

About a Role of Microorganisms in Destruction of Rock Structure of An Oil Reservoir

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Abstract

Microorganisms as the biotic factor are capable to participate in processes leaching of a rock of an oil layer directly, and also by secretion of various agents leaching -gases, acids, spirits, slime, etc. The basic mechanism leaching of a rock is formation of chelates by microbial agents with minerals of a rock. The order of carrying out of elements from minerals of rock of a class aluminosilicates basically is defined by structure and property of the mineral. The elements making crystalline a lattice of a mineral will least intensively be mobilized; isomorphically replaced or exchange ions which are taking place on peripheral sites of mineral particles will most intensively be mobilized. Knowledge of physical and chemical features of a collector - the nature and a cementing mineral of a rock, his maintenance in a rock, type of cement (basal or pore type etc.) and other parameters, in the certain degree allow to predict probability of shaking of structure of a rock of a collector and speed of his destruction during technological influence.

At selective leaching minerals of collector properties of rock can be modified both aside deterioration, and aside improvements of filtrational properties of pore spaces of a reservoir. Deterioration of collector properties can be shown, for example, in display sand recovery to wells-bottom (most likely in the first in sandy collectors with the small maintenance of a cementing material of montmorillonite type). In collectors with the high maintenance of a cementing material (basal or pore type of cement) leaching can promote substantial improvement of collector properties in connection with increase of permeability due to formation of secondary porosity.

Key words: Depleted oil reservoir; Enhanced oil recovery biotechnology; Microorganisms; Biofilter; Decomposition of organic substances; The formation of acids, alcohols; Rock leaching

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Till now one of practical measures of preliminary preparation of surface and oil-field sewage for injection in oil reservoir at flooding will consist in maximum full clearing from oxygen and microorganisms. As opposed to this, all modern biotechnological methods enhance of oil recovery assume introduction from the outside in a reservoir of microorganisms - producers of oil displacing agents (gases, bio-surfactants, solvents, bio-thickeners, etc.) and an intensification of their vital ability. Naturally thus to believe, that microorganisms as alive systems, can affect an oil collector not only by an intensification of bio-corrosion, but also participate in other sorts geology and chemical processes which final sum is destruction of rock forming minerals.

From the beginning of formation exposing and his operation with use of secondary and tertiary methods of influence it turns to open flowing system in which on an input surface waters and various agents of influence - alkalis and acids, surfactant and polymers, other organic matters are entered (12) But simultaneously in structure of these matter in a

reservoir microorganisms, as a rule, get. In of wells-bottom they survive and adapt for real physical and chemical stratum conditions, start to carry out the vital activity (3, 8). In due course under favorable physical and chemical conditions microorganisms can be distributed on all oil collector and occupy not only of well-bottom of injecting wells (so-called a zone of oxidation), but also the zones which have been removed enough from well-bottom (so-called a zone of restoration).

Specificity of an reservoir as inhabitancies of microorganisms will be, that it represents 3 phase system with very much advanced firm surface which adjoins to liquid and gas phases. After formation exposing and the beginning of technological influence (injecting surface waters, etc.) the oil reservoir will gradually be transformed and modified in 4 phase polydisperse system in which in addition to natural three phases the biogenic phase - "bio-film" (a complex aerobic and anaerobic microorganisms) is formed (3). "Bioreactor" in which complex processes of transformation of inorganic and organic matters as brought from the outside is carried out, and reservoir starts to function. Since this period microorganisms, alongside with physical and chemical factors, turn to the powerful bio-geological factor of influence on an oil collector. It results in transformation of phases, including of oil containing rocks. One of displays of such influence is decomposition (leaching) the cementing rocks minerals of a collector.

Process of leaching the cementing rocks minerals, irrespective of their character, can include physical and chemical (abiotic) and microbiological (biotic) factors, and also their joint influence.

Among physical and chemical processes of leaching the significant role belongs to processes of hydrolysis (5). Hydrolysis, leaching by water of mineral salts is the basic chemical mechanism of leaching of silicates (9). It has been confirmed with experiments on models of an oil reservoir. In conditions of a reservoir leaching rocks can be shown with the beginning of use flooding and intensity leaching with other things being equal - time of operation. So, with increase in claying and fine-grained fractions in a skeleton of the porous medium the specific surface of contact of agents leaching and rock forming minerals that promotes increase of quantity taken out with an oil phase of microparticles increases (6). Quantity of the microparticles secreted from production of wells of two various deposits, developed by a flooding method, but distinguished by duration of operation, sharply differed. So, in production of wells deposits Balachani-Sabuntchi-Ramani developed over hundred years, the maintenance of particles of rocks were made with 32-136 mg/l, and in deposit Guneshli, maintained with 1979r, the maintenance of particles has made all 0,02-0,08mg/l(7) Scales of leaching are quite often rather impressive: for example, in the central part of area Volgo-Kamsk with 1 km² annually are taken out about 3,5 t soluble salts (11)

Increase of speed of hydrolysis will be favourable to low values pH in microzones of a reservoir, with presence sour aniones. With rise in formation temperature speed of hydrolysis of mineral elements will be accelerated - she should be doubled at rise in formation temperature with 26 up to 30⁰C. Leaching of rock forming minerals with prevalence of the mechanism of hydrolysis can begin with the beginning intensive contour flooding a collector - most intensively will be leaching the minerals containing K, Ca and Mg in the exchange or isomorphically replaced form.

Agents of destruction of rocks be direct various agents, for example, solutions hydrochloric or the chamois of acids, carbonated waters, CO₂, etc., used in technological processes for processing of wells-bottom, and also the products formed at interaction of these matters with hydrocarbons, for example, sulfuric acids can also. Methods of displacement of oil by micellaric solutions are included with use isopropilic, butilic, geksilic spirit (12). They it is direct, and also their oxidized products, in turn, can render dissolving action on rock minerals.

In 1-2 years after the beginning of flooding by surface waters in case of intensive development of microorganisms (their number can reach up to 10³ - 10⁵ cells/ml) in an oil reservoir technical, physical and chemical processes leaching mineral elements can be supplemented and combined microbiological. In what essence and the basic laws microbial leaching minerals in an oil reservoir?

For maintenance of the vital activity in conditions of an reservoir to microorganisms, as well as all alive essences, alongside with organic substances are necessary also mineral.

Process of leaching gets the fundamental importance for microorganisms as the factor providing them with elements of a mineral nutrition. In conditions of a reservoir minerals of rock, in essence, unique, or nearly so their unique sources for microorganisms. Ways and mechanisms of influence of microorganisms on rock forming minerals can differ depending on specific features of microbial systems and physical and chemical properties of a collector. In an oil reservoir can take place direct and indirect influence of microorganisms on crystal lattices of minerals and transition of elements contained in them in a mobile condition.

As example of direct, direct influence can serve influence of microbial enzymes on the rocks containing in the structure elements with variable valency. The mineral elements contained in rocks, under influence on them of microbial enzymes are involved in oxidation-reduction reactions, that finally are the reason of destruction of a mineral. For example, iron in silicates (and carbonates) frequently is in the form restored Fe⁺². In wells-bottom in microzones where there is oxygen in necessary quantity, Fe⁺² can be oxidized in Fe⁺³ - considerably more mobile. Thus stability of a crystal

lattice is broken. Besides Fe can easily form iron - organic complexes with products of oxidation of hydrocarbons and other organic matters contained in injected surface waters and filterable streams to be taken out for limits of rock.

The most universal and effective means of extraction of minerals from oil rocks for microorganisms is, probably, indirect their influence on minerals. The question is about destruction of rocks with the help of the substances produced by microorganisms during a metabolism and representing strong chemical agents. Organic acids, various slime, biogenic alkalis, formers of chelate, etc. the substances, possessing strong reducing properties concern to their number.

The great value in destruction of rocks can have characteristic for many microorganisms slime –forming. Slime represents mostly polysaccharides, containing uronic acids. Available in their structure carboxylic and phenol groups are responsible for disintegration of crystall lattices of minerals (2). Reacting with the certain chemical elements, they form complex bindings that results in an output of corresponding substances from structure of crystall lattices and to their transition in a solution and to carrying out by a filterable stream for bound of medium. Besides bacterial slime, enveloping of part sand, released from cementing them minerals by similar to gel cover, as though greasing them, can plasticize of them, give to them the big mobility and ability to migration.

Among microbial acids there are such strong acids, as nitric and sulfuric. At selective absorption of cationes microorganisms releases of mineral acids which cause destruction of rock minerals. A source of biogenic alkalis in a reservoir can be mainly salts of weak organic acids and the strong bases brought in a reservoir at their operation (for example, at alkaline flooding a reservoir), and also carbonates and the bicarbonates contained in a stratum waters. Formed at decomposition of hydrocarbons and organic matters brought in a reservoir carbonates and bicarbonates cause increase pH in the medium therefore can be exposed leaching of alum silicates.

In an oil reservoir microorganisms are formed a various spectrum of organic acids at decomposition of hydrocarbons, and also in case of entering from the outside organic matters (biodegradable surfactant, carbohydrates, etc.). It can be both simple low-molecular, and high-molecular acids, including the cyclic nature. Ability to generation of acids is very widely distributed of heterotrophic microorganisms and, undoubtedly, plays the big role in destruction of a skeleton of rocks (1, 2, 4, 10). Formation of organic acids in quantity up to 340mg/l with prevalence of an acetic acid and significant - up to 55-1975 mg/l leaching magnesium, silicon, calcium and sodium from silicate sand is proved in model of an oil reservoir (9).

Besides organic acids and oxyacid's, formed by microorganisms, are capable to form intracomplex chelated type matters with released at destruction of minerals by elements. In complexes of this type ions of metals contact organic radicals in the form of cyclic substances, rather steady in a wide range pH, eh, etc. In result chelation many minerals are capable to be dissolved and further to be taken from rock, thus rendering on it destroying influence. Among products of an exchange of microorganisms there is a set of the organic matters capable to formation of complex bindings with the most various chemical elements. One only oxyacids form complexes more than with 60 elements.

For example, the 2-ketogluconic acid forming by bacteria from genus *Pseudomonas* sp., vigorously dissolves 1-17 % SiO₂, 13-63 % Ca, 3-54 % Mg, 16 % Al and 5 % K from their total maintenance in minerals. Active complex producing properties possess also the polyphenols which forming at microbial oxidation of hydrocarbons of an aromatics.

It is necessary to note, that ability of various elements to form complexes with products of vital activity of microorganisms, etc. organic substances is not identical. By the greatest activity of formation of complexes it is characterized Fe which with rare exception, entirely binds in complexes. SiO₂ and Al also vigorously enter complex compounds - from 10 up to 90% of the dissolved element are in the complex form, Ca and Mg binding in complexes a little bit more poorly. Development of complex producing is possible even at very small amounts of organic substance - 0,22% (13) . Presence of organic substances can stimulate formation of the organic -metal complexes described by high stability and mobility that will promote their migration in a reservoir in structure of filtered streams. Detection in stratum waters of Binagadi and Lok-Batan deposits up to 7-42mg/l of organic matters of the various nature can promote leaching of rock forming minerals (3) .

In general active complex producing chelates are the diversified organic matters containing of hydroxyl, carboxyl, amines, ketones, phenolic groups. The chelation is a primary factor of biochemical destruction of minerals.

One of factors, it is direct or indirectly influencing on rock forming minerals are also gases - CO₂, CH₄, H₂, forming as a result vital activity of microorganisms. For example, it is shown that when using eco-biotechnology, the effects on the oil formation by pumping they each ton of when in the bottom-hole zone of the formation forms over 39 m³ of carbon dioxide (Исмаилов, 2017). So, intensive formation CO₂ according to carbonate balance can be accompanied by his transition in stratum water as carbonate and bicarbonate the ions rendering dissolving influence on minerals. The certain part of gases can be in a free condition, sating of pore of a collector, they render effect of «an air ball», «dirigible balloon», promote decrease in specific density and increase in mobility of the sand released from cementing materials as a result of influence of hydrochemical and biological leaching factors.

At influence of microorganisms on aluminosilicates first of all get mobility alkaline metals, and then alkaline-earth,

at last - silicon and aluminum (2). Strong destruction are exposed some ferriferous minerals collapsing under influence of iron oxidizing and iron restoring microorganisms, and also the microorganisms producing matters, forming with iron mobile iron organic complexes. End-products of process of leaching can be or one-and-a-half oxides (R_2O_3), or silica (SiO_2). Accumulation of this or that product will depend on physiological features of the microorganisms participating in decomposition, character secreted by them in reservoir fluids of decomposition agents of rock forming minerals, conditions of development of process - temperatures, eh, presence of organic substances, character, rates and volumes of their receipt, etc.

Stability of crystals against dissolving their agents will be determined by structure of a crystal lattice, its total energy and character of binding between ions, and the order of carrying out of elements - chemical properties of the element, energy of formation of his oxide, conditions of medium. The great significance has also position of an element in a mineral lattice: isomorphically replaced ions, as a rule, are taken out much more intensively, than its basic components. The more poorly the potential of ionization of the ions making silicates, is easier these ions pass in a solution. And the more than such ions, that the crystal skeleton is less steady.

So, from a microwedge will be taken out most difficultly SiO_2 , K and Al, and most intensively - Mg, Ca and Fe, i.e. the elements present in a mineral in quality of isomorphically replaced ions or in structure of extraneous impurity. From biotite in all cases two elements - Ca (isomorphically replaced ion) and potassium, possessing, as is known, will be taken out by high chemical mobility most intensively. Other elements will be taken out more poorly, but nevertheless in the significant sizes that is caused by relative instability and a power unbalance biotite due to ion Fe^{+2} present in it.

The bentonite clay is cementing substance in terrigenous and other sedimentary rocks of oil collectors and concerns to group montmorillonite. As a rule, will be taken out more poorly from bentonite (SiO_2). Al and Fe, more intensively Mg and is the strongest K and Ca, that is connected by that in minerals montmorillonite groups Mg frequently is present at quality of isomorphically replaced ion and less often - in the exchange form; Ca usually is as an impurity of calcite or in an exchange condition, and K - it is almost extreme in the exchange form. Thus, the order of carrying out of elements from minerals of a class of aluminosilicates basically is defined by structure and property of the mineral; the elements making a crystal lattice of a mineral, and most intensively - isomorphically replaced or exchange ions which are taking place on peripheral sites of mineral particles will least intensively be mobilized.

Influence of microorganisms on rock, in essence, will not be limited to the centers of development of corresponding colonies of microorganisms, and to be shown and along a collector. Destruction of structure of rocks of an reservoir with participation of microorganisms differs one more feature: they influence on rock forming minerals mainly locally, in microzones, i.e. is direct in the centers of development of their microcolonies. Besides they not only chemically influence minerals included in its structure, but also mechanically her destroy.

Change of all structure of rock of an oil collector - process gradual and rather slow. In spite of even on minor alteration of a chemical compound of residual minerals, they are already characterized by the raised looseness and presence concerning unstable soluble products in water. Accumulation concerning unstable secondary formations in residual mineral weights specifies occurrence in them of new qualitative attributes and transition of a material in other form. Finally it results in process of plastiphization, shift of rock, migration of particles of sand under influence of differences of well-bottom and reservoir pressure, difficultly intense conditions of rock of wells-bottom, high viscosity, influence pulsatory an operating regime of wells, origin and development of dynamic loadings, etc.

Thus, it is possible to note the following sequence of the basic processes connected to destruction of structure of rock at technological influences on an oil reservoir with participation of microorganisms:

- Biological colonization of rock by microorganisms, active vital activity of various groups of microorganisms;
- Gradual decomposition of the minerals cementing rocks with simultaneous removal of products of aeration in structure of reservoir fluids at a filtration;
- Occurrence of horizons leaching and shaking of structures of rocks;
- Moving, migration, as soluble minerals - products of aeration, and in the certain conditions and the rock released from cementing materials.

Knowledge of physical and chemical features of a collector - the nature and a cementing mineral of rock, his maintenance in rock, such as cement (bazalic, pore, etc.) and other parameters, in the certain degree allow to predict probability of shaking of rocks structure of a collector and speed of his destruction during technological influence. For example, it is possible to assume, that sandy collectors in which a cementing material are minerals montmorillonite groups and their maintenance is insignificant will be less steady to biological leaching than minerals of caolinitic groups. It is connected first of all by that in minerals montmorillonite groups (their chemical formula $4SiO_2 \cdot Al_2O_3 \cdot nH_2O$) binding between packages weak, in interbatch space will easily penetrate water - hence, and cells of microorganisms contained in it and the organic substances necessary for their "destroying" vital activity. They are characterized by high dispersiveness, contain up to 60% colloidal particles and up to 80% of particles less 0,001mm, high capacity of

absorption - up to 80-120 mg/eqv. As against montmorillonite, caolinit (their chemical formula $2Si_2O \cdot Al_2O_3 \cdot nH_2O$) not swell since access of water in interbatch space is complicated because of strong binding between packages. Dispersiveness of it is low, capacity of absorption of only 20 mg /eqv. So, it is possible to predict relative stability to chemical and microbial leaching of rocks of horizons X, SP of Guneshli deposit , and also PK of deposits Balachani-Sabuntchi-Ramahi in which one of minerals cementing rock is minerals kaolin. In turn it gives the basis to consider, that on these deposits methods of biotechnology of influence on a reservoir for enhance of oil recovery can be used. Danger of destruction of structure of rocks at microbial influence for these horizons in long-term scale will be minimal.

At selective leaching minerals of collector properties of rock can be modified both aside deterioration, and aside improvements of filtrational properties of pore spaces of a reservoir. Deterioration of collector properties can be shown, for example, in display sand recovery to wells-bottom (most likely in the first in sandy collectors with the small maintenance of a cementing material of montmorillonite type). In collectors with the high maintenance of a cementing material (bazalic or pore type of cement) leaching can promote substantial improvement of collector properties in connection with increase of permeability due to formation of secondary porosity.

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