Mineral gels with a condensed dispersed phase

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Abstract. In the modern oil industry, water-polymer gels are widely used as drilling fluids. The main structural and mechanical units of these gels are macromolecules that participate in the construction of a single spatial structural grid due to donor-acceptor or ion bonds. The purpose of this work is to study the possibility of obtaining mineral hydrogels that combine high structural and mechanical characteristics characteristic of polymer hydrogels, but differ in the pseudoplastic flow model in combination with stability in the harsh thermobaric conditions of oil wells. Condensed hydrogels can potentially solve the most important problem in the production of liquid and gaseous minerals, which is to preserve the natural ecological balance and ensure the normal mode of biological self-purification of biogeocenoses in the areas of oil field development and disposal of drilling waste.

An example of an ionic mechanism for the formation of a polymer hydrogel is the coordination of functional groups of polyelectrolytes (carboxymethylcellulose (CMC), polyacrylamide (PAA), and others) around polyvalent metal cations [1] (Figure 1). The strength of such gels increases with an increase in the molar fraction of the complexing cation. In work [2], the mechanism of formation of spatially crosslinked polymer structures is presented due to substitutional interactions between functional groups of polyanions (CMC) and polyester chains of nonionic surfactants (polyoxyethylene (POE)).

Figure 1. Cross-linked polymer hydrogel.
In this case, polyoxyethylene groups of surfactants form an associated polycation with counterions (Na⁺), which is capable of forming a spatial structure due to interpolymer complexation with macromolecules of an anionic stabilizer. On the other hand, in aqueous solutions of xanthan biopolymer, hydrogen bonds are formed between neighboring macromolecules, characterized by regular alternation of branches of oligosaccharides (Figure 2).

![Figure 2](image)

**Figure 2.** Hydrogel with a branched structure of the base polymer forming a system of hydrogen bonds.

This ensures an optimal ratio of the structural and rheological properties of biopolymer gels, which, however, are highly unstable to thermobaric effects [3]. Polymer-dispersed gels formed by non-ionic polymers (hydroxyethylcellulose (HEC), PoE) and salts of transition and amphoteric elements (Fe, Ni, Al) have increased strength of the structure [4, 5].

Emulsion hydrogels based on concentrated surfactant solutions also have acceptable structure formation. In such solutions, macromycellar aggregates interact at a close distance by forming hydrogen, dispersion, or ionic bonds, forming a cellular structure. To ensure the necessary level of kinetic stability of supramicellar structures, a combination of three specially selected components is necessary: polyanion, an oxyethylated nonionic surfactant, and a relatively polar component, which uses acids from vegetable oils. In [6], the principal possibility of obtaining structured hydrogel systems by stabilizing solubilization microemulsions with polysaccharide derivatives that carry oxyethyl and carboxymethyl groups, and as a surfactant, an oil-soluble copolymer of ethylene and propylene oxides is shown.

For almost all types of washing liquids (suspensions and emulsions), the height of the electrostatic barrier that prevents the convergence and coagulation of dispersed particles is quite high. In other words, flushing fluids are aggregatively stable systems. If the depth of the far potential minimum is large enough, then, regardless of the height of the electrostatic barrier, there is a long-range interaction of two particles, fixed at a distance of about 10^3 Å, corresponding to the secondary potential minimum. In this case, 2 particles can neither disperse nor come close to each other and exist as a pair participating together in Brownian motion. When coagulating in the far minimum, the particles retain their individuality, and the system retains its dispersion and specific surface area, while when coagulating in the near minimum, the particles coalesce, which leads to a decrease in the specific surface area and surface energy of the system.

For concentrated washing liquids (weighted polymer-clay systems or hydrocarbon emulsions), the depth of the secondary potential minimum is more than 10 times higher than the energy of the thermal movement of molecules, so aggregates of dispersed particles formed by long-range interaction can only disintegrate if the kinetic energy of the particles is sufficiently large: the "Sol ↔ Aggregate" equilibrium is established. With a sufficient concentration of Sol (in conditions of high concentration of the clay phase or low-soluble salt), the fixation of dispersed particles in the far potential minimum
leads to the transformation of the Sol into a structured system. When the number of particles in the aggregate increases, the depth of the far minimum increases, which leads to the formation of "periodic colloidal structures" that have a far order and have a quasi-crystalline structure.

In the process of flushing flat and horizontal wells, pseudo-plastic flushing fluids have many technological advantages, since they reduce hydraulic losses when the solution circulates in the annular space, and also contribute to high-quality cleaning of the wall sections of the borehole from the drilled rock. For the transition from the binghamian to the pseudo-plastic rheological model, an adsorption-solvate barrier must exist between the dispersed phase particles, which provides the system with high viscosity, elasticity, and shear resistance. These properties prevent the interpenetration of the solvation layers at the convergence of particles. Strong hardening of solvate layers is achieved by adsorption on the surface of dispersed particles of long-chain surfactants or high-molecular compounds (HMC). In this case, adsorption-solvate layers are formed, covering even the far potential pit, and the washing liquid acquires the properties of a lyophilic system. The adsorption layers of the HMC have shear resistance, high viscosity and do not have time to "squeeze out" during the collision of particles, forming a structural and mechanical barrier that prevents coagulation.

Surfactants and HMC that create a structural-mechanical barrier are stabilizers of washing liquids. In contrast to surfactants, the cohesive strength of polymer adsorption layers increases over time (it reaches its maximum a few hours after the introduction of the polymer stabilizer into the system as a result of slow diffusion and orientation of macromolecules). Increasing the charge due to dissociation of ionogenic groups of macromolecules in the adsorption layer, which increases hydration, increases the repulsion forces between the macromolecules, reducing the lateral cohesion, and, consequently, the strength of the adsorption layers. Thus, you can control the stability of the washing liquid by changing the pH level, electrolyte concentration, and using stabilizers (surfactants and HMC).

To create an adsorption-solvate barrier on the surface of dispersed particles, which leads to the implementation of a pseudo-plastic model of the flow of the washing liquid, mainly non-ionic water-soluble polymers of the polysaccharide series and oxyethylated surfactants are used. Thus, the authors [7] link the appearance of pseudoplastic characteristics of a polymer-clay solution with the use of water-soluble polyethylene oxide oligomers in its composition. In [8], the implementation of pseudo-plastic properties of the emulsion system is associated with the use of an oil-soluble copolymer of ethylene and propylene oxides with an ethylene oxide content of no more than 15 % mol. as an emulsifier, and as a hydrocolloid filler - derivatives of cellulose and starch. In polysaccharide reagents (oxyethylcellulose, carboxymethylcellulose, etc.) are used to create pseudo-plastic properties of heat-resistant polymer washing systems, which are lined with aluminum and iron (III) salts.

The success of using low-charge and non-ionic polymers (starch, xanthan resin, hydroxyethylcellulose) in washing liquids is associated with ensuring the aggregate stability of the system, as well as with the formation of a three-dimensional structural grid. Stabilization of the dispersed system and structure formation are interrelated processes in which the polymer provides the implementation of structural-mechanical, sorption-solvate and electrostatic stability factors of the system. There are several mechanisms of structure formation involving a nonionic polysaccharide:

- in aqueous solutions of xanthan resin, there is a very strong tendency to macrostructure as a result of the formation of supramolecular spatial grids consisting of spiral structural units that contact by means of hydrogen and dispersion bonds. Macromolecules of xanthan resin, in addition to polar functional groups, also carry anionic carboxylate groups, the source of which is the structural links of pyruvic and glucuronic acids, located on the side branches inside the main (d) glucose helix. It is this screening of charged sections of the xanthan macromolecule that seems to explain the unique reversibility and shear strength of hydrated macromolecular structures that provide a solid, pseudoplastic character of the rheological behavior of xanthan flushing fluids. This is, in particular, confirmed by the fact that the maximum solubility of xanthan resin is observed at pH=4-6, while the solubility region of conventional polyanion stabilizers lies at pH>8.
- nonionic polymers (hydroxyethylcellulose, starch) form spatially structured systems when interacting with dispersed particles of high-grade bentonite as part of polymer-bentonite washing
fluids. An important property of such solutions is their pseudoplasticity, which is characterized by a pronounced dependence of the effective viscosity on the shear rate;
- polymer structured washing fluids are prepared by complexation using polyvalent metal ions characterized by a large charge and a small ionic radius. Metals whose ions have a large hydrate capacity include Cr, Al, Ca, Zr, and Ti. To enhance the thixotropic properties of xanthan resin solutions, trivalent chromium salts are introduced into them, the effect of which is due to the ability to form multi-core complex compounds, for example, aquacomplexes, in the inner sphere of which water molecules and hydroxyl groups are contained. The coordinating ability of cations depends on their ion potential (the ratio of the ion charge to its radius), according to the value of which the complexing agents are located in the following row: Al>Fe>Cu>Ni>Mn. The thixotropic properties and viscosity of polymer solutions containing a particular complexing agent are directly proportional to its ionic potential. Thus, Al3+ cations are able to coordinate very tightly the hydroxyl and carboxyl groups of polysaccharide derivatives in the pH range < 6, while a three-dimensional hydrogel structure can be formed on the basis of a complex of iron (III) salts and hydroxyethylcellulose.

The accumulated data on the physical, chemical and technological properties of polymer hydrogels with different spatial structure formation nature allow us to assert that these systems combine high structural and visco-plastic properties, as well as significant inhibitory and lubricating characteristics characteristic of saturated emulsion systems. However, polymeric hydrogels have several significant disadvantages associated with the peculiarities of their colloid-chemical structure. Thus, the lifetime of the polymer hydrogel is limited by the resistance of the base polymer to bio- and thermal degradation. In addition, purified varieties of carboxymethylated polysaccharides are required to produce polymer hydrogels, the market value of which is constantly growing.

The purpose of this work is to study the possibility of obtaining mineral hydrogels that combine high structural and mechanical characteristics characteristic of polymer hydrogels, but differ in the pseudoplastic flow model in combination with stability in the harsh thermobaric conditions of oil wells.

Mineral hydrogels are significantly cheaper than polymer analogues, since they are made from large-capacity products of processing and enrichment of rocks. The most commercially popular mineral hydrogel is a clay suspension, which is structured to achieve the effect of swelling and dispersion of smectite-type layered aluminosilicate in an aqueous medium. This kind of mineral hydrogels can be attributed to systems with a peptised dispersed phase (Figure 3).

Figure 3. Coagulation-type Hydrosols with a peptised dispersed phase (clay suspensions).

When condensed hydrogel is obtained in an aqueous solution supersaturated with polyvalent metal salts (a phosphate-carbonate complex of iron, magnesium, and aluminum), conditions are created for the formation of new phase microcrystals that grow to a certain limit. When the necessary size of the condensed phase particles is reached, which is sufficient to create a strong hydrogel macrostructure, a crystal growth inhibitor is introduced into the system – a surface-active substance that is adsorbed on the active centers of the dispersed phase particles and prevents their further enlargement.
Condensed hydrogels, in contrast to polymer structured systems, are characterized by high pseudoplastic characteristics (Figure 4, Table 1).

**Figure 4.** Flow curves of hydrogels based on a phosphate-carbonate (PhC) complex of magnesium and aluminum salts with a condensed microphase content of 3.7% wt. (curve 1) and 4.5% wt. (curve 2).

| Table 1. Structural and mechanical parameters of condensed hydrogels. |
|-------------------------------------------------|-----------------|-----------------|-----------------|
| Rheological parameters                           | 2,2 % wt. PhC   | 3,7 % wt. PhC   | 4,5% wt. PhC    |
| Yield strength ($\gamma$), dPa                    | 25              | 40              | 75              |
| Plastic viscosity, mPAs                           | 8               | 9               | 14              |
| Exponent $n$ in the model of Ostwald-Weyl        | 0,25            | 0,2             | 0,2             |

As a result of the research, the main features of the physical and chemical structure and technological properties of condensed hydrogels were formulated:
- hydrogels with a condensed solid phase form a structure due to the electrostatic interaction between the micron nuclei of condensation;
- the flow of the hydrogel is described by a pseudoplastic rheological model that provides optimal properties of the washing liquid;
- the structural and mechanical characteristics of the hydrogel are formed without the participation of organic polymers, which ensures the stability of the system to biodegradation;
- hydrogel has high coagulation resistance in the presence of acids and mineral salts;
- hydrogel is safe for the environment; gelling salt complex is used as a common mineral fertilizer.

Condensed hydrogels can potentially solve the most important problem in the production of liquid and gaseous minerals, which is to preserve the natural ecological balance and ensure the normal mode of biological self-purification of biogeocenoses in the areas of oil field development and disposal of drilling waste. The most consistent solution to this problem is the use of effective resource-saving methods for influencing the productive formation, which ensure maximum well flow rate with minimal initial opening time. This makes it possible to achieve a relatively low level of contamination of the drilled rock and drilling waste water, both with reservoir fluid and reagents in the composition of washing fluids. Hydrogel technology is designed to improve the productivity of oil reservoirs by upgrading the dispersion medium of washing liquids as a result of the use of environmentally friendly reagents that prevent colmatation and ensure the growth of oil recovery of the exposed layers.
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