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© PNRPU / ПНИПУ, 2022**Digital simulation of flow diverting technologies: a review of analytical models for describing the physicochemical properties of cross-linked polymer gels**

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**Цифровое моделирование потокоотклоняющих технологий: обзор аналитических моделей для описания физико-химических свойств сшитых полимерных гелей**

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flow diverting technologies, sweep efficiency, injectivity profile smoothing, water inflow limitation, polymer solutions, polymer cross-linked gels, digital modeling, ECLIPSE, CMG STARS, UTCHEM, WPOPE, SCORPIO, PC-GEL, POL-GEL, PUMAFLOW, IORCoreSim.

Information on the most common analytical models used in modern specialized software (ECLIPSE, CMG STARS, UTCHEM, WPOPE, SCORPIO, PC-GEL, POL-GEL, PUMAFLOW, IORCoreSim, etc.) for modeling physical and chemical properties. cross-linked polymer gels used in the framework of flow diverting technologies, was presented on the example of an in-situ gelation polymer composition based on partially hydrolyzed polyacrylamide and chromium (III) acetate. This polymer composition was considered within the framework of the article due to the fact that it had the most complete analytical description, and also due to the long period and widespread use. The article provides detailed information about the features of the analytical description of the physicochemical properties of polymer compositions of in-situ gelation. Within the framework of the above model, the process of injection of a polymer solution, the transient process of gelation, as well as the stage of the final placement of a cross-linked polymer gel in the pore space of the rock were considered as separate stages of modeling. For each stage of modeling, the existing analytical models describing the physical and chemical processes corresponding to this stage were considered. Based on the information given in the article, it was concluded that modern specialized software contained an analytical description of the rheological properties of cross-linked polymer gels, the mechanisms of retention of polymer solutions in the rock matrix (adsorption, precipitation), and the kinetics of gel formation reactions. However, many aspects of modeling the physicochemical properties of the described compositions, such as the mechanical and gravitational retention of polymer molecules in the pore space, the effect of the adsorption process on the kinetics of gel formation reactions, the analytical calculation of the pore volume inaccessible for filtering polymer molecules, the analytical description of the process of dehydration of a cross-linked polymer gel, still require further study.

**Ключевые слова:**

потокоотклоняющие технологии (ПОТ), коэффициент охвата пласта, выравнивание профиля приемности (ВПП), ограничение водопритока (ОВП), полимерные растворы, полимерные сшитые гели, цифровое моделирование, ECLIPSE, CMG STARS, UTCHEM, WPOPE, SCORPIO, PC-GEL, POL-GEL, PUMAFLOW, IORCoreSim.

Представлена информация о наиболее распространенных аналитических моделях, используемых в составе современного специализированного программного обеспечения (ECLIPSE, CMG STARS, UTCHEM, WPOPE, SCORPIO, PC-GEL, POL-GEL, PUMAFLOW, IORCoreSim и т.д.) для моделирования физико-химических свойств полимерных сшитых гелей, применяемых в рамках потокоотклоняющих технологий, на примере полимерного состава внутрипластового гелирования на основе частично гидролизованного полиакриламида и ацетата хрома (III). Данный полимерный состав рассматривается в рамках статьи по причине наличия у него наиболее полного аналитического описания, а также ввиду продолжительного периода и широкой распространенности применения. В статье приведены подробные сведения об особенностях аналитического описания физико-химических свойств полимерных составов внутрипластового гелирования. В рамках приведенной модели процесс закачки полимерного раствора, переходный процесс гелеобразования, а также этап окончательного размещения сшитого полимерного геля в поровом пространстве горной породы рассматриваются как отдельные этапы моделирования. Для каждого этапа моделирования рассмотрены существующие аналитические модели, описывающие соответствующие данному этапу физико-химические процессы. На основе приведенных в статье сведений сделано заключение о том, что современное специализированное программное обеспечение содержит аналитическое описание реологических свойств полимерных сшитых гелей, механизмов удержания полимерных растворов в матрице породы (адсорбция, выпадение в осадок), кинетики реакций гелеобразования. Однако многие аспекты моделирования физико-химических свойств описываемых составов, такие как механическое и гравитационное удержание молекул полимера в поровом пространстве, влияние процесса адсорбции на кинетику реакций гелеобразования, аналитический расчет величины недоступного для фильтрации молекул полимера порового объема, аналитическое описание процесса обезвоживания сшитого полимерного геля, по-прежнему требуют дальнейшего изучения.

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## Introduction

One of the most common tasks that petroleum engineers solve during the development of oil fields is the task to improve the efficiency of the oil displacement process using water injected into the formation: maintaining uniformity of the reservoir flooding front, increasing the formation sweep factor, leveling the injectivity profile of injection wells, limiting water inflow in production wells, reduction in the volume of produced water. This issue is especially acute for mature fields as well as for fields with a high degree of geological structure heterogeneity where washed zones and preferential filtration channels are usually formed, through which ones water injected into the formation breaks directly to production wells, bypassing oil-saturated wells not covered by waterflooding. areas of the deposit, as a result of this the efficiency of the oil displacement process is greatly reduced [1].

Traditionally, to solve this problem methods were used to optimize the well pattern and waterflooding scheme (drilling additional wells, killing wells), hydrodynamic methods (changing the operating mode of pumping equipment), hydraulic fracturing and repair and insulation work using resins and cement mortars [2, 3]. However, the limited effectiveness of the above technologies, the complexity of application and high cost, along with the growth in the number of fields with high production rates, have led to a growing need for new high-tech solutions.

As one of these decisions in the 70s of twentieth century several groups of researchers proposed to reduce the permeability of preferred water filtration channels by injecting specialized process fluids into these areas of the formation.

This engineering solution was subsequently called "flow-diverting technologies" (FDT).

One of the first proposed liquids for use as such specialized there were polymer solutions and cross-linked gels based on them. Polymeric substances (PAM, Polyacrylamide), xanthan gum (xanthan), guar gum (guar), etc.) from the very beginning of the developing new technology began to be considered as an effective flow diverter agent due to the experience of their successful use in within the framework of polymer flooding. Possessing the necessary physical and rheological properties and being widely available for purchase on the commercial market of chemical raw materials, these substances became the basis for the developing the technology for cross-linking polymer gels that can effectively solve the problem of increasing formation coverage through in-situ treatments (large-volume injections) as well as leveling the injector profile wells and limiting water inflow in production wells (low-volume injections).

Subsequently, cross-linked polymer gels which have the required properties at a low market cost became the most commonly used agent in flow diverter technologies [4].

A modern approach to study the applicability of a particular blocking composition, in addition to conducting laboratory studies in free volumes and filtration experiments in reservoir conditions, also requires the presence of a hydrodynamic modeling stage. At this stage, a general analytical model of the studied composition properties created on the basis of laboratory experimental data is used to scale key physical and chemical processes to the level of the field site [5]. The purpose of this approach is to select the optimal characteristics of the studied composition and the scheme of technological operations for further pilot work and subsequent application of technologies in the selected area of the field.

Today, there is a wide range of software products designed to perform digital modeling of physical and chemical processes occurring in the reservoir during the use of cross-linked polymer gels to block preferred water filtration channels. The main difference between these programs is expressed in the variety of analytical models used to describe the physicochemical properties of cross-linked polymer gels.

This article discusses existing analytical models for describing the physicochemical properties of cross-linked polymer gels using the composition of partially hydrolyzed polyacrylamide (HPAM) and chromium acetate as an example. The overviewing the list of existing analytical models a part of modern software products is provided, and little-studied aspects of digital modeling these polymer systems are identified.

### Specialized software for digital modeling physico-chemical properties of flow diverting technology compositions

In parallel with the development of new flow diverting technologies (FDT) using cross-linked polymer gels against the backdrop of the rapid developing computer technologies and numerical methods of data analysis in the second half of the 70s of last century, a number of research programs were launched to study the issues of digital modeling physical and chemical processes as part of the developing new production technologies and the application of enhanced oil recovery (EOR) methods.

Thus, in 1978 the first version of the three-dimensional multiphase multicomponent hydrodynamic simulator UTCHEM, was completed and presented to the scientific community. The basic code of the program was written by SHELL employees G. Pope and R. Nelson in FORTRAN. The program was originally created to simulate the process of oil displacement using process fluids used to enhance oil recovery. The initial version of the program made it possible to simulate oil production processes using surfactants (SAS) and polymer compounds. Subsequently, the program was constantly improved and supplemented with specialized modules for solving other modeling problems, such as the use of cross-linked polymer gels, alkaline solutions, foam systems, microbiological compositions, silicate solutions (liquid glass) as well as for tracer studies, for reservoir damage processes and geochemical processes. At the moment, the functionality of the program continues to be developed by researchers at the University of Texas at Austin (UT Austin).

In the 80s two simulators entered the commercial software market at once which later became industry standards in the field of hydrodynamic modeling oil and gas field development processes. In 1983 the private Canadian company Computer Modeling Group (CMG) introduced the STARS hydrodynamic simulator, originally intended for modeling chemical (polymer flooding, surfactant injection, alkali flooding) and thermal (steam injection, gravity drainage, cyclic steam injection, in situ combustion and etc.) methods for increasing oil recovery. Also during this period, the British company Exploration Consultants Limited released the ECLIPSE simulator in the ECLIPSE 300 modification (a compositional simulator that allows you to simulate physical and chemical processes within the framework of EOR). Currently, the service company Schlumberger is distributing, improving and supporting ECLIPSE.

In 1987 the first mentions of the hydrodynamic simulator SCORPIO (Simulator for Chemical Oil Recovery and Polymer Injection) produced by the British company AEA Petroleum Services appeared in scientific publications. This multiphase multicomponent fluid dynamics simulator was developed to calculate the performance of oil displacement processes using chemical reagents including polymer solutions and cross-linked gels, alkaline solutions and surfactants.

In 1993 as part of a joint project between the Illinois Institute of Technology (IITRI) and the National Fuels and Energy Research Institute

USA (NIPER) released a three-dimensional three-phase hydrodynamic simulator PC-GEL developed on the basis of the previously released BOAST simulator as a new version adapted for the personal computer platform. A priority in the development of PC-GEL was to create software for simulating EOR technologies using polymer formulations. The simulator made it possible to simulate polymer flooding and injection of cross-linked polymer gels.

Subsequently, the following were also released: the BPOPE hydrodynamic simulator which is a modified version of the UTCHEM simulator by British Petroleum employees the POL-GEL simulator developed by the Research Institute of Petroleum Exploration and Development of the People's Republic of China (RIPED), the PUMAFLOW hydrodynamic simulator from Beicip-Franlab and the French Petroleum Institute (IFP), VIP simulator from Landmark and Halliburton, REVEAL simulator from Petroleum Experts, and IORCoreSim, a collaboration between the University of Stavanger (UiS), the Norwegian Research Center (NORCE) and the Norwegian Institute of Energy Technology (IFE).

Further we will consider the main analytical models used as part of these commercial and corporate software products for digital modeling of the physicochemical properties of cross-linked polymer gels.

#### Polymer cross-linked gels used within the framework of flow diverting technologies

In 1974 employees of Phillips Petroleum Co. (ConocoPhillips) proposed a technology for using water-soluble polymers (partially hydrolyzed polyacrylamide and acrylamide copolymers) in a mixture with multivalent calcium and aluminum cations to form a spatial structure of a cross-linked polymer gel inside the pore volume of a rock, capable of multiply increasing the hydraulic resistance of a formation selected area and redistributing filtration flows water injected into the reservoir [6]. The effectiveness of this approach is determined by the formation of spatially branched physicochemical bonds between cross-linker cations and high molecular weight polymer chains, which, in turn, leads to the formation of a deformation-resistant cross-linked polymer gel structure. The primary choice of polyacrylamide as the polymer base of the cross-linked gel was dictated by the experience of its successful use in polymer flooding, the high degree of knowledge in the physical, chemical and rheological properties of this polymer, as well as its availability on the commercial market in the 60–80s. In particular, polyacrylamide has been widely used in the paper industry.

A large number of different polymer compositions types were proposed and tested in the subsequent decade as the basic processes of the polymer gels formation as well as their filtration in the pore space of rocks were studied. The developers of new compositions sought to reduce the cost of the used solutions and improve their properties: increase temperature and mechanical stability, reduce sensitivity to salinity and hardness of formation water and waters of the reservoir pressure maintenance system, reduce the level of adsorption and general losses of the solution during filtration in the pore space of the rock, improve lubricating properties of solutions, increase injectivity, and be able to regulate within a wide range the duration of the solution gelation period [7]. The goals could be achieved in two main ways: by modifying polymer compounds known at that time or by searching for new substances to serve as the polymer base of the gel.

Therefore by the end of the 80s a large number of polymer compositions of two main types have been studied: synthetic polymers and biopolymers [8]. Synthetic polymers used in oil and gas production typically include the previously mentioned partially hydrolyzed polyacrylamide (HPAM), polyacrylamide copolymers as well as artificial polymers based on natural polysaccharides.

EOR biopolymers include xanthan (xanthan gum), guar (guar gum) and natural polysaccharides (cellulose, scleroglucan). In the course of research [9–13] it was established that there is a large number of polymer compositions suitable for use in the framework of EOR. However, among other synthetic polymers, the best ratio of applicability and cost has the now widely used HPAM and cross-linked gels based on it. The most effective and popular formulation is a gel based on HPAM and trivalent chromium acetate  $\text{Cr}(\text{CH}_3\text{COO})_3 \cdot \text{H}_2\text{O}$  as a cross-linking agent [14, 15],

patented in 1984 by Robert Sidansk under the name MARCITTM (Marathon Conformance Improvement Technology) [16]. This formulation makes it possible to obtain a composition with a relatively long gelation period, which makes it possible to pump the solution into remote washed areas of the formation if necessary.

Among biopolymers, xanthan gum is most widely used in oil and gas production [17–20] which has demonstrated better stability characteristics and better thickening ability. However, in general, the use of xanthan gum and gels based on it is much less common.

The entire variety of cross-linked polymer systems depending on the mechanism of gel formation inherent in them can be divided into the following main types [21, 22]:

1. In-situ gelling compositions. This group includes solutions of monomers that polymerize in the pore space of the formation in the presence of a catalyst or without it (first proposed by Halliburton in 1978) [23] as well as polymer solutions with a concentration in the range of 5000–10000 ppm, gelling inside the pore space during the crosslinking process in the presence of special additives (cross-linker substance 500–2000 ppm, reducing agent 100–1000 ppm). This type of cross-linked polymer gels includes solutions of HPAM and aluminum citrate [1], HPAM and chromium (III) acetate [16], solutions of PAA with tert-butyl acrylate (PATBA) and polyethylenimine (PEI) [24], etc.

The components of these solutions are supplied to the formation in the form of an aqueous solution prepared on the surface called gelant which viscosity is close to the water viscosity during injection which ensures the penetration of the mixture into the water-washed areas of the productive formation. The chemical composition of the gelant is selected in such a way that the cross-linking process reaches maximum intensity after the solution penetrates into the treated areas of the formation. The characteristics of the polymer gel cross-linking process and, as a consequence, the final result of the treatment (distribution of the gel in the reservoir, mechanical and rheological properties of the gel, etc.) strongly depend on reservoir conditions: temperature, dissolution of the gelant by reservoir fluids (concentration of reagents), effective pressure drops and filtration rate (shear deformations), adsorption of components on the rock surface, mechanical destruction of polymer molecules, etc.

2. Colloidal dispersed gels. This group includes solutions of low concentrations of HPAM (100–1000 ppm) and chelated form of aluminum citrate (chromium citrate) as a crosslinking agent in a ratio of 20:1 to 100:1. Due to the low polymer concentration, the gel is structured in the form of unbound almost spherical colloidal particles with a diameter of up to 150 nm [25]. The characteristics of these solutions allow them to be used for treating formation areas at a great distance from the well at formation temperatures up to 90°C and salt concentrations in formation water up to 30,000 ppm. One of the first to introduce such solutions to the market was Tiorco Inc.

3. Pre-cross-linked granular Gels (PPGs). A class of solutions first developed and introduced by PetroChina in 1996 to solve the problems of treating flushed formation zones under conditions of high formation temperatures and high salinity of formation waters. To form particles of such a solution, the initial gel based on acrylamide monomer, cross-linker (N, N'-methylene-bis-acrylamide), initiator (sodium peroxydisulfate) and other additives (bentonite, etc.) is mechanically crushed, then the resulting particles are dried and sifted to obtain the desired fraction (dimensions on a millimeter scale). The particles are injected into the formation as a stable brine-based suspension and are resistant to formation temperatures of up to 120°C for long periods of time (up to one year), as well as high salinity solutions (up to 300,000 ppm).

Pre-cross-linked granular gels have increased swelling ability (increase in size up to 100 times); as a result, the particles become elastic which facilitates their movement through the formation [26]. In this case, as the speed of



particle movement decreases away from the well, gel clogging occurs in the watered, highly permeable intervals of the formation which leads to the redistribution of filtration flows into the unwashed intervals of the productive section [27–29].

4. Microgels. Gels consisting of pre-cross-linked micron-scale polymer aggregates whose characteristics are comparable to those of polymer molecules. They were first introduced in 1999 under the STARPOL brand in the form of cross-linked polymer gel particles based on acrylamide and zirconium lactate. This group also includes the so-called Small Microgels (SMG) [30, 31]. The mechanism for reducing the permeability of gels is based on the formation of a mono- or multimolecular gel layer on the surface of the rock. Such gels have high mechanical, thermal and chemical stability [32, 33], and are also capable to selectively change the characteristics of relative phase permeability to water [34, 35] isolating highly permeable zones of the formation without penetrating into the low-permeability rock matrix due to precise control of particle size during manufacturing.

5. Thermogels/gels with thermal activation. This type of gel was developed as a result of research programs by British Petroleum, Chevron, Texaco and Nalco in 1997. This technology later formed the basis for the products offered by Tiorco-Nalco under the name Bright Water. Gels of this type are intended for injection into flushed, highly permeable zones of productive formations remote from wells in order to block them [36, 37]. The gel particles have submicron sizes (0.1–1.0  $\mu\text{m}$ ), a high degree of swelling (up to 10 times), and consist of cross-linked chains of sulfonated PAM. Gel particles are injected into the formation in the form of an aqueous solution whose temperature is lower than the formation temperature. The injected aqueous solution has viscosity values close to the viscosity of water, thus, the solution is filtered into highly permeable washed layers. After penetration into remote zones of the formation, the solution temperature is compared with the formation temperature, which resulted the cross-linking agent of the polymer gel using which the particles are formed dissociates, the chemical bond density of the gel decreases, and the particles absorb the surrounding water and swell blocking the mouths of the washed zones pore channels [38]. Gels are mainly intended for use in terrigenous rocks in the range of formation temperatures up to 150°C, with formation water salinity up to 260,000 ppm [39], with permeability of washed zones up to 25 Darcy [40].

Historically, it was the in-situ gelation compositions that were the first proposed engineering solution in the field of flow diverter technologies which later partly determined their wider use and a high degree of studying their properties in comparison with the other types of cross-linked polymer gels mentioned above. The relative ease of use, low cost and acceptable efficiency of this technology for a wide range of deposits explains the predominant using this type of composition within the framework of FDT [41].

This fact, in turn, explains the presence of the most complete analytical describing the physicochemical properties of such polymer systems as part of modern specialized software designed for FDT digital modeling.

For these reasons, the article discusses the main analytical models used for digital modeling the physicochemical properties of in-situ gelling polymer compositions based on HPAM and chromium (III) acetate.

#### Features of the analytical describing properties of in-situ gelation polymer compositions

Of all the above-mentioned variety of gel polymer solutions used in the framework of FDT, the most complete analytical description has been developed to date for in-situ gelling compositions based on HPAM and a cross-linker in the form of chromium (III) acetate due to the long period of their use and the large amount of accumulated data.

A feature of the physical and mathematical describing the composition of in-situ gelation is the variability of the solution aggregative state during its injection into the formation and further filtration. This fact, in turn, affects the solution viscosity of the and the filtration mode. For convenience, the process in in-

situ gelation of solution injected into the considered formation is usually divided into three stages [42]:

1. Gellant filtration. Gellant is a mixture of a polymer and a cross-linking agent with additives that improve the filtration characteristics of the mixture. The properties of such a mixture at the stage preceding the start of gelation are extremely close to the properties of the polymer solution [43, 44]. To describe the filtration of such a mixture in the pore space of a rock, it is necessary to take into account the rheological properties of the polymer solution, the phenomenon of adsorption and retention of the polymer and cross-linking agent in the pore space, as well as the presence of a pore volume inaccessible for filtration.

Rheological properties. One of the main parameters characterizing the rheological properties of a polymer solution is the resistance factor, equal to the ratio of the pressure drop during filtering a polymer solution to the pressure drop during filtering water at the same specified flow rate:

$$Fr = \frac{dP_p}{dP_w}, \quad (1)$$

where,  $Fr$  – resistance factor;  $dP_p$  – pressure drop during filtering a polymer solution;  $dP_w$  – pressure drop during water filtration.

Recent studies confirm that the resistance factor depends on the type and concentration of the polymer in the solution, the salinity of the solution, and the shear rate during filtration. Unlike xanthan gum solution which exhibits pseudoplastic properties (the resistance factor decreases with increasing shear rate), the HPAM solution behaves as a Newtonian fluid at low shear rates, as a pseudoplastic fluid in the medium speed range, and as a dilatant fluid (the resistance factor increases with increasing shear rate) liquid in the region of high shear rates. The boundaries of the ranges are determined mainly by the concentration of the polymer, the salinity of the water and the permeability of the porous medium, the presence of cracks and highly permeable filtration channels. The higher the polymer concentration in the solution, the earlier the solution begins to exhibit its dilatant properties with increasing filtration rate. In turn, an increase in water salinity leads to the fact that the dilatant properties of the solution become more pronounced [45–50].

Retention of polymer and cross-linker. During the gellant filtration in the pore space of the rock, the phenomenon of retention of the polymer material and cross-linking substance has a significant impact on the chemical composition of the substance in the washed zones and its final placement in the formation. The main mechanism for retaining gellant components in rock is adsorption, characterized by the mass of a substance (polymer) adsorbed per unit mass of rock. Mathematically, the process of polymer adsorption in most cases is quite accurately described by the Langmuir isotherm. However, recent studies [51, 52] indicate the need to take into account the influence of other mechanisms of substance retention in the rock, such as the formation of bridges in the pore space, the formation of substance clots, and getting stuck in dead-end filtration channels. According to researchers [53], retention of the cross-linker is, a combination of various physicochemical mechanisms, such as ion exchange and precipitation of the substance. The intensity characteristics of these processes are related to the pH of the environment, the concentration of substances dissolved in water and the lithological composition of the rock.

Inaccessible pore volume. Since the beginning of studying the characteristics of polymer solutions, researchers [54] have noted the fact that part of the volume of the rock pore space is available for filtering water molecules but is not available for filtering large polymer molecules. The main mechanisms that determine and characterize this physical phenomenon are: 1) the impossibility of penetrating large polymer molecules into the mouths of small pores, 2) the forming a layer of adsorbed polymer on the walls of the pore space; 3) the phenomenon of polymer molecules repulsion from the rock surface; 4) the difference between the in-situ rheology of the

polymer and the rheology in the free volume [55]. To date, there is no single generally accepted model that describes this phenomenon. Based on previous studies [52], we can conclude that the inaccessible pore volume is directly proportional to the residual oil saturation, the molecular weight of the polymer and inversely proportional to the resistance factor and the amount of polymer retention in the porous medium.

The process of gelling a polymer solution includes two sub-processes: internal cross-linking and external cross-linking. The process of internal cross-linking involves the formation of two-dimensional polymer structures as a result of the joining two polymer chains by atoms of the cross-linking agent. Further stitching of the resulting two-dimensional structures into three-dimensional structures is called external cross-linking. These processes can be described by the corresponding equations of the kinetics of the chemical reaction between the polymer and the cross-linker. To date, several models have been developed that describe these processes [56, 57].

One of the most important characteristics of the composition is the gelation period which determines the duration of the composition transition from a liquid mixture of components to a gel. To apply the composition within the framework of the FDT technology, it is important that its dynamic viscosity remains relatively low during injection into the formation, while internal cross-linking reactions mainly occur inside the gellant, and after placing the composition in the washed zone of the formation, external cross-linking reactions are triggered causing a sharp increase in the dynamic viscosity. Thus, the most important thing within the framework of the gelation process mathematical model is the description of the transition from internal to external cross-linking of the composition. The main characteristic of this transition is the moment when external cross-linking begins—the so-called gelation point [58]. The HPAM formulation and Cr(III) cross-linker require several hours to reach the gelation point and another couple of hours to complete the gelation process of the formulation [59]. The process can be slowed down using special additives [60, 61].

Also, to describe the gelation process, it is necessary to determine the rate of chemical reactions occurring at each stage of the process. As one of the first models to describe the kinetics of chemical reactions of a HPAM/Cr(III) solution, it was proposed to use the Arrhenius equation [62]. Subsequently, the proposed model was improved and simplified in order to be used for more complex compositions [63]. As part of modern research, it is proposed to describe the kinetics of internal and external cross-linking using separate models [64].

After completion of the gelation process, further penetration of the cross-linked gel into the pore space of the rock is difficult; the gel mass can penetrate into nearby areas of the formation mainly through cracks in the rock and large filtration channels. At this stage of modeling, it is necessary to describe the further process of penetration and retention of the gel in the formation. The residual resistance factor ( $Frr$ ) is used to describe the phenomenon of reduced rock permeability due to gel retention.

Gel penetration. The mechanism of penetrating the gel into the rock is extremely different from the mechanism of gellant filtration due to the difference in the physical and rheological properties of the formed gel. To mobilize the gel mass, a certain threshold pressure drop must be present. The pressure drops required for gel movement significantly exceed the pressure drops characteristic of gellant filtration [65, 66].

Gel retention. Gel retention in the formation can occur as a result of a combining many factors and mechanisms: large molecular sizes of the cross-linked polymer gel, chemical adsorption on the rock surface, mechanical retention in penetration channels due to the increased gel viscosity, gravitational sedimentation, entrapment in dead-end voids of the pore space, formation of bridges etc. [67].

Gel dehydration. During the penetrating the gel into the rock under the influence of mechanical stress, water can be squeezed out of the gel mass into the pore space of the rock matrix, into cracks or filtration channels which, in turn, affects the process of forming the filter cake and retention of the gel in the rock. Currently, research into this process is ongoing [68].

Residual resistance factor. This parameter is widely used during laboratory studying characteristics of various polymer solutions and gels. During filtrating a polymer solution, as a result of its components retention in the pore space, a decrease in the permeability of the rock is observed. The residual resistance factor is the ratio of the rock permeability value before exposure to the polymer composition to the permeability value after exposure:

$$Frr = \frac{K_1}{K_2}, \quad (2)$$

where  $Frr$  is the residual resistance factor;  $K_1$  – rock permeability to water before exposure to the polymer composition;  $K_2$  – rock permeability to water after exposure to the polymer composition;

The residual resistance factor can be represented as a constant value for a given polymer concentration or as a function of the concentration parameter (as a linear [69] or exponential [70] function).

Gel destruction. The factors that reduce the  $Frr$  value after the formation of the gel in the pore space are mainly chemical decomposition, mechanical destruction under the influence of stresses, gel desorption, oil penetration, etc.

In addition to the factors listed above, it is also important to take into account the phenomenon of a disproportionate decrease in rock permeability for water ( $Frrw$ ) and oil ( $Frr_o$ ) as a result of the gels influence, the effect of changing the characteristics of relative phase permeabilities. The mechanism of the disproportionate decrease in permeability is partly explained by the chemical destruction of the gel under the oil influence [71]. Several models have also been proposed for the mechanism of changes in the characteristics of relative phase permeabilities [72, 73].

### Existing analytical models describing the physicochemical properties of in-situ gelling polymer compositions

In this section, we consider physical and mathematical models used as part of commercial and corporate software to calculate the properties of in-situ gelling polymer compositions based on HPAM and chromium (III) acetate, used within the framework of FDT [42, 74–78].

1. Simulating gellant filtration. The rheological properties of a polymer solution depend on many factors including polymer concentration, shear rate and maximum Newtonian viscosity of the polymer. The rate of shear deformation in a polymer solution depends on the rate of its filtration, porosity and permeability of the rock (the geometry of the pore space).

The maximum Newtonian viscosity of a polymer solution depends on the type of polymer used and its concentration. To model the maximum Newtonian viscosity of a polymer solution, Thurston proposed using a linear regression model that takes into account the parameters of the polymer concentration in the solution and the water viscosity [79]:

$$\mu_p^0 = \mu_w \left[ 1 + (A_{p,1} C_p + A_{p,2} C_p^2) \right], \quad (3)$$

where  $\mu_p^0$  – maximum Newtonian viscosity;  $\mu_w$  – water viscosity;  $C_p$  – polymer concentration;  $A_{p,1}$  и  $A_{p,2}$  are model parameters.

In the PC-GEL simulator model, the dependence between the Newtonian viscosity of a polymer solution and the polymer concentration is specified by a polynomial of the 2nd or 3rd degree:

$$\mu_p^0 = \mu_w + A_1 C_p + A_2 C_p^2 + A_3 C_p^3, \quad (4)$$

where  $\mu_p^0$  – maximum Newtonian viscosity;  $\mu_w$  – water viscosity;  $C_p$  – polymer concentration;  $A_{p,1}$  и  $A_{p,2}$  are model parameters.

In the UTCHEM simulator model, this dependence is supplemented with parameters taking into account salinity and water hardness:

$$\mu_p^0 = \mu_w \left[ 1 + (A_{p,1} C_p + A_{p,2} C_p^2 + A_{p,3} C_p^3) C_{SEP}^{SP} \right], \quad (5)$$

where  $\mu_p^0$  – maximum Newtonian viscosity;  $\mu_w$  – water viscosity;  $C_p$  – polymer concentration in the aqueous/microemulsion phase;  $A_{p,1}$  и  $A_{p,2}$  are model parameters.

Parameter  $C_{SEP}^{SP}$  describes the dependence between the viscosity of the polymer composition and salinity and hardness.

Subsequent studies were devoted to supplementing this model with a function describing the kinetics of gelation [69] as well as parameters for taking into account the salt content in the solution [80].

The rheological properties of a polymer solution also depend on the porosity and permeability of the rock matrix, since the topology of the pore space determines the values of shear strain rates observed in the solution during filtration. One of the first models that established the relationship between the shear rate in a solution, the porosity and permeability of the medium was the Hirasaki–Pope model [81] where the value of the shear rate for a single-phase flow is specified by a function of the following form

$$\gamma = F \left[ U (k \varphi)^{0.5} \right], \quad (6)$$

where  $\gamma$  – shear strain rate;  $U$  – linear fluid filtration rate;  $k$  – absolute permeability of rock;  $\varphi$  – rock porosity.

Chauveto and Zaitoun [82] proposed a different type of dependence:

$$\gamma = F \left[ U (1 - \varphi) / (k \varphi)^{0.5} \right]. \quad (7)$$

In the case of two-phase filtration (water/oil) considered in a number of works, the effective shear rate was presented as a function of the shear coefficient, flow rate of the aqueous phase, water saturation of the porous medium, effective phase permeability to water and porosity [83]:

$$\gamma_e = C \left( \frac{3n + 1}{4n} \right)^{\frac{n}{n-1}} \left( \frac{U_w}{\sqrt{K k_{rw} S_w \varphi}} \right), \quad (8)$$

where  $\gamma_e$  – effective shear rate;  $C$  – Cannella constant;  $n$  – shift factor;  $U_w$  – flow rate of the aqueous phase;  $K$  – absolute permeability;  $k_{rw}$  – relative phase permeability to water;  $S_w$  – water saturation;  $\varphi$  – porosity.

This formula supplemented by various correction factors for specific models is used in most modern simulators.

To describe the non-Newtonian rheology (pseudoplastic properties) of polymer solutions, a number of software products (UTCHEM, BPOPE, PC-GEL) use the Meter equation [84, 85]:

$$\mu_{app} = \mu_w + \frac{\mu_p^0 - \mu_w}{1 + \left( \frac{\gamma_{eq}}{\gamma_s} \right)^{P_\alpha - 1}}, \quad (9)$$

where  $\mu_{app}$  – apparent viscosity value of the polymer solution;  $\mu_p^0$  – maximum Newtonian viscosity;  $\mu_w$  – water viscosity;  $\gamma_{eq}$  – equivalent shear rate;  $\gamma_s$  – shear rate value corresponding to the average viscosity of the polymer solution between  $\mu_p^0$  and  $\mu_w$ ;  $P_\alpha$  – model settings.

In turn, the equivalent value of the shear rate  $\gamma_{eq}$  for the selected phase  $l$  ( $l = w$  – water,  $o$  – oil) is calculated from the augmented Blake–Cozeny equation (UTCHEM):

$$\gamma_{eq} = \frac{\gamma_c |U_l|}{\sqrt{k k_{rl} \varphi S_l}}, \quad (10)$$

where  $\gamma_{eq}$  – equivalent shear rate;  $\gamma_c = 3,97C$ ,  $C$  – correction factor to take into account the effects of non-ideal solution and porous media;  $U_l$  – linear phase  $l$  filtration rate;  $k_{rl}$  – phase permeability of phase  $l$ ;  $\varphi$  – porosity;  $S_l$  – degree of saturation of the pore space with phase  $l$ ;  $k$  – average permeability value calculated by the formula

$$\bar{k} = \left[ \frac{1}{k_x} \left( \frac{U_{xl}}{U_l} \right)^2 + \frac{1}{k_y} \left( \frac{U_{yl}}{U_l} \right)^2 + \frac{1}{k_z} \left( \frac{U_{zl}}{U_l} \right)^2 \right]^{-1}, \quad (11)$$

where  $k_x, k_y, k_z$  – permeability vector components;  $U_{xl}, U_{yl}, U_{zl}$  – components of the phase filtration velocity vector  $l$ ;  $U_l$  – value of the phase  $l$  filtration rate.

There is also a generalized Seright model [43] which includes pseudoplastic models:

- Bird power law [86] (UTCHEM, BPOPE);
- Carreau model [87] (UTCHEM, BPOPE, IORCoreSim);
- Chauveteau model [82];
- Cannell model [83] (UTCHEM, BPOPE);
- Wilhite empirical model [88],

as well as dilatant models:

- Heemskerck power law dependence [89];
- Hirasaki-Pope model [81] (UTCHEM, BPOPE);
- Durst-Byrd model [90].

In his work, Delshad [91] combined the experimental data of Hirasaki–Pope [81] and Masuda [92] with the Carreau model to formulate a mathematical model to describe the rheology of a HPAM solution:

$$\mu_{app} = \mu_\infty + (\mu_0 - \mu_\infty) \left( 1 + (\lambda \gamma)^\alpha \right)^{\frac{n-1}{\alpha}} + \mu_{max} \left[ 1 - \exp \left( -(\lambda_2 \tau_r \gamma)^{n_2 - 1} \right) \right], \quad (12)$$

where  $\mu_{app}$  – apparent viscosity value of the polymer solution;  $\mu_0$  – Newtonian viscosity of a polymer solution at zero shear rate;  $\mu_\infty$  is the Newtonian viscosity of the polymer solution at an infinite shear rate;  $\mu_{max}$  – maximum viscosity of the polymer solution during filtration;  $\gamma$  – effective shear strain rate;  $\lambda$ ,  $\lambda_2$ ,  $\alpha$  – model settings;  $\tau_r$  – shear stress;  $n$  – pseudoplastic shear coefficient;  $n_2$  – shear coefficient of dilatant deformations.

This model allows us to describe the Newtonian, pseudoplastic and dilatant properties of a polymer solution. The model is implemented within the UVM module (Unified Viscosity Model) of the UTCHEM simulator.

Lone in his work [93] studied the effect of stretching polymer chains on the dilatant properties of a polymer solution; based on the results of his work, he proposed a model for describing the pseudoplastic and dilatant properties of polymer solutions:

$$\mu_{app} = \mu_p^0 + (\mu_{thin} - \mu_p^0) \mu_{thick}, \quad (13)$$

where  $\mu_{app}$  – apparent viscosity value of the polymer solution;  $\mu_p^0$  – maximum Newtonian viscosity;  $\mu_{thin}$  – pseudoplastic component of viscosity:

$$\mu_{thin} = \mu_p^0 \left( 1 + (\lambda \gamma)^x \right)^{\frac{n}{x}}, \quad (14)$$

where  $\lambda$  – relaxation time corresponding to pseudoplastic properties;  $\gamma$  – shear rate;  $x$ ,  $n$  – model parameters;  $\mu_{thick}$  – dilatant component of viscosity

$$\mu_{thick} = \left( 1 + (\lambda_2 \gamma)^{x_2} \right)^{\frac{m+n}{x_2}}, \quad (15)$$

where  $\lambda_2$  – time parameter corresponding to dilatant properties;  $x_2$ ,  $m$  – model tuning parameters.



The pseudoplastic component of this model is based on the Carreau–Yasuda model, the dilatant component is represented by a power law.

To calculate the viscosity of a solution containing several components, within the framework of the CMG STARS software model, a specialized function  $F(x)$  is used, which describes the change in the viscosity of the composition depending on the content (mass fraction)  $x$  of each  $i$ -th component and complements the basic rules for calculating the viscosity of mixtures from several components. This function allows you to take into account a wide range of factors of nonlinear changes in viscosity and allows you to simulate the behavior of polymer solutions with sufficient accuracy. The final form of the function is specified by the software user.

$$F(x) = \frac{\left( (1-x_i) \ln(\mu_p^0) - \sum_{j \neq i}^{n_c} x_j \cdot \ln(\mu_j) \right)}{\left( (1-x_i) \ln(\mu_i) - \sum_{j \neq i}^{n_c} x_j \cdot \ln(\mu_j) \right)}, \quad (16)$$

where  $F(x)$  – viscosity function of a multicomponent solution;  $x$  – mass fraction of the component;  $\mu$  – viscosity of the solution component;  $i, j$  – indices of the components of the aqueous solution;  $p$  – index of the parameter of the polymer component of the solution;  $n_c$  – number of solution components.

The ECLIPSE and IORCoreSim simulators use the Todd–Longstaff model equation to calculate the effective viscosity of a polymer solution:

$$\mu_{p,eff} = \mu_m (C_p)^\omega \cdot \mu_p^{1-\omega}, \quad (17)$$

where  $\mu_{p,eff}$  – effective viscosity of the polymer solution;  $\mu_m(C_p)$  – function of the dependence of the viscosity of a polymer solution on the polymer concentration;  $\mu_p$  – the maximum value of the viscosity of the polymer solution (i.e. the value of the viscosity of the initial solution without loss of polymer concentration);  $\omega$  – model coefficient.

This model, however, does not take into account the influence of the parameters of salt concentration and water hardness on the viscosity value.

In the SCORPIO and PUMAFLOW simulator, the physical and rheological properties of polymer solutions and gels are determined through laboratory studies and are specified in tabular form (depending on the polymer concentration and shear strain rate). The PUMAFLOW simulator model also takes into account the effect of water salinity on the rheological properties of the solution.

**Inaccessible pore volume.** Modules for accounting for the presence of inaccessible pore volume of a porous medium of each simulator have their own characteristics. Thus, in the hydrodynamic simulator ECLIPSE 300 [94], within the framework of the model, to take into account the value of the inaccessible pore volume (IAPV – Inaccessible Pore Volume), a correction factor is introduced for the effective water saturation (the value of the effective water saturation decreases with increasing IAPV).

In the POL-GEL simulator [95], the presence of inaccessible pore volume is taken into account by reducing the effective volume of the polymer and, as a consequence, the effective concentration of the polymer.

In the CMG STARS, PC-GEL, PUMAFLOW simulator model [76, 77, 96], the presence of IAPV is taken into account by reducing the value of the effective pore volume occupied by the polymer in the mass conservation equation of the simulator.

Despite the differences in approaches, all simulators take into account the IAPV value as a constant value specified by the user.

**Retention of polymer in porous media.** The most commonly used model for the retention of polymer and cross-linking agent in a porous medium is the Langmuir adsorption model (UTCHEM, BPOPE, PC-GEL, PUMAFLOW) which specifies the relationship between the concentration of the

adsorbed polymer and the polymer concentration in water as well as water salinity [97]:

$$C_{ads,p}^w = \left( tad1 + tad2 C_{sep,p}^w \right) \frac{C_p^w}{1 + tad3 C_p^w}, \quad (18)$$

where  $C_{ads,p}^w$  – adsorbed polymer concentration;  $C_{sep,p}^w$  – effective salinity;  $C_p^w$  – polymer concentration in the aqueous phase;  $tad1, tad2, tad3$  – specified model parameters.

In his work Stavland [69] proposed a more complex model for the retention of a crosslinker substance in a porous medium, including taking into account ion exchange and precipitation of the substance:

$$\frac{\partial C_{Cr}}{\partial t} = R_{Cr} (C_{H^+} + H_{Cr0})^\beta \left\{ 1 - \left( \frac{C_{Cr} \cdot C_{OH}^3}{K_{Crsp}} \right)^\alpha \right\}, \quad (19)$$

where  $\frac{\partial C_{Cr}}{\partial t}$  – rate of precipitating the cross-linker substance;  $R_{Cr}$  – reaction constant;  $\alpha, \beta$  – model settings;  $C_{H^+}$  – ion  $H^+$  concentration;  $C_{Cr}$  – crosslinker concentration;  $C_{OH}$  – OH ion concentration;  $K_{Crsp}$  – reaction equilibrium constant;  $H_{Cr0}$  – model tuning parameter.

This model is included in the mathematical apparatus of the UTCHEM simulator [98].

The SCORPIO simulator allows you to set the level of adsorbing polymer material on the walls of the pore space using a functional dependence on the concentration of all basic chemical reagents during the polymerization process.

The mass density  $m_i$  for each adsorbed component  $i$  can be written in the following form:

$$m_i = r_w S_w C_w^i + \frac{\rho_R \Gamma_i (C_w^i, T)}{\varphi}, \quad (20)$$

where  $m_i$  – mass density of adsorbed component  $i$ ;  $\rho_w$  – aqueous phase density;  $\rho_R$  – rock density;  $S_w$  – degree of water saturation;  $C_w^i$  – concentration of the  $i$ -th component in the aqueous phase;  $\vec{C}_w$  – vector function of the concentration of the  $i$ -th component in the aqueous phase;  $\Gamma_i$  – adsorption function of the  $i$ -th component;  $T$  – temperature;  $\varphi$  – porosity.

Thus, within the framework of the SCORPIO model, a system of nonlinear equations is solved for the vector function  $\Gamma(C_w, T)$  and, as a consequence, for the function  $C_w$  for a given vector function of mass density  $\vec{m}$ :

$$\vec{m} = \rho_w S_w \vec{C}_w + \frac{\rho_R \vec{\Gamma}(\vec{C}_w, T)}{\varphi}. \quad (21)$$

Adsorption of crosslinking agents and redox substances is not taken into account.

**2. Simulating the gelation process.** Simulating the gelation process requires a mathematical description of the process of transition of an aqueous solution and a cross-linking agent through the internal cross-linking phase (the appearance of small aggregates of two-dimensional cross-linked structures) to the external cross-linking phase (the formation of a three-dimensional cross-linked gel structure).

In his work Scott [63] proposed to use the Arrhenius equation for the reaction rate to take into account the kinetics of gelation. The proposed method assumed that 1 mole of polymer substance and 1 mole of cross-linker substance form 1 mole of cross-linked gel:

$$\frac{\partial C_g}{\partial t} = (K_g C_p^m C_{Cr}^n), \quad (22)$$

where  $\frac{\partial C_g}{\partial t}$  – speed of the gelation chemical reaction;  $C_p, C_{Cr}$  – polymer concentration, chromium concentration;  $m, n$  – reaction order ( $m = n = 1$  Scott model);

The reaction frequency coefficient  $K_g$  is calculated by the formula

$$K_g = A \cdot \exp\left(\frac{E_a}{R} \left(\frac{1}{T_0} - \frac{1}{T}\right)\right), \quad (23)$$

where  $A$  – the Arrhenius constant;  $E_a$  – activation energy;  $R$  – universal gas constant;  $T_0$  – standard temperature value;  $T$  – current temperature value.

The method converted gelation time measured in the laboratory into a reaction frequency ( $K$ ) value which is a function of temperature, activation function, universal gas constant, and Arrhenius constant. This method is used within the CMG Stars software.

The solution to this equation is the formula for calculating the gelation time:

$$t_g = \frac{1}{KC_p C_{Cr}}, \quad (24)$$

where  $t_g$  – gelling time;  $K$  – frequency of gelation reaction.

In the SCORPIO simulator, to calculate the rate of a chemical reaction, a table function (specified by the user) or a power law formula for the concentration of all components participating in the chemical reaction in question can be used:

$$\frac{\partial C_a^i}{\partial t} = a_0 (C_a^1)^{a_1} \dots (C_a^j)^{a_j} \dots (C_a^N)^{a_N} \cdot \exp\left(-\frac{a_{N+1}}{T}\right), \quad (25)$$

where  $C_a^i$  – concentration of the  $i$ -th component dissolved in phase  $\alpha$ ;  $N$  – number of components;  $a_0 \dots a_{N+1}$  – model constants;  $C_a^1 \dots C_a^N$  – concentrations of components dissolved in phase  $\alpha$ ;  $T$  – temperature.

The last term of this equation describes the temperature dependence.

In his work Stavland [69] considers this transition in relation with the changing properties of the polymer solution, some of which acquires the properties of a cross-linked gel. This technique avoids the need to introduce additional gel components into the model.

$$\frac{\partial F_g}{\partial t} = a (C_p (1 - F_g))^{\text{expp}} C_{CrOH}^{\text{expp}} C_H^{\text{expp}} \times \exp\left(\frac{E_a}{R} \left(\frac{1}{T_0} - \frac{1}{T}\right)\right), \quad (26)$$

where  $F_g$  – polymer fraction that has acquired gel properties;  $C_p$  – polymer concentration;  $C_{CrOH}$  – the concentration of chromium atoms chemically bonded to the hydroxyl groups of polymer molecules;  $C_H$  – hydrogen ion concentration;  $\text{expp}$ ,  $\text{expx}$ ,  $\text{epph}$  – model parameters;  $E_a$  – activation energy;  $R$  – universal gas constant;  $T_0$  – standard temperature value;  $T$  – current temperature value.

3. Simulating penetration and placement of cross-linked gel. Gel penetration. To calculate the viscosity of an aqueous solution containing a gel in the UTCHEM, BPOPE simulator model, the Flory–Huggins equation is used with an additional term in the equation describing the rheology of the gel:

$$\mu_g = \mu_w \left[ 1 + (A_{p1} C_p + A_{p2} C_p^2 + A_{p3} C_p^3) \times C_{SEP}^{Sp} + A_{g1} C_g + A_{g2} C_g^2 \right], \quad (27)$$

where  $\mu_g$  – viscosity of the polymer gel;  $\mu_w$  – water viscosity;  $A_{p1}$ ,  $A_{p2}$ ,  $A_{p3}$ ,  $A_{g1}$ ,  $A_{g2}$  – model constants;  $C_p$  – polymer concentration;  $C_g$  – gel concentration;  $C_{SEP}^{Sp}$  – dependence of the polymer composition viscosity on salinity and hardness.

In the PC-GEL simulator the viscosity of a polymer gel is estimated according to the method outlined by Kenneth Sorby using an additional third-order component introduced to describe the smooth but rapid increase in the solution viscosity at the moment of gelation:

$$\mu_g = \mu_w + \beta_1 C_g + \beta_2 C_g^2 \text{ при } (C_g < CGC), \quad (28)$$

$$\mu_g = \mu_w + \beta_1 C_g + \beta_2 C_g^2 + \beta_3 (C_g - CGC)^3 \text{ при } (C_g > CGC), \quad (29)$$

where  $\mu_g$  – gel viscosity;  $\mu_w$  – water viscosity;  $\beta_1$ ,  $\beta_2$ ,  $\beta_3$  – model constants;  $C_g$  – gel concentration;  $CGC$  – critical gelation concentration.

While studying the issue of a cross-linked polymer gel penetration into cracks inside the rock, Seright [99] found that when a certain pressure drop is reached, the resistance factor  $Fr$  for the cross-linked gel remains constant which characterizes this gel as a Bingham fluid. The volumetric flow rate of the gel can be calculated using the formula

$$q = \frac{h_f w_f^3 \Delta p}{12 \mu_g L} \left( 1 - \frac{3y_0}{w_f} + \frac{4y_0^3}{w_f^3} \right), \quad (30)$$

where  $q$  – volumetric flow;  $h_f$  – half-length of the crack;  $w_f$  – crack width;  $\mu_g$  – gel viscosity;  $L$  – model length;  $\Delta p$  – pressure drop;  $y_0$  – gel filter cake thickness.

In further work Wang and Seright [100] used a power function to describe the dependence between the volumetric flow rate of the gel  $q$  and the resistance factor  $Fr$  at three different values of polymer concentration in solution. The pressure drop was calculated using the following formula:

$$\frac{\Delta p}{L} = a \left( \frac{q}{h_f} \right)^{n_1} \frac{1}{w_f^{n_2}}, \quad (31)$$

where  $a$ ,  $n_1$ ,  $n_2$  – model settings.

It was also proposed to use the Herschel–Bulkley rheological model [101] which demonstrates better agreement with the research results to describe the movement of a cross-linked gel. Within this model consumption is calculated using the following formula:

$$q = 2h_f A \left( \frac{w_f}{2} - y_0 \right) - 2h_f \frac{A}{-\frac{\Delta p}{\mu_0 L} \left( 1 + \frac{1}{n} \right) \left( 2 + \frac{1}{n} \right)} + 2h_f y_0 A, \quad (32)$$

where

$$A = \frac{\left( -\frac{\Delta p}{\mu_g L} \frac{w_f}{2} - \frac{\tau_0}{\mu_g} \right)^{1+\frac{1}{n}}}{\left[ -\Delta \left( \frac{1}{n} + 1 \right) \right]}, \quad (33)$$

$\tau_0$  – fluid yield strength;  $y_0$  – gel filter cake thickness;  $n$  – shift factor.

Gel retention. To model the process of retaining a cross-linked gel inside a rock during its penetration, Stavland [69] proposed using mathematical dependencies based on the Langmuir equation. In the proposed model, the coefficient  $Q_m$  was introduced to take into account the degree of gel cross-linking (gel fraction). During further testing of the model, it turned out that it does not accurately describe the entire mechanism of the phenomenon, since it does not take into account the processes of gel clots formation and substance getting stuck in dead-end filtration channels. The general form of the model equation was as follows:

$$C_{g,ads} = \frac{Q_m b C_{p,aq} C_{adsm}}{b C_{p,aq} + 1}, \quad (34)$$

where

$$Q_m = Q_p + C_{pt} \times \left[ A_{ga} (F_{gs} - A_{g0}) + B_{ga} (F_{gs} - B_{g0}) \right]^2 \sqrt{\psi/k}, \quad (35)$$



$F_{gs}$  – aqueous fraction of the gel;  $A_{g0}$  – minimum value  $F_{gs}$ ;  $A_{ga}$ ,  $B_{ga}$  – model tuning parameters to take into account the amount of adsorbed and filtered gel;  $B_{g0}$  – parameter responsible for describing the formation of a rigid structure of a cross-linked gel (a sharp increase in the intensity of the adsorption process) during filtration;  $C_{adSm}$  – adsorption activity;  $b$  – a specified model parameter depending on the salinity of the solution;  $C_{p,aq}$  – the proportion of polymer dissolved in the aqueous phase;  $C_{pt}$  – total amount of polymer;  $\varphi$  – porosity;  $k$  – permeability.

Unfortunately, at the moment there are no scientific works in periodicals that would propose more complete mathematical models that describe more aspects of cross-linked gel retention in the pore space of rock. Various retention mechanisms were studied in his works by Launay [102], such as retention of polymer molecules at the mouths of pores and lining the surface of the pore space for the case of penetration of polymer drilling fluid into rocks. The work presented formulas for calculating the retention value (in pore volumes) for both mechanisms:

$$R_{trap} = \frac{U_w}{\varphi S_w} (\lambda_1 C_t - \lambda_2 \sigma), \quad (36)$$

$$R_{line} = \lambda_3 C_g (C_{adSm} - C_{g,ads}) - \lambda_4 C_{g,ads}, \quad (37)$$

where  $R_{trap}$  – amount of polymer retained at pore mouths;  $R_{line}$  – the amount of polymer adsorbed in the pore space;  $C_t$  – polymer concentration at time  $t$ ;  $\sigma$  – average retention value (in pore volumes);  $U_w$  – linear flow velocity;  $\varphi$  – porosity;  $S_w$  – degree of water saturation;  $\lambda_1$  – locking parameter;  $\lambda_2$  – drag parameter;  $\lambda_3$  – adsorption parameter;  $\lambda_4$  – параметр десорбции;  $\lambda_1$ ,  $\lambda_2$ ,  $\lambda_3$ ,  $\lambda_4$  measured in fractions of polymer retained per unit length of movement.

Dehydration of the gel. Several analytical models are available to describe the gel dehydration process. The most common use is the Carter model [103], which assumes that the filter cake is formed uniformly over the entire surface of the crack during gel dehydration. The model equation is given below:

$$U_1 = 0,05t^{-0,55}, \quad (38)$$

where  $U_1$  – rate of dehydration;  $t$  – dehydration time.

In the course of further research [104], a model was proposed where the assumption that the filter cake is formed uniformly was replaced by the diametrically opposite one. This model received experimental confirmation through MRI analysis [105].

The rate of dehydration according to this model can be found from the following equation:

$$U_1 = \frac{U_m}{1 + \frac{\int U_1 dt}{w_f}}, \quad (39)$$

where  $U_1$  – rate of dehydration;  $U_m$  – rate of dehydrating the gel moving part;  $w_f$  – crack width.

Reduced permeability. The effect of reducing the permeability of the porous medium is calculated based on the characteristics of the gel retention and dehydration process. In a large number of proposed models, the effect of reducing permeability is proposed to be taken into account using the coefficient of reduction in permeability of the aqueous phase calculated on the basis of the value of the residual resistance factor  $F_{rr}$  measured in the laboratory. Similar models are used within ECLIPSE 300, CMG STARS, UTCHEM, SCORPIO. The most commonly used linear dependence on  $F_{rr}$ :

$$RKW = 1 + (F_{rr} - 1) \cdot \frac{C_{ad}}{C_{ad,m}}, \quad (40)$$

where  $RKW$  – aqueous phase permeability reduction coefficient;  $F_{rr}$  – residual resistance factor;  $C_{ad}$  – concentration of adsorbed gel;  $C_{ad,m}$  – adsorption capacity.

In the PC-GEL simulator model, the rock permeability reduction factor is introduced:

$$k_c = k/F_{rr}; \quad (41)$$

where  $k_c$  – permeability reduction factor;  $F_{rr}$  – residual resistance factor;  $k$  – absolute permeability of rock.

The  $F_{rr}$  parameter is calculated using the formula:

$$F_{rr} = 1 + \sum_{i=1}^5 l_i g_i(\Gamma_i), \quad (42)$$

$$g_i = 0 \left( \Gamma_i \leq \Gamma_i^* \right),$$

$$g_i = \Gamma_i - \Gamma_i^* \left( \Gamma_i > \Gamma_i^* \right),$$

where  $\Gamma_i$  – amount of adsorbed  $i$ -th component;  $\Gamma_i^*$  – critical amount of adsorbed component  $i$  where the process of blocking the pore canal begins;  $l_i$  – model parameters determined on the basis of laboratory studies.

There are more complex integrated models [69] that take into account the influence of rock porosity and permeability as well as the proportion of cross-linked gel in the polymer solution on the permeability reduction coefficient:

$$RKW = \frac{a_{Frr} (C_{g,ads} - C_{p,ads}) F_{ga} b_{Frr} k^{\frac{1}{2}} \varphi^{\frac{3}{2}}}{1 + b_{Frr} k^{\frac{1}{2}} \varphi^{\frac{3}{2}}}, \quad (43)$$

where  $RKW$  – aqueous phase permeability reduction coefficient;  $a_{Frr}$  – model tuning parameter;  $b_{Frr}$  model tuning parameter;  $C_{g,ads}$  – adsorbed gel concentration;  $C_{p,ads}$  – adsorbed polymer concentration;  $F_{ga}$  – a function describing the gelation process for the adsorbed part of the polymer solution;  $k$  – rock permeability;  $\varphi$  – rock porosity.

In the IORCoreSim simulator the effect of permeability reduction is modeled using the parameters of effective water porosity, unavailable pore volume and shear coefficient:

$$RKW = \left[ 1 - f_{rkw} \cdot \frac{C_{g,ads}}{1 - IAPV} \left( (\varphi_{sw} - 1) f_{sh} + 1 \right) \right]^{-2}, \quad (44)$$

where  $RKW$  – aqueous phase permeability reduction coefficient;  $f_{rkw}$  – tuning parameter;  $f_{sh}$  – shear coefficient (functional dependence on the Carreau – Yasuda shear rate);  $C_{g,ads}$  – adsorbed gel concentration;  $IAPV$  – inaccessible pore volume;  $\varphi_{sw}$  – gel swelling coefficient.

Gel destruction. Modeling process the destruction of cross-linked gel is usually performed taking into account two main mechanisms: chemical destruction and mechanical destruction. The rate of chemical destruction reaction ( $R_{cd}$ ) is usually calculated according to the Arrhenius-type kinetic equation for first-order reactions ( $m = 1$ ):

$$R_{cd} = K_{cd} C_g^m, \quad (45)$$

where  $R_{cd}$  – chemical destruction reaction rate;  $C_g$  – gel concentration;  $K_{cd}$  – frequency of the chemical reaction of gel destruction.

Due to the low reaction rate of chemical gel destruction this model allows us to simulate the dependence between the value of the residual resistance factor and time.

Among the methods for modeling the process of gel mechanical destruction, one can highlight the Scott model [63], according to which the destruction process was considered as a decrease in the mass of the cross-linked gel and was set by a constant value of the rate of this process, determined on the basis of laboratory studies.

Stavland [69], as part of his work, took into account the effect of mechanical destruction of the gel using the residual resistance factor multiplier  $F_{rrf}$ :

$$F_{rrf} = 1 - (P - P_0) \cdot k_f, \quad (46)$$

where  $F_{rrf}$  – residual resistance factor multiplier;  $P$  – effective pressure drop;  $P_0$  – the minimum pressure drop required to

begin the process of mechanical destruction of the gel;  $k_f$  – model tuning parameter.

Launay [93] considered the process of mechanical destructing a cross-linked gel as a decrease in the molecular weight of its three-dimensional structure depending on the effective mechanical shear stress ( $\tau$ ), the rate of destruction ( $r_{deg}$ ), the current value of the molecular weight ( $M_g$ ) and the hydraulic radius of the polymer molecule ( $R_p$ ):

$$\frac{\partial M_g}{\partial t} = -M_w \cdot (r_{deg} \tau)^{\alpha_d} \cdot \frac{2M_g}{R_p}, \quad (47)$$

where  $M_g$  – molecular weight of a polymer molecule;  $t$  – time;  $M_w$  – viscosity-averaged molecular weight of a polymer;  $r_{deg}$  – destruction rate;  $\tau$  – effective shear stress;  $\alpha_d$  – tuning factor;  $R_p$  – hydraulic radius of a polymer molecule.

## Conclusion

As it becomes clear from the information provided in the article, the analytical description and digital modeling of the physicochemical properties of polymer composing in-situ gelation used within the framework of flow diverter technologies EOR, is a complex multi-level task, implying the need for continuous calculating the characteristics of a wide range of processes accompanying changes in the aggregate state of the studied material. substance during its filtration in the porous medium of the productive formation.

The most complete physical and mathematical description has been obtained by polymer compositions of in-situ gelation, in particular compositions based on HPAM and chromium (III) acetate. A wide range of analytical models are available to describe the rheological properties of these crosslinked polymer gels including Newtonian, pseudoplastic, and dilatant properties.

Modern software products also make it possible to simulate the mechanisms of retenting polymer compositions in the rock matrix, including the phenomena of adsorption and precipitation of solution components. However, within the framework of the presented models, there is no describing the mechanical retention of the polymer substance in the filtration channels due to increased dynamic

viscosity, gravitational sedimentation, sticking of polymer molecules in dead-end channels of the pore space and the formation of bridges.

The used physicochemical and stoichiometric models make it possible to describe the kinetics of interaction reactions of a large number of basic components involved in the formation of a polymer gel. However, under conditions of gelant filtration through the pore space of the rock, it is also necessary to take into account the influence of pH indicator of the area, gelation time, residual resistance factor as well as changes in the concentrations of components due to retention in the pore space on the kinetics of the considered chemical reactions.

The presented models lack an analytical describing factor of inaccessible pore volume. The value of this parameter is usually specified by the user as a constant value corresponding to the results of laboratory tests.

Models describing the possible penetration of a cross-linked gel into a productive formation, for example, for cases of highly permeable unconsolidated rock or in the presence of a system of fractures, are currently at the stage of active development; existing models are poorly represented in commercial software products. The situation is similar with models describing gel dehydration and the effect of a disproportionate decrease in water and oil permeability [42].

Currently, in periodicals you can find information about scientific work and software developments in the field of modeling the filtration of polymer solutions based on analytical models for microgels, pre-crosslinked granular gels (PPG) and thermogels [38, 106, 107]. In particular, the analytical model for microgels is included in the basic functionality of the PUMAFLOW simulator, and the model for PPG gels formed the basis of the UTGEL software product, developed on the basis of the UTCHEM simulator.

Thus, despite the presence of an impressive list of specialized software products designed to simulate the physicochemical properties of cross-linked polymer gels, a long history of research and development related to this field of knowledge, many mechanisms and aspects of modeling still require further study in order to formulate new analytical models.

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