielded by thermal coal decomposition [108] in the presence of H_2O . The process proceeds by a “low-temperature” (500-1000 °C) carbide cycle aided with nanoparticles, which in technogenic conditions promote catalytic transformation of Fe_2O_3 from IASOMs into nano- and then into microdisperse magnetite, on the surface of which nanoparticles of arsenates and phosphates are accumulated [371]. Consequently, in natural metamorphic conditions fine-disperse magnetite and thermodisrupted silicates formed first from sedimentary IASOMs are transformed into ferroquartzites (jaspelites) [22] or into ferrosilicates carbonized with nano-carbon particles (schungites) [372] as a result of sintering at high temperatures and pressures in the Earth’s crust. Nanochemical processes in such conditions at 500-1000°C, including according to “low-temperature” carbide cycle mechanism [106] can be characterized by the following reactions [106, 371]:



Similar reactions, running above 500 °C on catalytically active surface of iron-silicate structures, such as saponites, nontronites and other disperse iron-

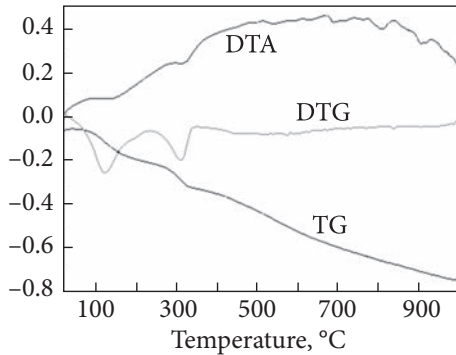


Fig. 5.3. Thermogram of IASOM mixed with coal powder at 4:1 ratio

containing silicate minerals contained in IASOM composition as admixtures, lead to formation of schungites [372] in conditions of natural metamorphism and at carbon surplus in the Earth's crust, and to formation of carbonized nanoporous sorbents [344] in technogenic conditions. The above data directly points

on the dependence of described processes on the conditions of sediment formation usually occurring in seas and oceans [11, 18-22, 106, 108, 368-371], as IASOM dispersion defines direction and efficiency of their transformation [106, 108, 369-371]. According to [21], such processes are also substantially affected by biocolloid (microbiological and colloid) processes in dispersions of IASOM pelagic sediments. Biogeocenosis or bioosteal aggregates formed according to the biogeochemistry laws as a result of interaction of selective microorganisms with mineral particles are transformed into oolites, which are the basis of sedimentary iron-oxide-silicate and other ore deposits [11, 21, 22]. Sedimentary IASOMs in the inorganic structure of bioosteal aggregates or oolites contain also organic substances, microorganism waste products along with living organisms. Metabolic processes of the latter are accompanied with formation of various organic substances including nanostructured surface-active substances (SAS) [18, 22]. Such organic compounds take part in above described high-temperature reduction metamorphic processes in the Earth's crust and, in technogenic reduction condition, in IASOM transformations, along with disperse coal or gaseous hydrocarbons obtained also from outside sources [106, 108, 369-371]. However, at the same time the role of living organisms in IASOM sediment transformation processes in aqueous medium and environment temperature lower than 38 °C, has not yet properly clarified.

Investigations of microorganisms of different eco-trophic groups [17], first of all, iron-reducing bacteria, in pelitic sediment samples indicate the sediment ability to restore its physicochemical properties after their reactivation. Changes in viscosity and yield stress in the course of sediment activation for 90-100 days indicate also realization of hydrolytic dispersion mechanism [20] under the action of substances like surfactants excreted by microorganisms during Fe^{3+} reduction to Fe^{2+} (Fig. 5.4).

The data from Fig. 5.4 also shows that Fe(II) quantity in disperse medium increases by 0.07% during reduction processes (30-100 days), while the Fe(III)

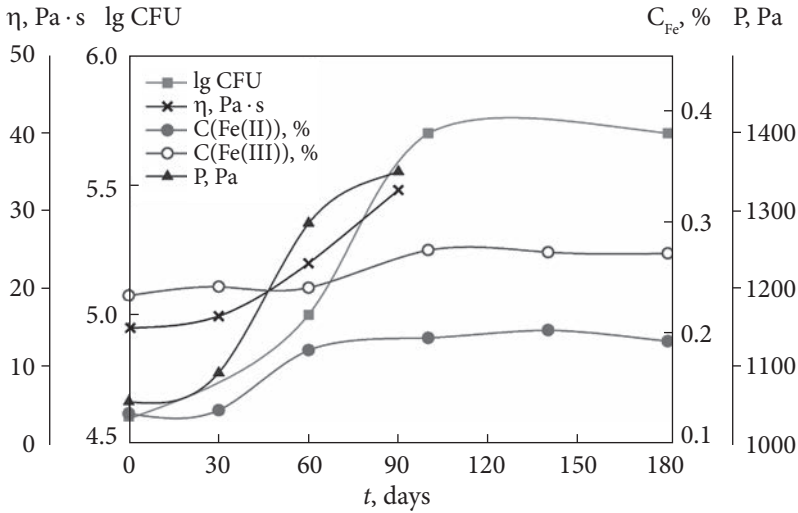
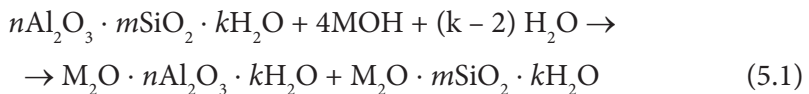


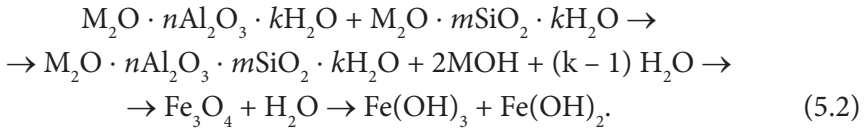
Fig. 5.4. Dynamics of viscosity (η), shear stress (P) and of microbiological composition ($\lg\text{CFU}$) of partly reactivated iron-containing pelitic sediment suspensions during their activity in subsequent maturation, as well as change in Fe(II) and Fe(III) concentrations in the disperse medium

concentration increases synchronously by 0.03% at the expense of partial oxidation of the reduced iron by oxygen from air, and it gives 0.1% in sum. Thus, at total 2.7% Fe concentration in sediment in terms of elemental iron, the part of mineral disruption mainly up to nanoparticles [371] reaches approximately 4% in 90-100 days during the period of reduction processes. It substantively affects the increasing suspension yield stress and viscosity at the same period due to the fact that formed iron-containing nanophases take part in contact processes, followed by coagulation condensation transformations.

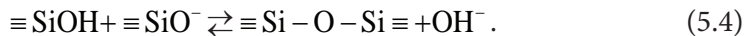
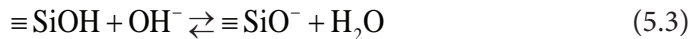
High-temperature and microbiologic effects on pelitic IASOM sediments are also preceded by apparently connected with them physicochemical and geochemical transformations of iron-containing ores, which should be considered in detail to show their role in posterior processes. Pelitic sediment formation in long-term natural geological conditions in alkalescent disperse medium [368] is indeed preceded by mechanical and mechanochemical transformations of iron-containing ores accompanied by formation of nano- and microparticles, and proceeds according to the laws of physicochemical geomechanics (PCGM) [17, 20]. Here with, according to [20, 23, 373, 374], accelerated chemical processes can take place in 10-100 nm nanocracks as provided by the following equations:



Then reaction (5.1) products react according to the following schemes:



Crystalline hydrate formed by reaction (5.2) has higher volume than that of the initial product participated in reaction (5.1). Thus, the emerging crystallization pressure bursts (splits chemically) the crack subjected to sinter promotion by outer mechanical stress. Water, which additionally enters a micrometer-broadened initial crack, hydrolytically destructs reaction (5.2) product at the following stage with releasing alkali diffusing into newly-formed secondary crack in the form of solution. The process goes the same way as liquid phase penetration through intergranular boundaries, but few grades faster and it is now being measured not by years but hours [23, 373]. It is also promoted, in addition to (5.1) and (5.2), by nanochemical interactions and characterized by the reactions [373]:



Reactions (5.3) and (5.4) are conditioned by transformations of disperse medium in soluble silicates and affect IASOM suspension viscosity (Fig. 5.5).

Reaction (5.4) is a reaction of polymerization and leads to formation of insoluble polysilicate nanostructures on the solid phase crack surface. Released hydroxyl ions take part in reactions (5.1) or (5.3). Therefore, reactions (5.3) and (5.4) are intermediate for the processes (5.1) and (5.2), and colloid-chemical interactions at the nanolevel on the solid surface of iron-containing silicate ore are closely associated with chemical transformations in the disperse medium.

The process proceeds stepwise, which was shown experimentally on “iron-containing aluminosilicate and alkaline component” model system. Rheological data shown in Fig. 5.6 (as well as data from the previous chapters) demonstrate that this stepwise process is more intensive in low-motion conditions of porous disperse ore, but in the case of increasing plastic flow velocity, it is smoothed.

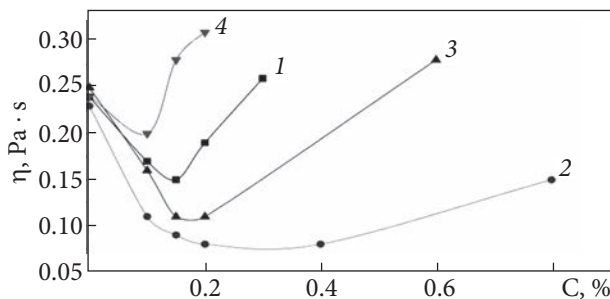


Fig. 5.5. Influence of the NaOH : $Na_2Si_3O_7$ ratio on IASOM suspension viscosity (η) depending on the concentration (C) of alkaline mixture in the following conditions: 1 — without NaOH; 2 — NaOH : $Na_2Si_3O_7$ = 1 : 2; 3 — NaOH : $Na_2Si_3O_7$ = 1 : 1; 4 — NaOH : $Na_2Si_3O_7$ = 1.5 : 1

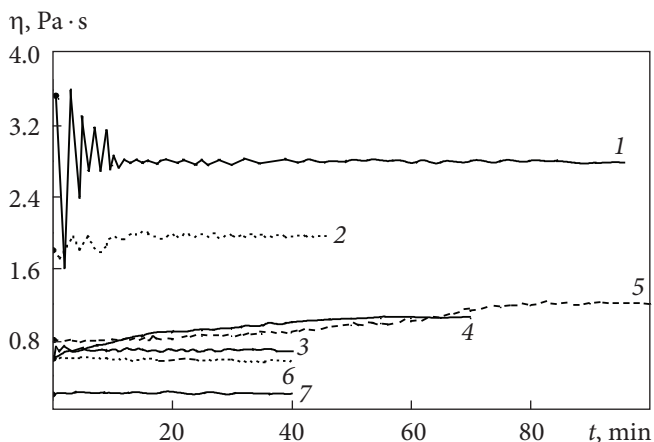


Fig. 5.6. The process kinetics for iron-containing aluminosilicate ore accompanied by reactions (5.1) and (5.4) at shear rates of (s^{-1}): 1 — 1.0; 2 — 1.8; 3 — 3.0; 4 — 27.0; 5 — 81.0

The formation mechanism of such a process in model disperse technogenic materials, whose analogues can be formed in natural conditions in zones of volcanic activity, almost does not differ from the mentioned stepwise processes in rocks [23, 373, 374], which has been proven by independent investigation [375]. The key point of the process is the fact that external nanocracks in disperse material work as channels for penetration of reaction alkaline substances into them, i.e., they are phase-formation zones. When the volume of such a new phase is bigger than initial phase then a disjoining pressure appear which leads to disruption of initial particles by nanocracks. Then the process is repeated at the new dispersion level, which can be seen in rheograms (Fig. 5.6) as a stepwise process. As a result of new phase formation, it is characterized not only by self-activating stepwise behavior, but also by proceeding like mechano-geochemical and nanochemical processes described in [17, 23, 106, 317, 368, 373-375].

The findings of the experimental part of the work along with known ideas [11, 17-20, 22, 23, 106, 108, 367-371, 373-375] make it possible to offer a generalized scheme of physico-geochemical, mechanochemical, and biocolloidal metamorphism and transformation processes of rock iron-oxide-silicate ore materials into pelitic (sedimentary) IASOMs and iron quartzites aided with nano- and microdisperse structures (Fig. 5.7). SEM images of structures formed at different process stages are presented on Fig. 5.8.

The scheme of iron-containing rock metamorphism and nanochemical transformation aided with nanostructures and microorganisms as well as in high temperature conditions (Figs 5.7 and 5.8) with formation of IASOMs like pelitic sediments and nanocrystal jaspelites, proposed on the basis of analytic-experimental investigations, allowed to provide scientific explanation of further technological processes of high-temperature solid-phase iron ore metallization as well as separation and concentration of metallized products from non-metallic admixtures. Ac-

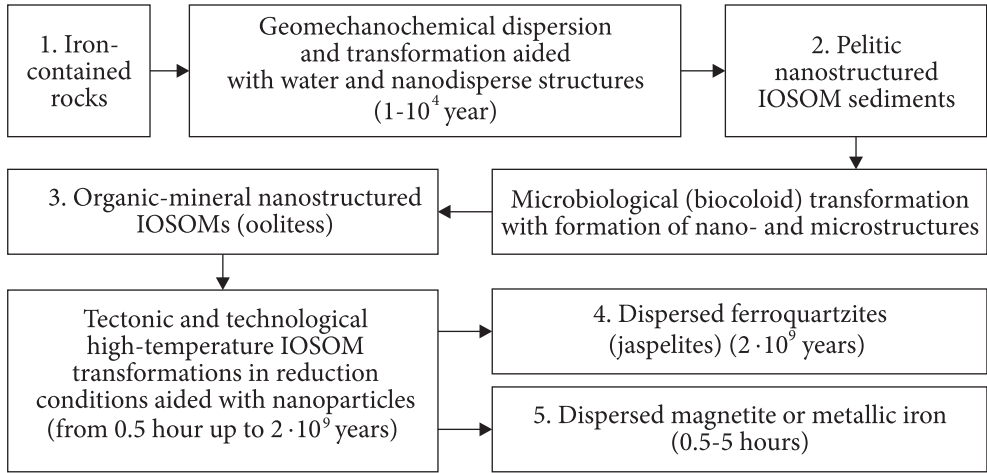


Fig. 5.7. Scheme of natural and technogenic iron-containing rock transformation into pelitic sediments, jaspelites, and metallized materials

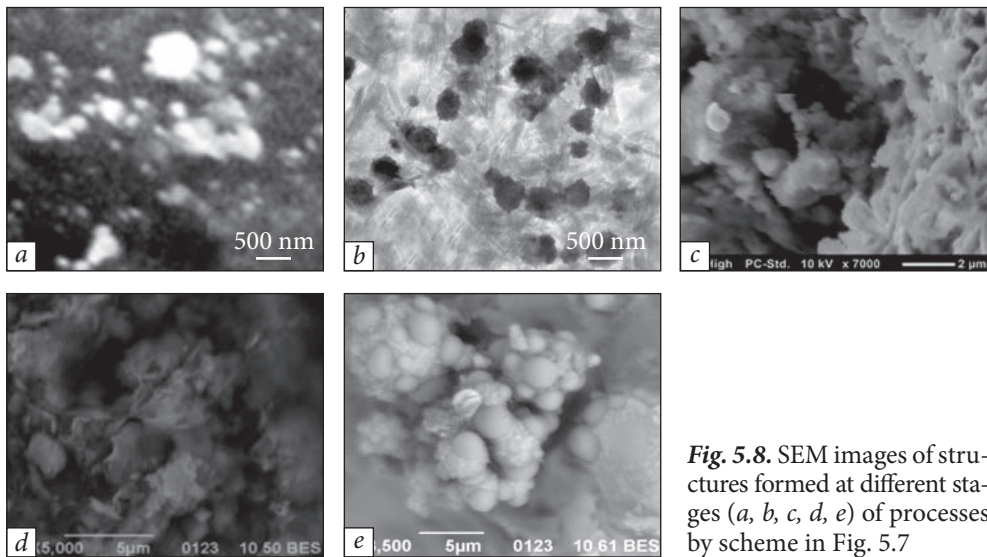


Fig. 5.8. SEM images of structures formed at different stages (a, b, c, d, e) of processes by scheme in Fig. 5.7

According to [367], the metallized product is obtained via direct reduction of iron ore raw material by carbon reducer at 900-1300 °C. For example, there can be used oxidized pellets of the following composition (wt%): 67.83 Fe_{total}; 2.50 FeO; 94.12 Fe₂O₃; 1.79 SiO₂; 0.72 Al₂O₃; 0.31 CaO; 0.12 MgO; 0.11 MnO; 0.31 TiO₂; 0.01 P₂O₅; 0.01 SO₃ (general admixture content is 3.38%), with flux addition for sulfur removal, for example, limestone containing (wt%): 1.59 SiO₂; 0.74 Al₂O₃; 57.70 CaO; 0.48 MgO; 0.05 P₂O₅; 0.23 SO₃ and 43.21 baking loss, and a reducer,

for example, brown coal. Metallized product obtained from such a mixture contains (wt%): 92.23 Fe_{total}; 5.93 FeO; 87.63 Fe_{MET}; 2.43 SiO₂; 0.98 Al₂O₃; 0.42 CaO; 0.17 MgO; 0.42 TiO₂; 0.15 MnO; 0.006 P; 0.004 S; 1.85 C (general admixture content is 4.58%).

A shortcoming of the process is the fact that it uses iron ore raw material concentrate with high content of iron (67-69%) for metallization process and it needs considerable costs for preliminary grinding, concentration and purification of raw iron ore material. Herewith, the obtained metallized product contains 87.3% of metallic iron; 5.93% of FeO; 1.85% C and 4.58% of admixtures, i.e., concentration of admixtures is even higher than it was in the initial iron concentrate (3.38%). It means that during the process, the impurities content in the final product increases by 1.2%, and their removal needs valuable capital, material and energetic costs and new technologies for this have not yet designed.

The chemical analysis results of brown ore and, for comparison, of tobacco ore are listed in Table 5.1. The comparison shows their similarity.

The XRD patterns given in Figs. 5.9 and 5.10 for tobacco and brown ores show that both ores contain goethite and saponite admixtures as general minerals.

Table 5.1. Chemical analysis results for (1'KA, 1''KA) tobacco and (2'KA, 2''KA) brown ores

Con- tent, wt%	Sample				Con- tent, wt%	Sample			
	1'KA	1''KA	2'KA	2''KA		1'KA	1''KA	2'KA	2''KA
Ag	<0.01	<0.01	<0.01	<0.01	Mg	0.45	0.45	0.29	0.25
Al	1.55	1.52	1.16	1.11	Mn	0.56	0.70	7.18	6.09
As	0.12	0.13	0.10	0.11	Mo	<0.01	<0.01	<0.01	<0.01
B	<0.01	<0.01	<0.01	<0.01	Na	0.07	0.07	0.13	0.12
Ba	0.05	0.07	0.14	0.11	Ni	0.02	0.02	0.11	0.11
Be	<0.01	<0.01	<0.01	<0.01	P	2.01	2.03	0.76	0.79
Bi	<0.01	<0.01	<0.01	<0.01	Pb	0.02	0.02	0.01	0.01
Ca	1.62	1.53	1.12	1.18	S	0.04	0.04	0.07	0.09
Cd	<0.01	<0.01	<0.01	<0.01	Si	5.31	5.44	5.74	6.07
Co	<0.01	<0.01	<0.01	<0.01	Sn	<0.01	<0.01	<0.01	<0.01
Cr	<0.01	<0.01	<0.01	<0.01	Sr	0.04	0.04	0.07	0.06
Cu	<0.01	<0.01	<0.01	<0.01	Ti	0.12	0.11	0.09	0.08
Fe	36.11	37.70	27.01	26.82	V	0.05	0.05	0.05	0.05
Ga	<0.01	<0.01	<0.01	<0.01	W	<0.01	<0.01	<0.01	<0.01
K	0.23	0.23	0.29	0.27	Zn	0.03	0.03	0.03	0.03
Li	<0.01	<0.01	<0.01	<0.01	Zr	<0.01	<0.01	<0.01	<0.01

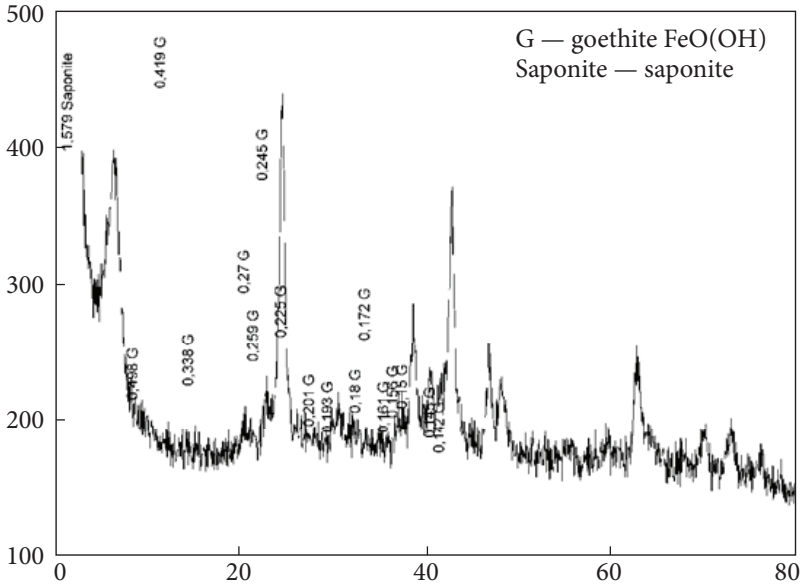


Fig. 5.9. XRD pattern of tobacco ore No. 1KA

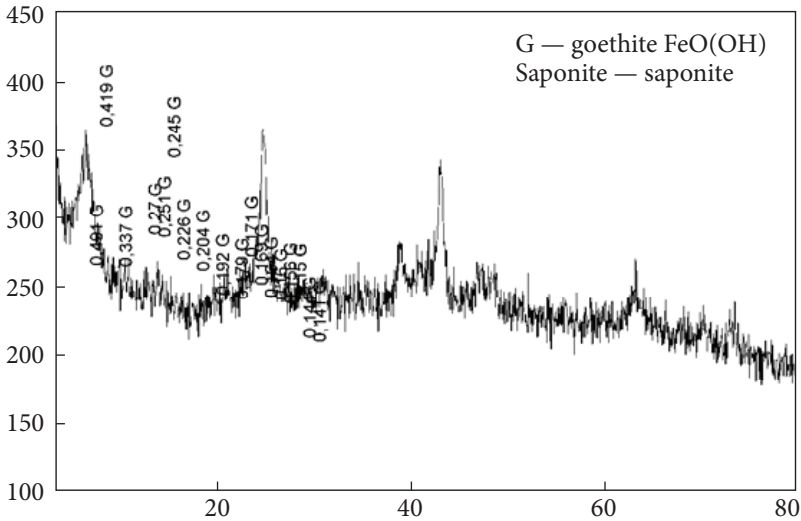


Fig. 5.10. XRD pattern of brown ore No. 2KA

The thermograms of samples (Figs. 5.11 and 5.12) also show similar thermic parameters except for mass loss. Tobacco ore lost 17.1% of initial mass at 1000 °C, while brown ore sample lost 23.5% at the same temperature. The mass loss in their mixture with coal (Figs 5.13 and 5.14) was 30.8% and 36.6%, respectively.

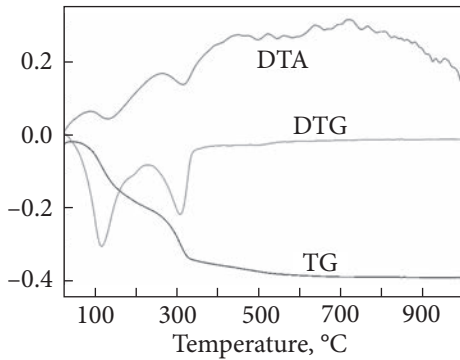


Fig. 5.11. Thermograms of tobacco ore

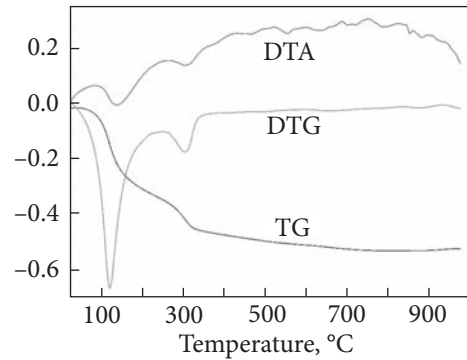


Fig. 5.12. Thermograms of brown ore

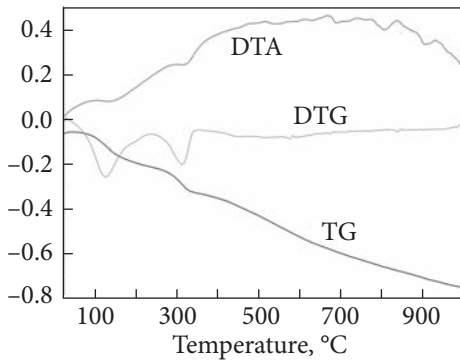


Fig. 5.13. Thermograms of tobacco ore with coal at ratio 4 : 1

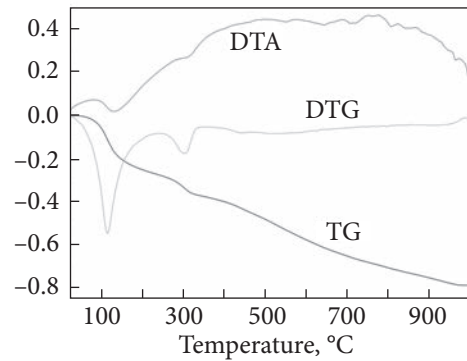


Fig. 5.14. Thermograms of brown ore with coal at ratio 4 : 1

Metallization process of brown ore was investigated in the same conditions as tobacco ore. The results are shown in Table 5.2. They indicate that brown ore metallization occurs similar to that of tobacco ore.

Chemical analysis results for red ore are summarized in Tables 5.3 and 5.4.

The XRD pattern in Fig. 5.15 shows that ore contain goethite, and admixtures of quartz and saponite as basic minerals.

The thermograms of pure sample and the same sample with addition of coal are given in Figs. 5.16 and 5.17. The mass loss at 1000 °C is 19.1% and 33.2%, respectively.

Metallization process of red ore was investigated in a similar way as for tobacco ore. The results are listed in Table 5.5.

These results agree with the data of differential thermal analysis. Thus, comparison of the DTA curves for pure ore (Fig. 5.16) and mixed with coal (Fig. 5.17) shows that the metallization process starts at 990-1000 °C.

The proposed method, based on analysis of experimental data in Figs 5.9-5.26 on iron ore (especially of sedimentary origin) processing, which considers established conditions of metamorphism and transformation of iron-containing rocks into nano- and microstructured iron-oxide ore materials, uses such materials without any preliminary enrichment [106, 108, 369-371]. The developed technology considers that obtained burnt cake can be easily purified from general part of inorganic impurities during dry enrichment and, as follows, the separation process is additionally activated during wet alkaline enrichment and phos-

Table 5.2. Brown ore metallization process

Temperature of reducing burning, °C	990	1100	1150	1200	1250
Metallization degree, %	0	56	74	83	95

Table 5.3. Chemical analysis of red ore

Element or oxide	Fe + Mn	Al ₂ O ₃	SiO ₂	P	As
Content, wt%	37.3	3.04	11.9	1.1	0.11

Table 5.4. Results of chemical analysis of red ore (3'KA, 3"KA)

Element	Content, wt %		Element	Content, wt %	
	3'KA	3"KA		3'KA	3"KA
Ag	<0.01	<0.01	Mg	0.36	0.23
Al	1.29	1.29	Mn	8.81	9.04
As	0.12	0.13	Mo	<0.01	<0.01
B	0.01	<0.01	Na	0.22	0.20
Ba	0.58	0.62	Ni	0.11	0.12
Be	<0.01	<0.01	P	1.39	0.94
Bi	<0.01	<0.01	Pb	0.02	0.02
Ca	1.29	1.00	S	0.13	0.12
Cd	<0.01	<0.01	Si	5.68	5.63
Co	0.04	0.04	Sn	<0.01	<0.01
Cr	<0.01	<0.01	Sr	0.11	0.11
Cu	<0.01	<0.01	Ti	0.09	0.10
Fe	25.50	26.33	V	0.05	0.05
Ga	<0.01	<0.01	W	<0.01	<0.01
K	0.33	0.31	Zn	0.03	0.03
Li	<0.01	<0.01	Zr	<0.01	<0.01

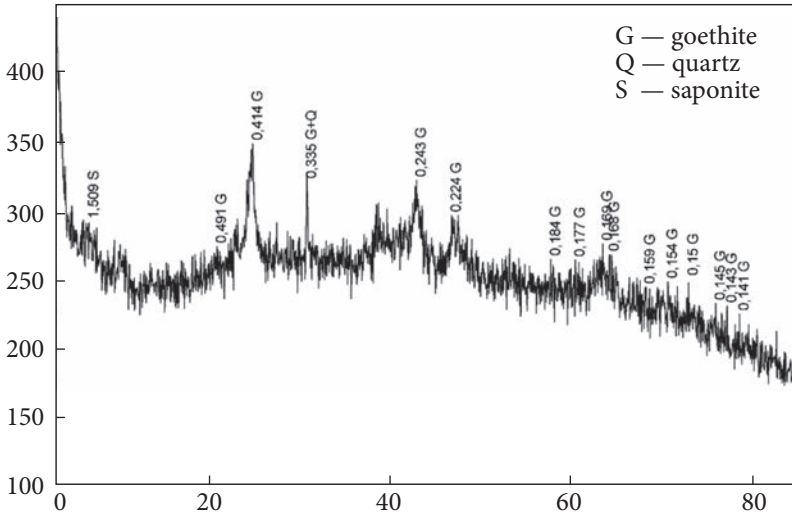


Fig. 5.15. XRD pattern of red ore

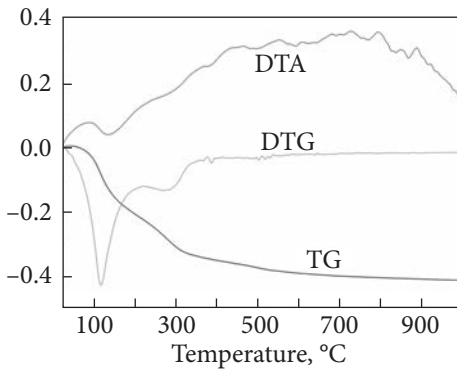


Fig. 5.16. Thermogram of red ore

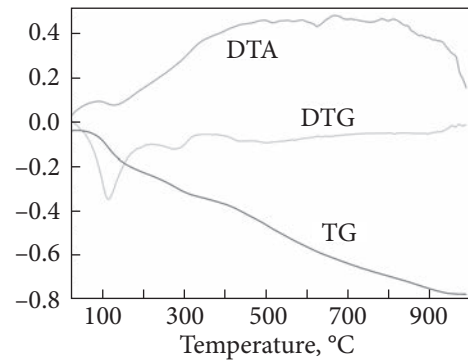


Fig. 5.17. Thermogram of red ore mixed with coal at ratio 4 : 1

phorus and arsenic impurities separation [369-371]. For example, from arsenic- and phosphorus-containing IASOMs reduced at 1200 °C and having the chemical composition (wt%): 32.88 Fe; 4.78 Mn; 1.38 P; 0.12 As; 0.09 S; 1.13 CaO; 1.88 Al₂O₃; 11.11 SiO₂, a high-purity concentrate can be obtained after enrichment, separation and purification of cake with the composition (wt%): 95.71 Fe; 0.09 P; <0.007 As; 0.002 S; 0.23 CaO; 0.32 Al₂O₃; 1.73 SiO₂, 1.84 C (Table 5.8). Such results were reached also thanks to the established fact that for iron ores contaminated with silicates, phosphorus and arsenic, the maximal arsenic extraction and its separation from phosphorus can be reached in conditions of catalytic solid-phase carbide transformation of iron oxide at 600-980 °C with concurrent process

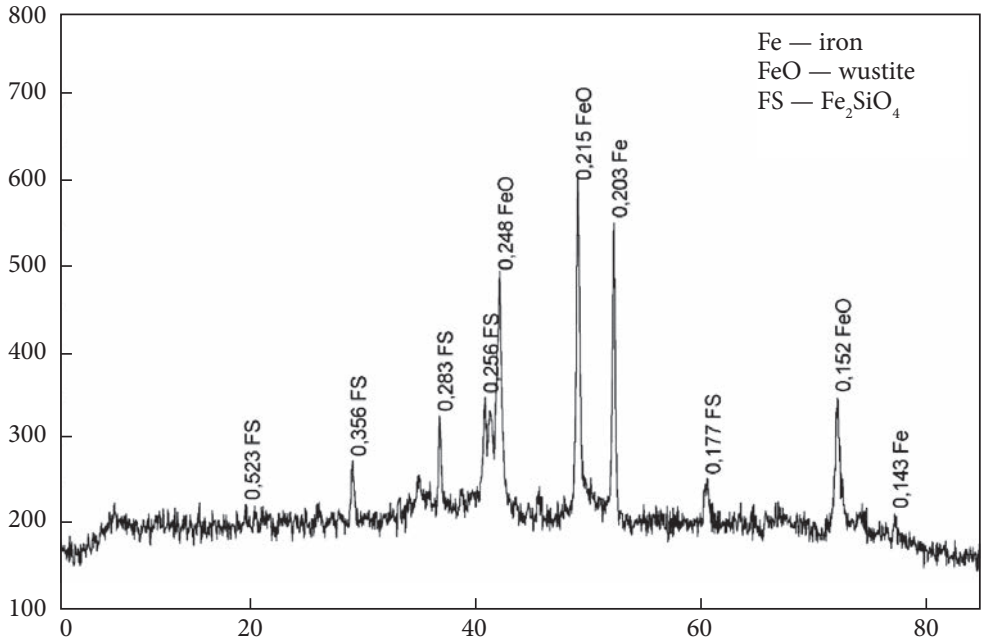


Fig. 5.18. XRD pattern of magnetic concentrate of averaged Kyz-Aul ore sample reduced by coal at 990 °C

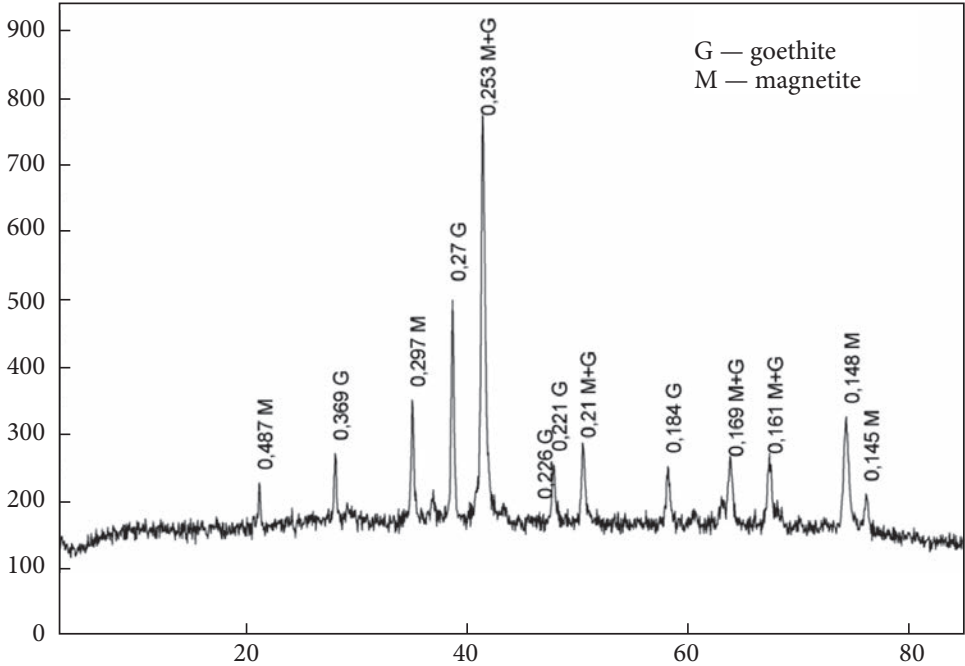


Fig. 5.19. XRD pattern of low-magnetic wastes of averaged Kyz-Aul ore sample reduced by coal at 990 °C

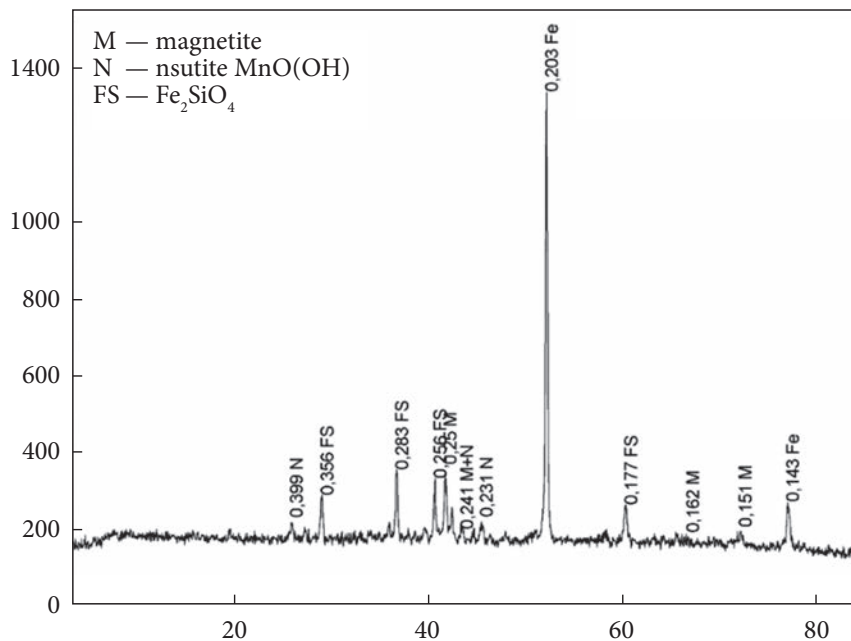


Fig. 5.20. XRD pattern of low-magnetic concentrate of averaged Kyz-Aul ore sample reduced by coal at 1050 °C

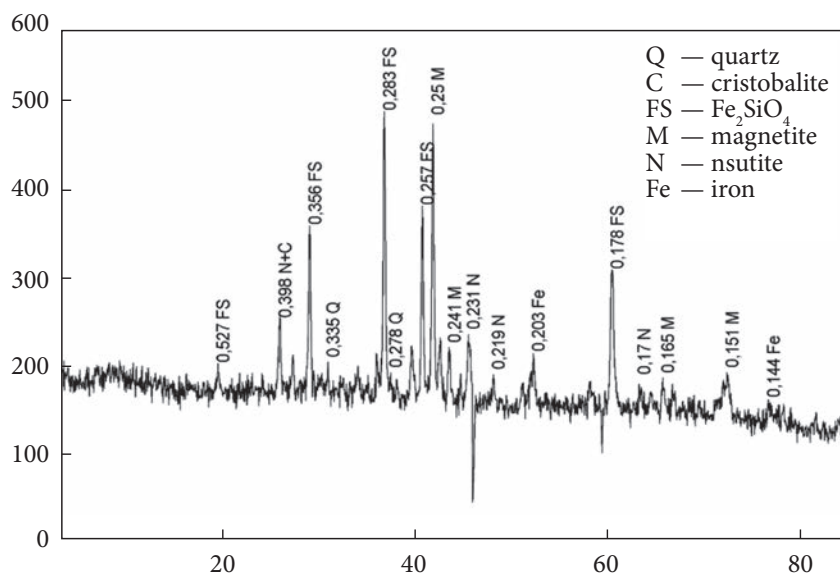


Fig. 5.21. XRD pattern of low-magnetic wastes of averaged Kyz-Aul ore sample reduced by coal at 1050 °C

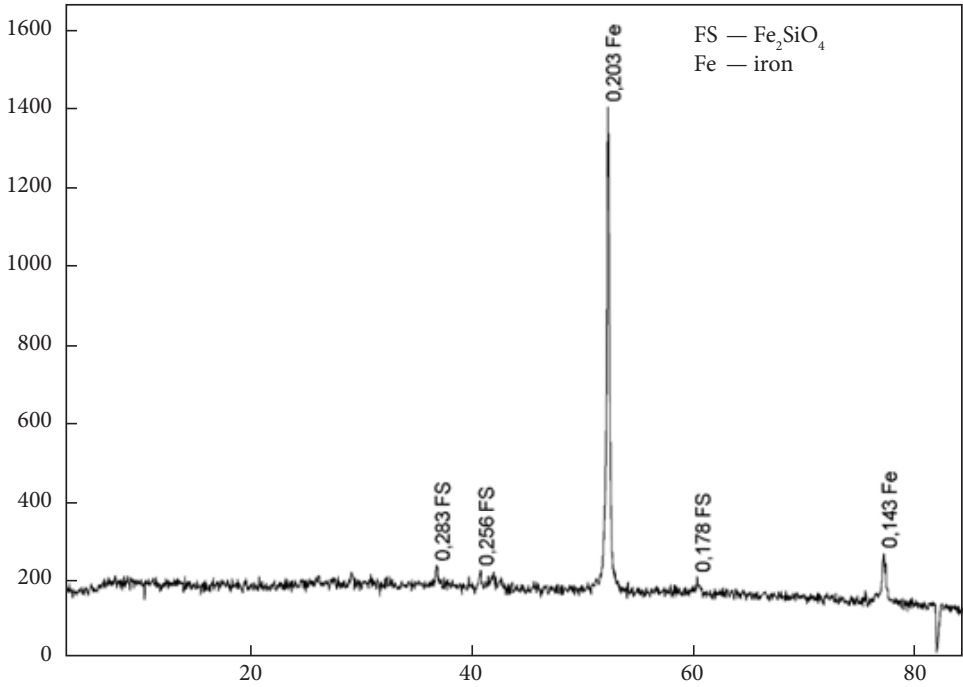


Fig. 5.22. XRD pattern of magnetic concentrate of averaged Kyz-Aul ore sample reduced by coal at 1150 °C

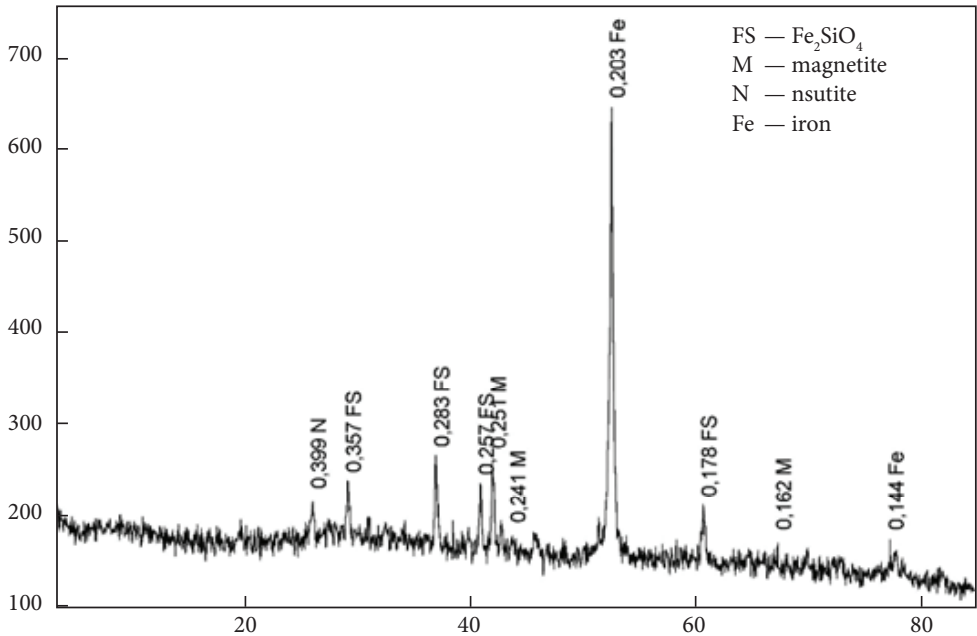
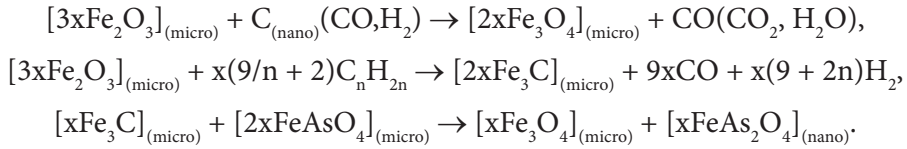


Fig. 5.23. XRD pattern of low-magnetic wastes of averaged Kyz-Aul ore sample reduced by coal at 1150 °C

of magnetite formation and conversion of insoluble As(V) compounds into alkali-soluble As(III) ones, for example, by the following scheme:



Analysis of results given in Table 5.8 allows making the following conclusions: proposed technology which considers geological IASOM transformation history can be used for component separation, enrichment, and purification of

Table 5.5. Results of red ore metallization

Temperature of reducing burning, °C	990	1100	1150	1200	1250
Ore metallization degree, %	0	5	63	82	95

Table 5.6. Results of chemical analysis of the averaged sample reduced by coal at 990 °C and conducted to dry magnetic enrichment. 73.3.1' and 73.3.1'' correspond to magnetic concentrate, 73.3.2' and 73.3.2'' — to low-magnetic enrichment wastes

Element	Content, wt%				Element	Content, wt%			
	73.3.1'	73.3.1''	73.3.2'	73.3.2''		73.3.1'	73.3.1''	73.3.2'	73.3.2''
Ag	<0.01	<0.01	<0.01	<0.01	Mg	0.52	0.54	0.49	0.42
Al	1.93	2.00	2.70	2.46	Mn	0.93	0.96	1.95	1.88
As	0.23	0.23	0.07	0.07	Mo	<0.01	<0.01	<0.01	<0.01
B	<0.01	<0.01	<0.01	<0.01	Na	0.06	0.07	0.31	0.31
Ba	0.25	0.26	0.46	0.58	Ni	0.04	0.03	<0.01	<0.01
Be	<0.01	<0.01	<0.01	<0.01	P	2.01	2.05	1.35	1.40
Bi	<0.01	<0.01	<0.01	<0.01	Pb	0.03	<0.01	<0.01	<0.01
Ca	0.88	0.91	1.13	1.09	S	0.55	0.40	0.23	0.22
Cd	<0.01	<0.01	<0.01	<0.01	Si	3.47	3.50	9.26	9.35
Co	<0.01	<0.01	<0.01	<0.01	Sn	<0.01	<0.01	<0.01	<0.01
Cr	<0.01	<0.01	<0.01	<0.01	Sr	0.04	0.04	0.07	0.07
Cu	0.06	0.05	0.06	0.06	Ti	0.08	0.08	0.17	0.17
Fe	53.48	55.42	32.84	33.41	V	0.09	0.09	0.04	0.04
Ga	0.02	<0.01	<0.01	<0.01	W	<0.01	<0.01	<0.01	<0.01
K	0.04	0.04	0.57	0.56	Zn	0.03	0.03	0.04	0.04
Li	<0.01	<0.01	<0.01	<0.01	Zr	<0.01	<0.01	<0.01	<0.01

Table 5.7. Results of chemical analysis of the averaged sample reduced by coal at 1200 °C and conducted to dry magnetic enrichment. 71.4.3' and 71.4.3'' — < 0.1 mm fraction; 71.4.4' and 71.4.4'' — < 0.16 mm fraction; 71.4.5' and 71.4.5'' — metallized residue of 0.16—0.5 mm size; 71.4.6' and 71.4.6'' — low-magnetic enrichment wastes

Element	Content wt%							
	71.4.3'	71.4.3''	71.4.4'	71.4.4''	71.4.5'	71.4.5''	71.4.6'	71.4.6''
Ag	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Al	1.57	1.64	1.30	1.41	1.58	1.65	3.60	3.02
As	0.21	0.21	0.23	0.22	0.21	0.21	0.09	0.09
B	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Ba	0.40	0.41	0.28	0.28	0.27	0.29	0.62	0.59
Be	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Bi	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Ca	1.28	1.30	1.00	1.04	0.89	1.00	2.22	1.90
Cd	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Co	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Cr	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Cu	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Fe	55.74	56.45	63.00	60.84	65.91	64.86	28.69	28.30
Ga	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
K	0.28	0.29	0.19	0.19	0.19	0.19	0.53	0.51
Li	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Mg	0.28	0.30	0.24	0.28	0.36	0.34	0.77	0.61
Mn	1.47	1.51	1.16	1.11	1.30	1.32	2.34	2.31
Mo	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Na	0.19	0.19	0.14	0.13	0.13	0.13	0.32	0.30
Ni	0.03	0.03	0.04	0.04	0.04	0.04	<0.01	<0.01
P	2.31	2.29	2.38	2.29	2.54	2.52	1.83	1.81
Pb	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
S	0.45	0.28	0.30	0.16	0.32	0.21	0.62	0.59
Si	5.78	6.01	4.31	4.18	4.75	4.77	10.02	9.86
Sn	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Sr	0.06	0.06	0.05	0.05	0.05	0.05	0.09	0.09
Ti	0.12	0.013	0.09	0.09	0.10	0.10	0.20	0.20
V	0.06	0.07	0.06	0.06	0.06	0.06	0.08	0.08
W	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Zn	<0.01	0.02	<0.01	<0.01	<0.01	<0.01	0.03	0.03
Zr	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

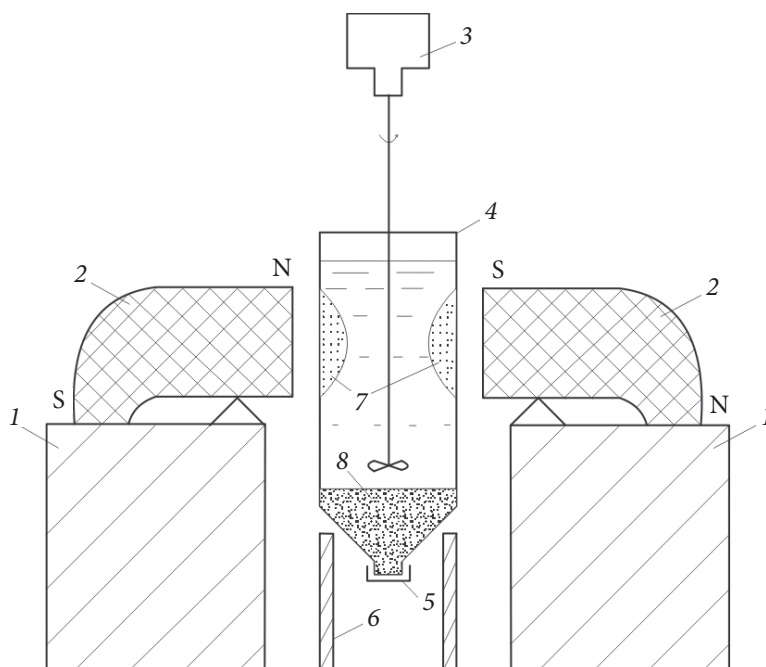


Fig. 5.24. Bench test installation for enrichment and hydrochemical leaching of admixtures from iron ores after reducing burning: (1) stand; (2) magnets; (3) mixer; (4) working tank for disperse cake suspension; (5) tank plug; (6) stand for the tank; (7) magnetic sediment; (8) non-magnetic sediment

Table 5.8. Influence of NaOH and NaCl concentration on enriched metallized cake purification

Concentration, %		Chemical composition of purified concentrate, %						
NaOH	NaCl	Fe	Mn	P	As	S	Al ₂ O ₃	SiO ₂
4	—	91.99	0.23	0.18	0.03	0.005	0.48	2.71
6	—	93.28	0.15	0.11	0.02	0.004	0.37	2.03
8	—	95.04	0.07	0.10	0.01	0.003	0.35	1.87
12	—	95.71	0.00	0.09	0.01	0.002	0.32	1.73
14	—	95.79	0.00	0.09	0.01	0.002	0.33	1.75
12	10	95.75	—	0.10	0.009	—	—	—
12	15	95.81	—	0.08	0.007	—	—	—
12	20	95.99	—	0.07	0.007	—	—	—
12	30	96.03	—	0.06	0.007	—	—	—
12	35	95.77	—	0.07	0.008	—	—	—

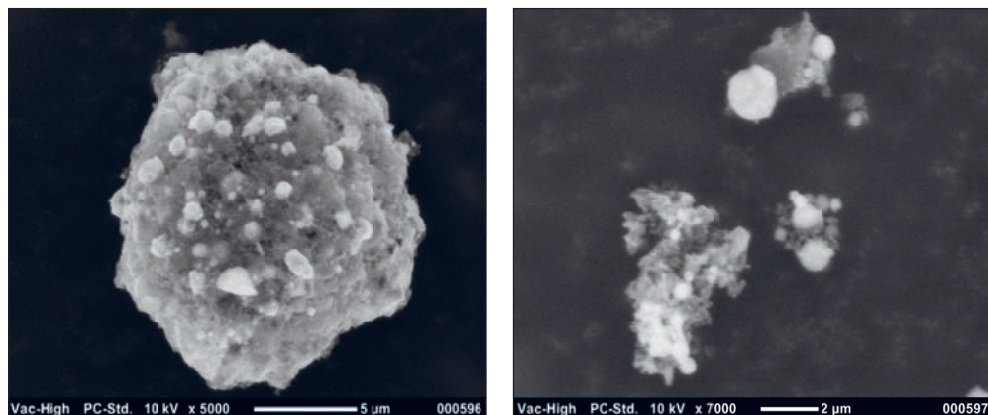
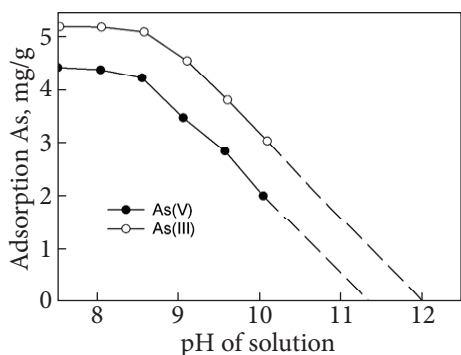


Fig. 5.25. SEM images of metallized cake particles (surface is covered by slag microparticles and nanoparticles of S, P and As compounds)



◀ *Fig. 5.26.* Adsorption limits for As(III) and As(V) for metallized product

metallized iron ore raw materials of almost any composition and origin, from metallurgic sludge to rich concentrates. The most effective application of the method maybe to sedimentary ores of biocolloid origin which usually contain 35-40% of iron and manganese and high concentration impurities like phosphates, arsenates and silicates. Such ore processing via other known methods is not effective because of insufficient removal of phosphorus and arsenic compounds.

In resuming the performed studies, it should be mentioned that thanks to using advances of physicochemical geomechanics, colloid and biocolloid chemistry, and experimental results of XRD, thermogravimetric, SEM, rheological, and microbiologic methods the dependences of mechanochemical, nanochemical and microbiological metamorphism processes of rocks on their conversions into nano- and microstructured iron oxide-aluminosilicate ore materials with the following processing, separation and enrichment have been established. Metamorphic processes at the intermediate stage of rock transformation into iron ores can also run with formation of nanostructured pelagic sediments aided with microorganisms and their excreted surface-active metabolic products. Optimal effec-

tive ways to the realization of reducing burning for sedimentary nanostructured iron-aluminosilicate ores with further separation and purification of obtained components have been shown.

Conclusions. Analytical (using advances of physicochemical geomechanics) and experimental analysis of the obtained data (by rheological, SEM, XRD, thermogravimetric, chemical and microbiologic methods) allowed us to determine the general role of physico-geomechanical, mechanochemical, biogeochemical, and biocolloid processes in metamorphic transformations of IASOM rocks. A limiting influence of nano- and microstructures, contained or formed during the processes, on the IASOM transformation at all interrelated stages of natural metamorphism and technogenic transformations was revealed. It was shown that, according to the established relationships, natural and technogenic processes in IASOM run almost in the same way, which made it possible to give science-ground interpretation of the methods of IASOM processing and purification from silicate, arsenic, phosphorus, and sulfur admixtures.

Practical realization of the designed technological methods based on complete investigations has allowed producing highly enriched magnetite and iron-containing (metallized) concentrates purified up to 90-95% from arsenic and phosphorus [106, 108, 369-371] and from poor iron-silicate ore materials and also to make predictive recommendations for improving IASOM processing aided with nanotechnologies.

GENERAL CONCLUSIONS

The influence of physical, colloid-chemical, nanochemical, geomechanical, and microbiocolloidal factors on the nanostructural contact formation and rheological behavior of real and model iron-aluminosilicate mineral materials (IASMs) with formation of nano- and microstructured systems (NIASSs and IASSs) has been investigated at experimental and theoretical-model levels. The formation of different NIASSs from IASSs and IASMs was shown to be similar and lead to the final formation of goethite (α -FeOOH) or magnetite (Fe_3O_4) along with other minerals, which agrees with the conclusions of the carried out geomineralogical studies. The role of rheological phenomena and physicochemical geomechanics in nano- and microstructural transformations of iron-aluminosilicate formations in catastrophic conditions was considered. For the first time, the role of mechanical and wind factors, and the role of IASMs dispersion in their initial nanostructural and mineralogical contact transformation have been revealed. It was indicated that the existence of Green Rust compounds does not last over 75-100 h and needs special conditions for the formation. Therefore, their role in processes of mechanogeochemical transformations is not significant. It was shown that microbiological processes in iron oxide-silicate structures lead to the formation of goethite or magnetite depending on pH, which was also confirmed by the observation that biocolloidal transformations occur due to inorganic chemical reactions aided with the surface-active products of microorganism metabolism. The general recommendations for controlling stress (beginning from the NIASSs suspension fracturing at the nanocontact level) and further catastrophic phenomena due to changing rheological parameters of the dispersions have been made. Moreover, it is indicated that a precise solution of the stability problem for pelitic-turbiditic sediment compositions on marine slopes and for dam material requires determination of individual composition parameters (physical, rheological, concentration and type of microorganisms, their influence on biocolloidal and geomechanical characteristics, etc.), which in turn, needs proper analytical consideration of the obtained findings to make a choice of an optimal biogeoecological method for protection from stress and catastrophic phenomena.

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Розглянуто сучасні уявлення колоїдної і біоколоїдної нанонауки про складні трансформаційні процеси в поширених дисперсіях залізоалюмосилікатних мінералів. Уперше показано, що такі процеси впливають на катастрофічні явища в морських турбідітно-пелітових осадах і ґрунтах гребель на основі залізоалюмосилікатів, обґрунтовано рекомендації стосовно їх запобігання. Викладено фундаментальні результати досліджень нано- і мікроструктурних трансформацій дисперсних залізоалюмосилікатних композицій та обґрунтовано можливості їх використання в: 1) будівництві захисних споруд на основі екологічно прийнятних біогеотехнологій, 2) курортології і медицині, 3) металургійній промисловості, 4) розвитку проблеми збереження екологічної рівноваги в морській гідросфері, 5) створенні нового наукового напрямку — біоколоїдної морської геоecології. Наведено реологічні характеристики багатьох мулових глинистих суспензій, лиманних і морських осадів. Обґрунтовано вперше встановлений ефект ультрааномальної в'язкості концентрованих дисперсій, який впливає на хід стресових і катастрофічних процесів.

Монографія розрахована на широке коло спеціалістів, які працюють в хімічній, геологічній, будівельній, металургійній, медичній і курортній сферах.

Наукове видання

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