Synthesis and investigation of preformed particle gels based on acrylic monomers to reduce water cut in oil wells

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Oil production, which often involves the extraction of relatively large quantities of water, causes a number of environmental and mechanical problems, particularly in oil reservoirs. One way to mitigate this problem is to use polymer gels as plugging agents. This article describes a method for synthesizing acrylamide-based hydrogel particles using *N,N*-methylenebisacrylamide as a crosslinking agent and the addition of bentonite to prepare the hybrid composite hydrogel. FTIR spectroscopy data confirmed the formation of an acrylamide-based hydrogel. The swelling capacity of the hydrogels was studied as a function of the change in the concentration of the components contained in the composition. The swelling capacity is also estimated as a function of change in temperature, salinity and acidity of the medium. The results show that the investigated hydrogel particles exhibit remarkable swelling and have a high mechanical strength. The thermogravimetric analysis indicates stability of the hydrogel particles of up to 200°C.These particles may definitely serve as a robust sealant. They show high resistance to heat and salt exposure as well as stability in acidic and alkaline conditions. Considering physicochemical properties discussed in this paper, hydrogel particles can be utilized as a cost-effective potting agent.

Keywords: hydrogel; preformed particle gel; oil; oil wells; polyacrylamide; bentonite.

Мұнай ұңғымаларының суланууын төмендету үшін акрил мономерлері негізіндегі алдын ала қалыптасқан дисперсті гельдерді синтездеу және зерттеу

Г.Т. Елемесова[1*], А.Н. Кливенко[1], Л.К. Оразжанова[1], А.Н. Сабитова[1], А.В. Шахворостов[2], В.О. Асеев[3]

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Мұнай өндіру кезінде жиі кездесетін айтарлықтай үлкен көлемдегі судың шығуы, әсіресе мұнай қабаттарында бірқатар экологиялық және техникалық мәселелерді тудырады. Бұл мәселені шешудің бір жолы – полимерлі гельдерді тығындаушы агенттер ретінде пайдалану. Бұл мақалада тігілген агент ретінде *N,N*-метиленбисакриламидті қолдану және гибридті композиттік гидрогельді алу үшін бентонит қосу арқылы акриламид негізіндегі гидрогель бөлшектерін синтездеу әдісі сипатталған. ИҚ-фурье спектроскопиясының деректері акриламид негізіндегі гидрогельдің түзілуін растады. Гидрогельдердің ісіну қабілеті композиция құрамындағы компоненттер концентрациясының өзгеруіне байланысты зерттелді. Сондай-ақ, ісіну қабілеті ортаның температурасына, минералдануына және қышқылдығына байланысты бағаланды. Нәтижелер зерттелген гидрогель бөлшектерінің ерекше ісіну қабілеті мен жоғары механикалық беріктікке ие екенін көрсетеді. Термогравиметриялық талдау гидрогель бөлшектерінің 200°C-қа дейінгі температурада тұрақтылығын көрсетеді. Бұл бөлшектер сенімді герметик ретінде қызмет ете алатыны анық. Олар жылу мен тұз әсеріне жоғары төзімділік, сондай-ақ қышқылды және сілтілі жағдайларда тұрақтылық танытады. Осы жұмыста қарастырылған физика-химиялық қасиеттерді ескере отырып, гидрогель бөлшектерін үнемді герметизациялаушы агент ретінде пайдалануға болады.

Түйін сөздер: гидрогель; алдын ала қалыптасқан дисперсті гель; мұнай; мұнай ұңғымалары; полиакриламид; бентонит.

Синтез и исследование предварительно сформированных дисперсных гелей на основе акриловых мономеров для снижения обводненности нефтяных скважин

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Добыча нефти, часто сопровождающаяся извлечением относительно больших объемов воды, вызывает ряд экологических и технических проблем, особенно в нефтяных пластах. Одним из способов решения этой проблемы является использование полимерных гелей в качестве тампонирующих агентов. В данной статье описывается метод синтеза частиц гидрогеля на основе акриламида с использованием *N,N*-метиленбисакриламида в качестве сшивающего агента и добавлением бентонита для получения гибридного композиционного гидрогеля. Данные ИК-фурье-спектроскопии подтвердили образование гидрогеля на основе акриламида. Степень набухания гидрогелей была изучена в зависимости от изменения концентрации компонентов, входящих в состав композиции. Степень набухания также оценивалась в зависимости от изменения температуры, минерализации и кислотности среды. Результаты показывают, что исследованные частицы гидрогеля обладают значительной способностью к набуханию и высокой механической прочностью. Термогравиметрический анализ указывает на стабильность частиц гидрогеля при температуре до 200°C. Эти частицы определенно могут служить надежным герметиком. Они проявляют высокую устойчивость к термическому воздействию и воздействию солей, а также стабильность в кислых и щелочных условиях. Учитывая физико-химические свойства, обсуждаемые в данной работе, частицы гидрогеля могут быть использованы в качестве экономичного герметизирующего агента.

Ключевые слова: гидрогель; предварительно сформированный дисперсный гель; нефть; нефтяные скважины; полиакриламид; бентонит.

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Article

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1. Introduction

The oil production industry faces a major challenge as excessive irrigation leads to reduced oil production and increased residual oil [1,2]. The increase in the fluid rings other problems, including the need for wastewater treatment and environmental issues [1]. Water produced along with hydrocarbon fluids contains harmful elements such as salts, heavy metals, radioactive materials and dissolved organic substances that pose a serious threat to the environment. This not only shortens the life of oil wells, but also increases the costs associated with corrosion, separation and water purification. Therefore, there is an urgent need to control excess water. Typically, different methods, known as conformance control, are employed to manage unwanted water production and enhance well output [2]. These methods involve using various materials, such as polymer plugging, gel treatments, surfactants, foam injection, and others [3,4]. A recent breakthrough in this area is the use of preformed particle gels (PPG) [5-7].

The main advantage of this approach is the ability to produce appropriately sized materials tailored to the cracks and roughness of the oil reservoir. This method involves the production of hydrogels through the use of a crosslinking agent.

PPGs are synthesized on the ground prior to injection, which overcomes certain disadvantages of polymer-based in-situ gels, such as the lack of a defined gelation time and the uncertainty of the gelation process [8]. PPGs range in size from micrometers to centimeters, making them well suited for use in fractured reservoirs [9].

Typically, the PPG used must withstand the harsh conditions in petroleum reservoirs, including high temperatures, salinity and increased acidity. The author's experiment [10] shows that hydrogels based on polyacrylamide (AAm) lead to higher oil recovery compared to solutions containing only AAm. According to the review [11], despite the influence of reservoir conditions, the structure of PPG remains stable even under high salinity and elevated temperatures for several months. The authors' studies [12] demonstrate that the incorporation of sodium silicate and graphene nanoplatelets enhances the thermal stability of PPG. The review [13] noted that polyacrylamide–chitosan hydrogels exhibit a high swelling capacity, while an increase in chitosan content and neutral pH enhance the elastic modulus; however, due to non-covalent interactions, their mechanical strength decreases, and degradation occurs under high-salinity conditions.

This article describes the synthesis of a hydrogel based on AAm/Sodium Acrilate (SA)/MBAA/Bentonite and presents the results of gravimetric, mechanical and thermogravimetric test methods. The introduction of monomers into a hydrogel is achieved by chemical methods, in particular by using ammonium persulphate (APS) as initiator and N,N-methylene bisacrylamide (MBAA) as crosslinking agent. These components of the initiator and the crosslinking agent play a decisive role in determining the properties of the final polymerization product. Bentonite, a layered silicate [14], can be incorporated into hydrogels to reduce costs and improve mechanical and swelling properties.

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2. Experiment

2.1 Materials

The following monomers were used to synthesize the hydrogel particles: AAm and SA. MBAA was used as a crosslinking agent. All reagents were purchased from Sigma Aldrich and used without additional purification. APS and TMED from Reachim (Russia) were used as polymerization initiators. Bentonite clay (Zhejiang Qinghong New Material Co., Ltd.) was incorporated to improve the mechanical properties of the hydrogel particles.

2.2 Synthesis and study of PPG

2.2.1 Synthesis of PPG

PPGs of different compositions based on AAm/SA/MBAA/Bentonite were synthesized by free radical copolymerization [15]. The required amount of monomers (AAm, SA and MBAA) and bentonite were dissolved in distilled water with constant stirring. The calculated amount of APS initiator was then added to the solution and mixed until complete dissolution. The resulting reaction mixture was transferred to a vessel for synthesis and purged with argon for 15-20 min to remove dissolved oxygen. Free radical polymerization was carried out at 60°C for 3 h with constant stirring of the solution. The hydrogels were immersed in distilled water for one week to remove any unreacted residues. The resulting hydrogel was cut into equal pieces of 0.5 cm thickness, dried under ambient conditions at room temperature and used for further studies.

As a result of the synthesis, a series of samples with variable initial composition was obtained. The variations of the starting mixtures are shown in Tables 1 and S1-S3.

2.2.2 FTIR-spectroscopy

The characterization of the functional groups of the hydrogel was performed with a Cary 660 IR spectrometer from Agilent, USA. The infrared (IR) spectra were recorded at room temperature within the wavelength range of 700-4000 cm^{-1}. The dried hydrogel was prepared by pressing in the form of a disk or granules. The disk was then positioned in a special IR spectrometer holder to facilitate the incidence of the IR beam on the sample disk for analysis.

2.2.3. Thermal analysis of hydrogels

Thermogravimetric analysis was used to investigate the thermal stability of hydrogel particles.

The evaluation of the thermal stability of the hydrogel was carried out using the ThermoGravimetric Analyzer GTA 1250 from FPS in China. The heating process range from room temperature to 400°C, using a heating rate of 10°C/min in an air atmosphere.

2.2.4 Investigation of mechanical properties

The mechanical properties of the hydrogels prepared in this way were examined using the Texture/Mechanical Analyzer TA.XTplus Stable Micro Systems (Mason Technology, UK). Each hydrogel sample was measured 3 times at room temperature and the results were averaged. The stress-strain diagrams of hydrogels were generated in compression mode. A cylindrical stainless steel probe P/75 with a diameter of 75 mm was used to press on the hydrogel sample and track the change in compressive force as a function of distance/time. The measurement parameters were: Cylindrical probe pre-test speed 1 mm/s, test speed 0.5 mm/s, release force 0.2 g, remote target mode with a distance of 1.5 mm. The tension value (force per unit area) was calculated from the maximum force value:

$$Stress = \frac{Force\ (g)}{Area(mm^2)} \quad (1)$$

Since the stress curve is proportional to the strain, the slope is Young's modulus. This means that the gel material only deforms elastically in this area [16].

2.2.5 Swelling experiments

The kinetics of hydrogel swelling, based on AAm/SA/MBAA/Bentonite, were determined through the gravimetric method, involving the measurement of the hydrogel's mass before and after swelling.

The gravimetric method for swelling kinetics involved placing a dried gel sample in a 100 ml glass of water. After 5 minutes, the hydrogel was removed, excess liquid was eliminated, and the sample was weighed. Subsequently, the sample was placed back into the same glass, and its mass was measured at intervals of 5, 10, 15, 30, 60, 120, 180, 1440, 2880 min, etc., until a constant mass was achieved. The swelling kinetics was calculated using the following formula:

$$SD = \frac{m - m_0}{m_0} \quad (2)$$

where, is the degree of swelling, $g \cdot g^{-1}$; is the mass of the swollen hydrogel at a time, g; is the mass of the dry hydrogel, g.

Table 1 – Masses of reagents for the synthesis of hydrogels with a change in the concentration of monomers

Composition of the initial monomer mixtures	Concentration of monomers, %				
	$[AAm\text{-}SA]_{5\%}$	$[AAm\text{-}SA]_{10\%}$	$[AAm\text{-}SA]_{15\%}$	$[AAm\text{-}SA]_{20\%}$	$[AAm\text{-}SA]_{25\%}$
	Mass, g				
Bentonite	0,5	0,5	0,5	0,5	0,5
Water	9	8,5	8	7,5	7
MBAA	0,0107	0,0214	0,0321	0,0428	0,0535
AAm	0,4442	0,8885	1,3327	1,7770	2,2112
SA	0,0450	0,0901	0,1351	0,1802	0,2253

The determination of the degree of swelling in hydrogels was also carried out using the gravimetric method. In this approach, the dried hydrogel sample was immersed in a glass of water for a day. After 24 hours, the sample was extracted, excess liquid was removed, and its weight was measured. The degree of swelling of the hydrogels was evaluated under various conditions, including:

– ambient temperature: Measurements were conducted at different temperatures, specifically 20°C, 40°C, 60°C, and 80°C;

– salt concentrations in solution: Swelling experiments were performed in solutions with varying salt concentrations, ranging from 1 $g \cdot L^{-1}$, 10 $g \cdot L^{-1}$, 25 $g \cdot L^{-1}$, 50 $g \cdot L^{-1}$, 75 $g \cdot L^{-1}$, 100 $g \cdot L^{-1}$, to 150 $g \cdot L^{-1}$;

– pH levels: Swelling studies were carried out at different pH, uncluding pH 2, 4, 6, 8, 10 and 12.

3. Results and Discussions

3.1 Synthesis of PPG

The hydrogel particles based on AAm/SA/MBAA/Bentonite were synthesized using the radical copolymerization method, as depicted in Figure 1.

The synthesis process took into consideration variations in the concentrations of monomers in the initial composition (IC), the crosslinking agent, and bentonite. Additionally, adjustments were made to accommodate changes in the percentage of AAm and SA.

Figure 2 illustrates hydrogel samples with variations in bentonite concentration and change to the AAm/SA ratio in the initial monomer mixture.

As depicted in Figure 2, hydrogels exhibit an inhomogeneous structure at both low and high concentrations of bentonite (1%, 2%, 3%, 4%, 10%). In Figure 2b, it is observed that a decrease in the amount of acrylamide leads to the formation of a hydrogel with a heterogeneous structure. Subsequent investigations focused on samples demonstrating a homogeneous structure. Notably, since the hydrogel sample with a 5% content is identical to the hydrogel sample with a 5% concentration of monomers (refer to Table 1), it is not further examined as a separate sample.

3.2 FTIR spectroscopy results

In the FTIR spectra (Figure 3), the absorption bands in the range of 2800-3000 cm^{-1} correspond to the asymmetric and symmetric stretching vibrations of CH groups. In particular, the band at 1590 cm^{-1} is attributed to the vibrations of N-substituted groups, characteristic of the amide II band. The distinct absorption band at 1656 cm^{-1} corresponds to the stretching vibration of the C=O bond, confirming the presence of carbonyl groups in the polymer structure. Furthermore, the band at 1452 cm^{-1} is associated with the bending vibrations of CH groups, while the band at 1414 cm^{-1} corresponds to the symmetric stretching of $–COO^-$ groups, indicating the presence of carboxyl groups. The strong absorption band observed at 1036 cm^{-1} is assigned to the Si–O stretching vibrations typical of bentonite.

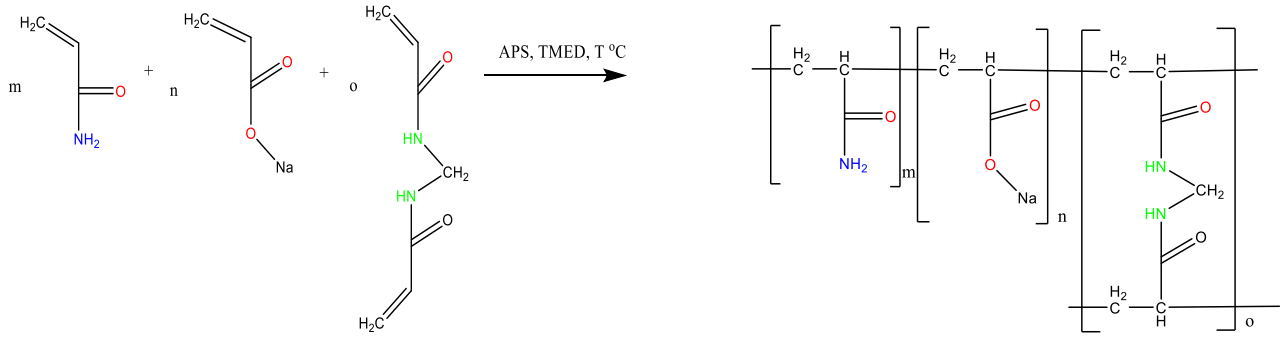

Figure 1 – Scheme for the synthesis of hydrogels based on AAm/SA/MBAA/Bentonite

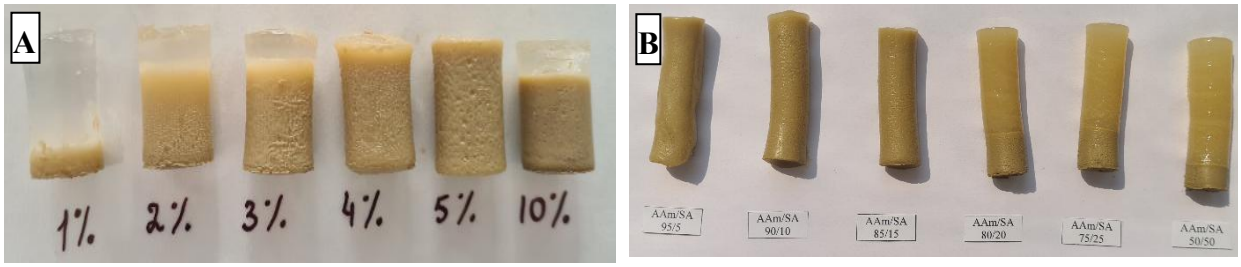

Figure 2 – Hydrogels based on AAm/SA/MBAA/Bentonite: A) the impact of varying bentonite concentration in the initial mixture (%), and B) the influence of altering the ratio of AAm/SA in the initial monomer mixture, expressed in percentages

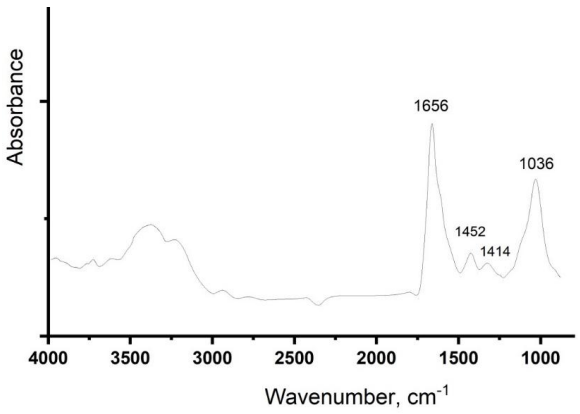

Figure 3 – FTIR spectra of hydrogel based AAm/SA/MBAA

3.3 Mechanical analysis of PPG

The mechanical properties of freshly prepared gels were investigated to demonstrate the strength of polyelectrolyte hydrogels with the inclusion of bentonite, along with an exploration of the impact of composition on their properties. The Young's modulus was calculated for various hydrogel variations, and the results are presented in Figure 4.

At different monomer concentrations, the elastic modulus (Young's modulus) of AAm/SA/MBAA/Bentonite composite hydrogels increased from 64 to 283 Pa with a higher monomer content in the initial mixture, indicating an enhancement in the mechanical properties of the samples. The strength of hydrogels is determined by the crosslink density in their network structure, which is directly dependent on the monomer concentration. At elevated monomer concentrations, more reactive centers are available for crosslinking reactions during polymerization. As a result, a greater number of covalent bonds are formed between polymer chains, leading to the development of a denser crosslinked network. However, when the monomer concentration exceeds the optimal level (15%), the mechanical strength of the hydrogel decreases, which is attributed to excessive crosslinking, structural heterogeneity, and increased brittleness. An increase in crosslink density improves the physical integrity of the material, enabling the hydrogel to withstand mechanical stresses and resist deformation, thereby raising the elastic modulus from 32 to 171 Pa. As the concentration of monomer and crosslinking agent increases, the pore (cell) size between the crosslinked polymer chains decreases. The reduction in porosity contributes to the formation of a denser network, which restricts the mobility of water within the hydrogel matrix.

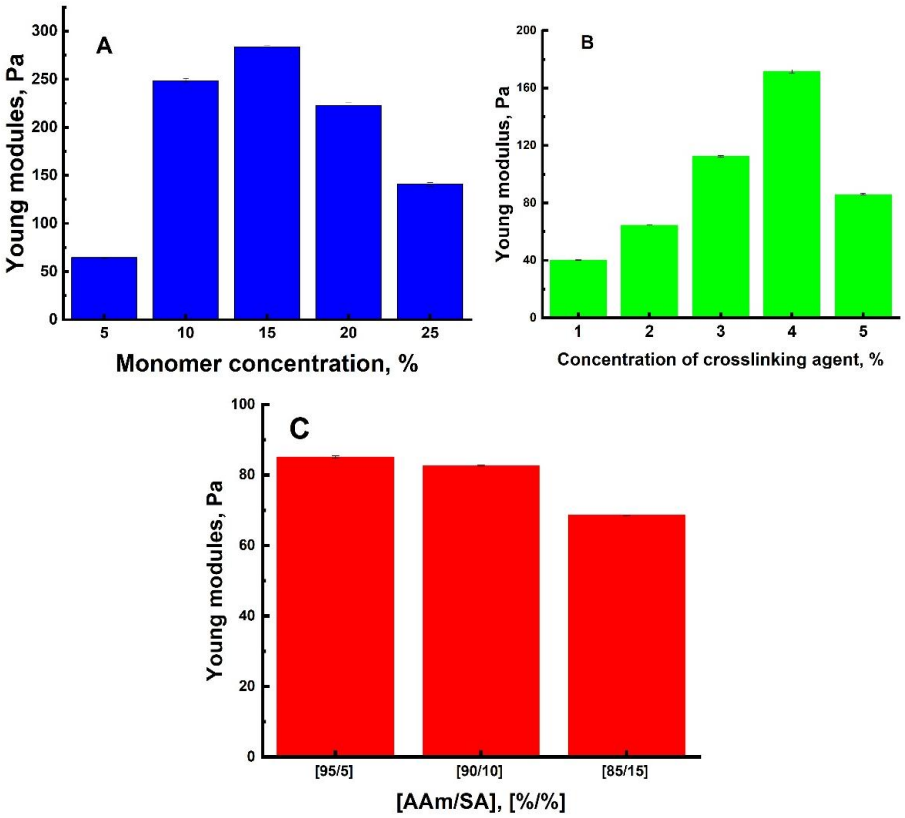

Figure 4 – Young's modulus of hydrogels depending on change: A) concentrations of monomers, B) concentrations of the crosslinking agent, C) ratios of monomers AAm/SA

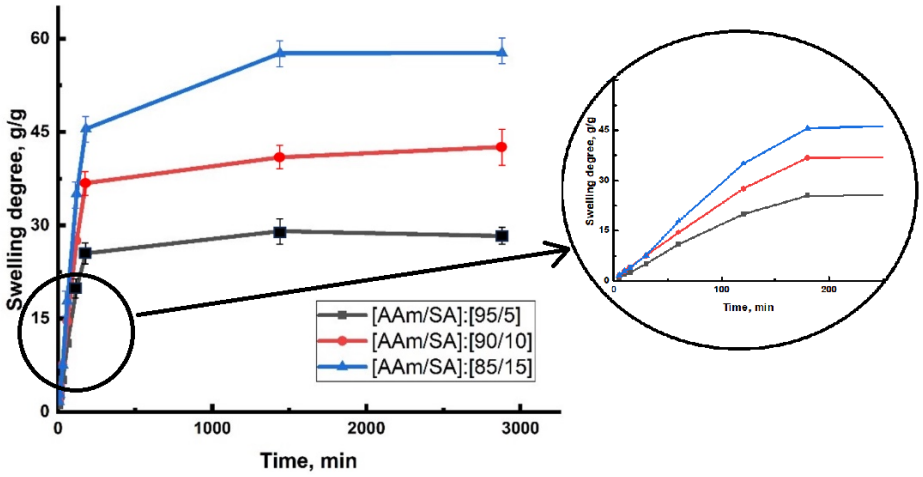

Figure 5 – Absorption of water by hydrogels depending on time

3.4 Analysis of swelling experiments

Given that hydrogels possess the capability to retain water through their three-dimensional (3D) polymer mesh, the swelling ability and rate of hydrogels are influenced by several parameters, including ionic strength, temperature, degree of crosslinking, monomer group types, and pH. While various kinetic models for swelling rate exist, many primarily describe diffusion or polymer relaxation as the dominant processes affecting the swelling rate.

The kinetics of hydrogel swelling in water have been examined using a gravimetric approach [17], and a subset of the results is depicted in Figure 5.

The hydrogel reaches equilibrium (Eq) degrees of swelling approximately after a day of swelling (Figure 5). To gain insights into the mechanism of water sorption by hydrogels, kinetic data were analyzed using a semi-empirical equation proposed by Rittger and Peppas [18].

$$\frac{SD_t}{SD_\infty} = k * t^n \quad (3)$$

where k – is a characteristic constant of a hydrogel, n – is a characteristic exponent of the transport mode.

Figure 6 shows the logarithmic dependence of the swelling degree (SD) of hydrogels on time

It's important to note that the Ritger and Peppas equation (3) is applicable only when $m_t/m_\infty \leq 0{,}6$. The parameter n in this equation offers insight into the mechanism of water sorption. When n < 0,5, it suggests that the sorption of water follows Fick's law. In this scenario, diffusion is the limiting factor, meaning it occurs much slower than the relaxation rate of polymer chains. When 0.5 < n < 1.0, it indicates that the process does not strictly follow the Fick's law, and water absorption is affected by both diffusion and relaxation of polymer chains. If n equals 1, then water absorption is primarily governed by the relaxation of chains, implying that the diffusion rate is greater than the relaxation rate of polymer chains. Table 2 contains data according to formula 3.

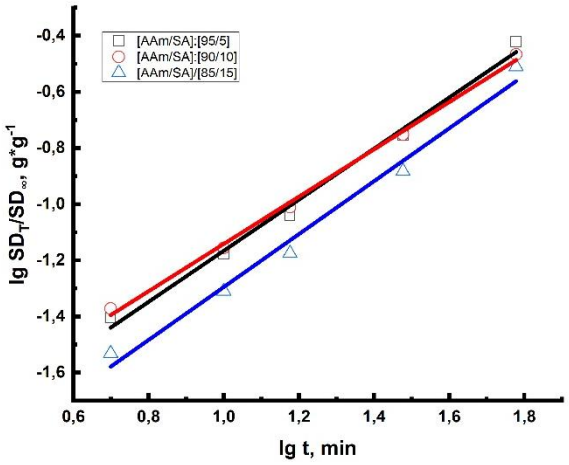

Figure 6 – Dependence of the EqSD of hydrogels on time in logarithmic coordinates

Table 2 – Constants of the Ritger-Peppas equation

Sample	S_e	A	N	R^2	Main process
[AAm]/[SA]:[95]/[5]	28.97	0.13	0.91	0.99	Relaxation and Diffusion
[AAm]/[SA]:[90]/[10]	42.24	0.14	0.84	0.99	Relaxation and Diffusion
[AAm]/[SA]:[85]/[15]	57.97	0.11	0.94	0.98	Relaxation and Diffusion

The data in Table 2 suggests that hydrogels exhibit characteristics of both processes—relaxation and diffusion. This dual nature implies that the absorption of water in hydrogels is influenced by both the relaxation of polymer chains and the diffusion of water molecules.

Despite the satisfactory description of the swelling kinetics and liquid transport angels provided by the Papas model in this case, it is worth noting that this model has limitations. It does not cover the entire interval of the swelling period and is only applicable for a restricted range of the SD. In a recent development, Yavari and Azizyan [19] introduced a new model for describing the kinetics of hydrogel swelling. This novel mixed model is capable of characterizing the swelling process across the entire range of degree of swelling values and allows assessment of whether the process is dominated by diffusion or relaxation.

Figure 7 illustrates the graphical dependence of the SD on time, constructed using the Yavari and Azizyan mixed model, and the corresponding calculation results are presented in Table 3.

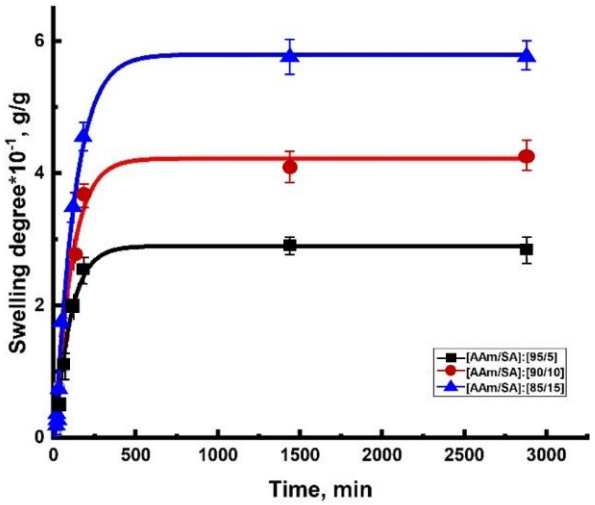

Figure 7 – Dependence of hydrogels SD on time

As depicted in Figure 7, the experimental measurement points closely align with the model curve, demonstrating a high degree of correlation (R^2=0.99).

This method affirms that the mechanism of gel swelling is influenced by both the diffusion of liquid into the gel volume and the relaxation of polymer macromolecules. The combined consideration of these factors provides a more comprehensive understanding of the kinetics and behavior of hydrogel swelling.

The EqSD is a crucial performance characteristic for hydrogels. In Figure 8, samples of hydrogels are presented in both dry and swollen states. It is evident even to the naked eye that the hydrogels exhibit a high swelling capacity.

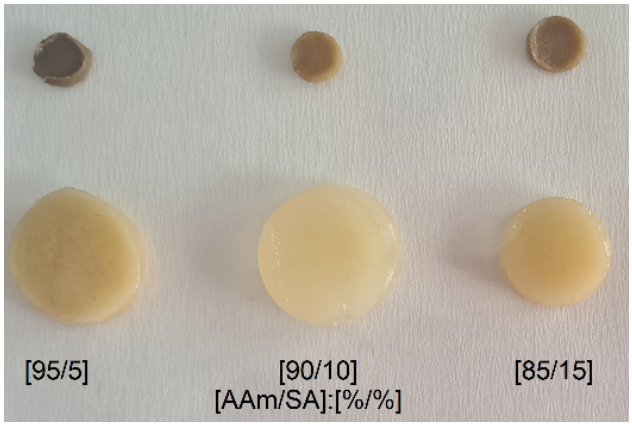

Figure 8 – Dried (upper row) and swollen (lower row) hydrogel samples

In Figure 9, it is observed that as the concentration of monomers (crosslinking agent) increases in the hydrogel, the degree of swelling decreases. Additionally, with an increase in the concentration of monomers, there is a noticeable breakdown of the hydrogel structure (Figure 10). This phenomenon may be attributed to the high density of monomer units leading to a reduction in the volume of pores. However, with an increase in the concentration of acrylamide in the hydrogel, the degree of swelling decreases. This is attributed to a decrease in the number of charged groups in the hydrogel structure, resulting in a reduction of their mutual repulsion from each other [20].

3.5 The effect of ionic strength on the EqSD of hydrogels

Figure 11 shows the dependence of the EqSD of hydrogels on the ionic strength of the solution.

As depicted in Figure 11, the EqSD in hydrogels shows significant variation only at the lowest concentration of salt in the solution; beyond that point, the EqSD appears to be independent of the salt concentration. The presence of salts in

Table 3 – Data on the swelling of hydrogels

Sample	S_e	k_1	k_2	R^2	Main process
[AAm]/[SA]:[95]/[5]	28.97	0.012	-0.023	0.99	Relaxation and Diffusion
[AAm]/[SA]:[90]/[10]	42.24	0.011	-0.019	0.99	Relaxation and Diffusion
[AAm]/[SA]:[85]/[15]	57.97	0.009	-0.021	0.99	Relaxation and Diffusion

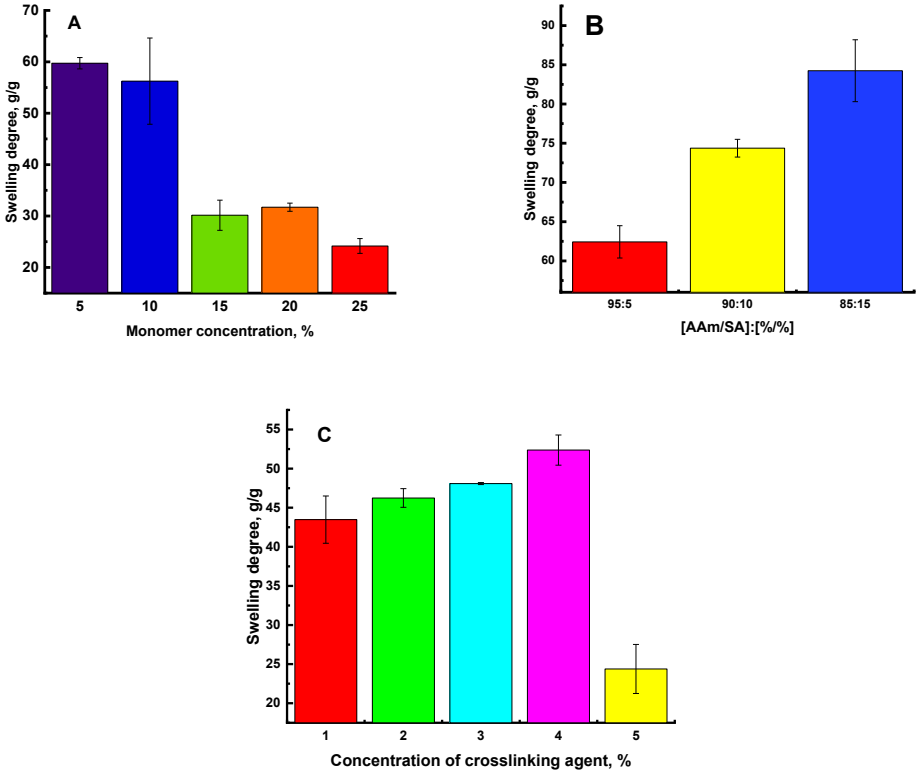

Figure 9 – Dependence of the swelling degree of hydrogels on various factors: A) the concentration of monomers, B) the ratio of AAm/SA, C) the concentration of the crosslinking agent

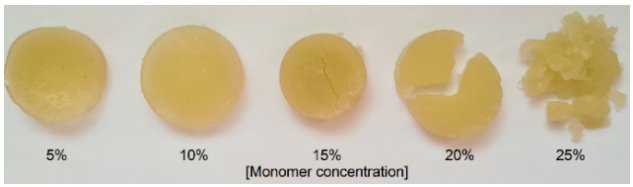

Figure 10 – Photos of swollen hydrogels

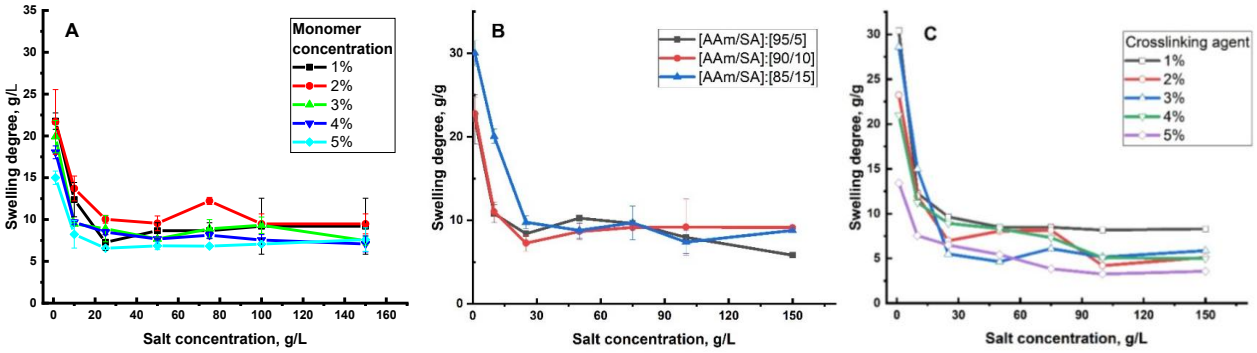

Figure 11 – Effect of the ionic strength on the EqSD of hydrogels on various factors: A) the concentration of monomers, B) the ratio of AAm/SA, C) the concentration of the crosslinking agent

the swelling medium increases their concentration, subsequently reducing the difference in osmotic pressure on the PPG membrane – the driving force behind absorbency. This reduction in osmotic pressure diminishes the ability of PPG to swell.

The increased concentration of positive ions (e.g., Na^+, Ca^{2+}, and Mg^{2+}) interacts with the negatively charged groups in PPG chains, leading to ion crosslinking and a shielding effect. This interaction reduces electrostatic repulsion, resulting in chain shrinkage and a decrease in the ability to swell. The swelling coefficients of various salt solutions remain nearly constant, as all positive ions react with negatively charged groups, reaching a state of charge balance. In this balanced state, further increases in salinity do not significantly affect the ability to swell. The same results have been observed by R. Elaf and co-workers [21] on the hydrogels made of AAm and chitosan.

An earlier study examined the relationship between the swelling of hydrogels and water salinity. The Table 4 presents comparative data, demonstrating how the degree of swelling in hydrogels is influenced by variations in water salinity.

The compression ratio of hydrogels was determined by dividing the EqSD of hydrogels with a change in salt concentration by EqSD of hydrogels in water. Table 4 reveals that the degree of swelling in hydrogels is composition-dependent. However, a noticeable decrease in the degree of swelling occurs when the ionic strength of the solution changes. The preformed hydrogel particle (PPG) highlighted in this study demonstrates comparable swelling abilities to other hydrogels, with the addition of bentonite resulting in a slightly higher compression ratio compared to its absence.

3.6 The effect of pH on EqSD of PPG

pH values of brine water in Kazakhstan oil fields are ranges or varies between 6 and 9. The pH range may vary slightly depending on mineral composition of oil reservoir, salt concentration etc. Figure 12 shows the dependence of the EqSD of hydrogels on the pH value of the medium.

Table 4 – Composition of the SD of PPG depending on the composition and concentration of NaCl

#	Composition	Swelling degree	The SD in the saline solution (Concentration of NaCl)	Compression ratio	Reference
1	AAm/Sodium peroxydisulfate	120	50 (10 g/L)	0.41	[22]
2	AAm/SA/MBAA	> 100	20 (10 g/L)	0.2	[23]
3	SAP	250	20 (100000 ppm)	0.08	[24]
4	PEG-200	200	180 (100000 ppm)	0.9	[25]
5	AAm/SA/MBAA/bentonite	85	20 (10 g/L)	0.235	Present work

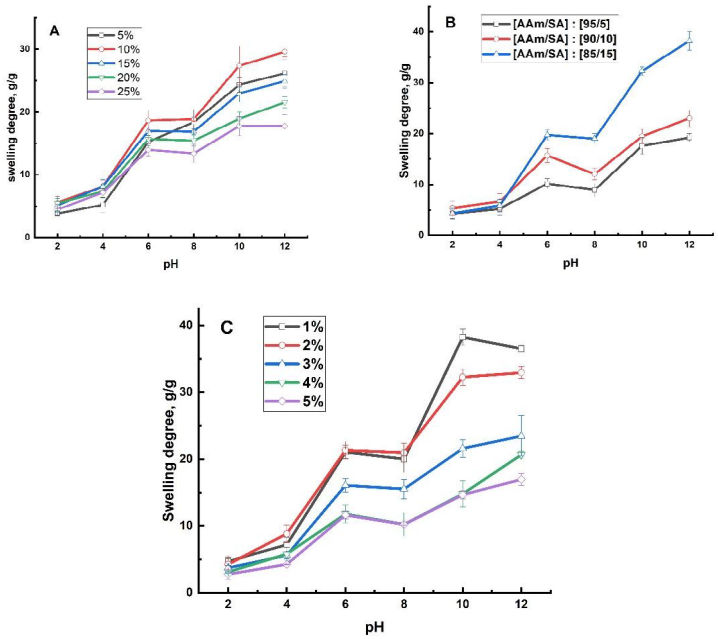

Figure 12 – Effect of pH on the EqSD of hydrogels on various factors: A) the concentration of monomers, B) the ratio of AAm/SA, C) the concentration of the crosslinking agent

As can be seen from Figure 12, in an acidic environment (pH = 2-6), the EqSD of hydrogels increases with increasing pH. The effect of pH may be due to the release of proton ions in an acidic medium, which shields the electric repulsive force of the charged group. What is described in the study [26]. At a pH value of 6-8, the EqSD practically did not change. This phenomenon can be explained by the cooperative relationship between the groups $^{-}$COOH and COO^{-}. At the specified pH range, COO groups turn into $^{-}$COOH groups. This reduces the repulsion of negatively charged groups and increases the association between $^{-}$COOH groups due to the formation of a hydrogen bond. Thus, water absorption will decrease due to the higher crosslinking density with increasing pH value. At a pH above 8, the $^{-}$COOH groups turn into COO^{-}, the polymers hydrolyze, which leads to a decrease in the polymer's resistance to water permeability and an increase in water absorption. Similar results were obtained by the authors [27].

3.7 The effect of temperature on the EqSD of PPG

Given the elevated temperatures of reservoir waters (60-80°C), it is imperative to choose a hydrogel composition that exhibits swelling capabilities at higher temperatures. Figure 13 illustrates the dependence of the EqSD in hydrogels on temperature. This information aids in selecting hydrogel compositions suitable for applications in environment with elevated temperatures, ensuring optimal performance under such conditions.

Figure 13 indicates that the swelling capacity of hydrogels increases with rising ambient temperature. Typically, for non-thermosetting hydrogels, an increase in temperature results in an augmentation of the EqSD. This phenomenon is primarily attributed to the enhanced kinetic energy of water molecules induced by higher temperatures, accelerating their diffusion into the hydrogel matrix. This observation aligns with the findings of the author [28].

The heightened diffusion rate of water molecules facilitates better penetration into polymer chains, leading to increased water absorption and swelling. The temperature increase weakens the interaction between polymer chains, promoting relaxation and expansion of polymer chains. This, in turn, facilitates greater penetration of water into the hydrogel, augmenting its ability to swell. In a broader context, the enhanced water absorption and expansion of the volume and structure of the hydrogel have significant implications potential for vapplications, such as the injection of preformed gel particles for compliance control in oil tanks.

3.8 Thermogravimetric and differential thermal analysis

The results of thermogravimetric and differential thermal analysis of AAm-SA hydrogels are shown in Figures 14 (A, B).

The thermogravimetric analysis showed that the samples are stable in the range from 25°C to 400°C, as shown in Figure 14A. No significant mass loss of the hydrogel particles was observed. The reason for the observed phenomenon is that the

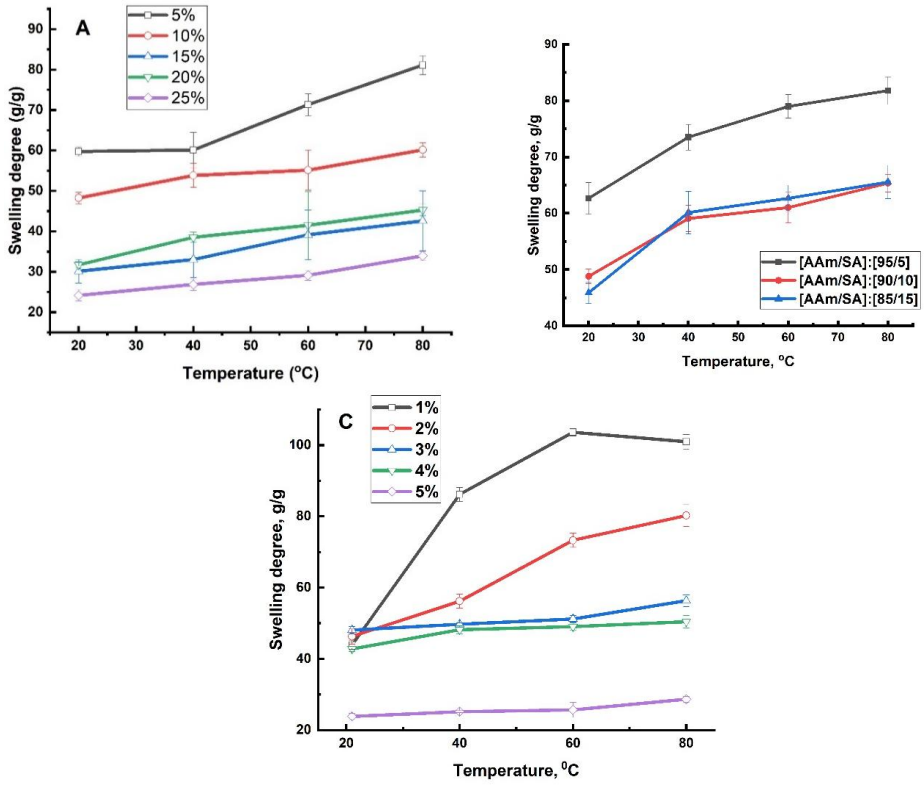

Figure 13 – Effect of temperature on the EqSD of hydrogels on various factors: A) the concentration of monomers, B) the ratio of AAm/SA, C) the concentration of the crosslinking agent

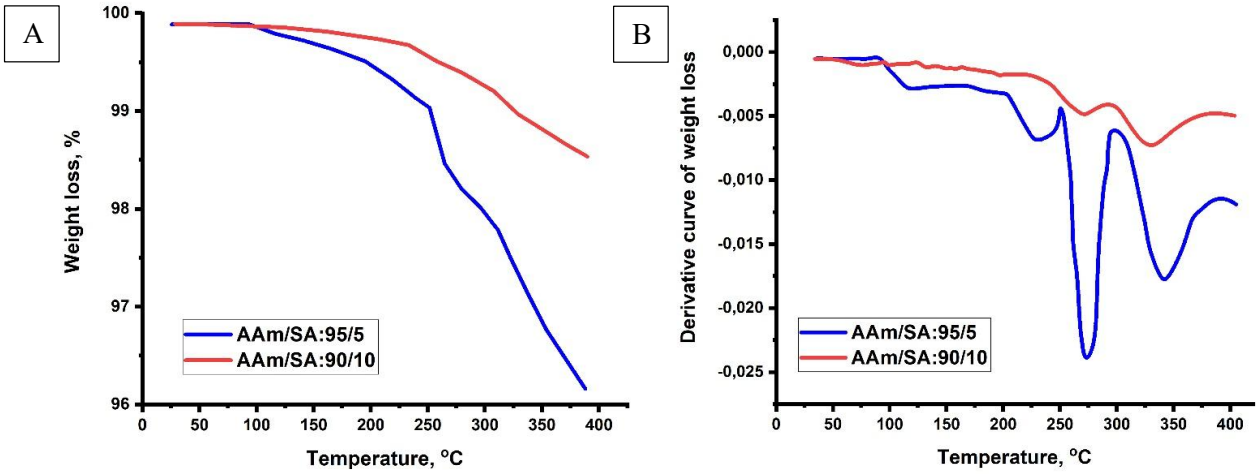

Figure 14 – TGA (A) and DTA(B) curves of hydrogels

sample was completely dried for analysis. As a result, the mass ratio of the polymer portion and the bentonite filler in the dried hydrogel was approximately 2 to 1. Consequently, the mass loss of the entire composite was no more than 3.5%.

Figure 14B shows the presence of temperature zones where significant mass loss of polymer hydrogels is observed: 257-264 °C and 322-332 °C. The first interval is associated with the dehydration of the amide groups, the second with the decomposition of the main chains of the polymer [23]. As can be clearly seen from the figure 14 b the T_{onset} of the samples is approx. 200 ˚C for [AAm:SA]- [95:5], and 220 ˚C for [AAm:SA]-[90:10]. The most important result of this experiment is that the obtained samples remain stable in the temperature range from room temperature up to 400 °C.

4. Conclusion

A series of hydrogels were synthesized with the further preparation of PPG. Their properties were investigated as a function of changing the concentration of the monomers and the crosslinking agent. The kinetic properties of swelling were investigated. The swelling capacity was also investigated as a function of temperature, salt concentration and acidity of the medium. This showed that the hydrogel particles have an excellent swelling capacity and can withstand harsh conditions such as high temperatures, high salt content in the solution and increased acidity of the medium. The thermogravimetric properties of the hydrogel particles indicate the possibility of their use at high temperatures, since the destruction of the gel begins at 200 °C and the average water temperature for collectors is 80 °C. The study of mechanical properties has shown that hydrogel particles have a high modulus of elasticity 283 Pa, which prevents damage when passing through oil formations.

The results of the study indicate that these hydrogel particles can serve as a cost-effective plugging agent in oil reservoirs, contributing to increased oil production and lower water content in the reservoirs, thus minimizing environmental impact. For optimal performance, hydrogel samples with monomer concentrations of 5% to 20% are recommended, and the crosslinker should not exceed 5%.

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CRediT authorship contribution statement

Gulnur Yelemessova: Investigation, Methodology, Writing – original draft; Alexey Klivenko: Methodology, Writing – original draft , Writing – review & editing, Data curation; Lyazzat Orazzhanova : Writing – review & editing; Alfira Saitova: Writing – review & editing; Alexey Shakhvorostov: Funding acquisition, Resources, Writing – review & editing; Vladimir Aseyev: Writing – review & editing.

Declaration of competing interests

Authors declare no conflicts of interest.

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