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Mathematical Modelling and Analysis of the Rheological Properties of a Polymer Modified Cementing Slurry

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ABSTRACT

The study presents mathematical modeling of the rheological properties of a cementing slurry with a water-to-cement ratio of W/C = 0.5 modified with various water-soluble polymers: polyacrylamide (PAA), xanthan gum and an AM/AMPS copolymer. Based on experimental data, second-order polynomial models were developed to describe the dependence of dynamic viscosity and shear stress on the concentration of polymer additives. It is shown that the effect of the polymers is nonlinear and is characterized by the presence of an optimal concentration range at which maximum rheological performance is achieved.

Keywords: Cementing slurry; Rheology; Dynamic viscosity; Shear stress; Polymer additives; Mathematical modeling

Introduction

The rheological properties of cementing slurries have a decisive influence on the efficiency of preparation, transportation and pumping processes of cement systems during the casing of oil and gas wells. Viscosity characteristics, shear stress and structural strength determine key technological parameters such as slurry pumpability, uniform filling of the annular space, prevention of solid-phase sedimentation and the quality of cement stone formation. Insufficient control of rheological parameters can lead to complications during cementing operations, reduced casing integrity and deterioration of well operational reliability[1,2].

Under modern field development conditions, characterized by increasingly complex geological settings, elevated temperatures and pressures and greater drilling depths, the requirements for the technological and rheological characteristics of cementing slurries are becoming more stringent. In this context, water-soluble polymer additives have gained widespread use, as they enable effective regulation of the structural and mechanical properties of cement systems[3,4]. Polymers of different chemical nature, such as polyacrylamide, xanthan gum and copolymers of acrylamide with AMPS, are capable of forming spatial networks, increasing resistance to shear and enhancing the stability of dispersed systems.

At the same time, the effect of polymer additives on the rheological properties of cementing slurries is complex and generally nonlinear. At low polymer concentrations, a significant improvement in rheological performance is observed due to system structuring, whereas exceeding a certain threshold concentration may lead to slurry oversaturation, macromolecular aggregation and disruption of the structure forming. This results in reduced modification efficiency and may negatively affect the technological properties of the slurry. Therefore, determining the optimal concentrations of polymer additives represents an important scientific and practical task[4,5].

One of the effective tools for analysing such dependencies is mathematical modelling, which makes it possible to generalize experimental data and obtain empirical equations describing the influence of modifier concentration on rheological parameters. Second-order polynomial models are widely used to describe smooth nonlinear relationships and allow the identification of extrema corresponding to optimal modification regimes[1,6-8].

In view of the above, the aim of this study is to investigate the effect of the concentration of polymer additives-PAA, xanthan gum and the AM/AMPS copolymer-on the dynamic viscosity and shear stress of a cementing slurry, as well as to develop and analyse empirical mathematical models describing the obtained relationships and enabling the determination of optimal dosing ranges for polymer components **(Figure 1)**.

Rheological properties of the cementing slurry (W/C = 0.5)

Effect of Polymers on Dynamic Viscosity and Shear Stress

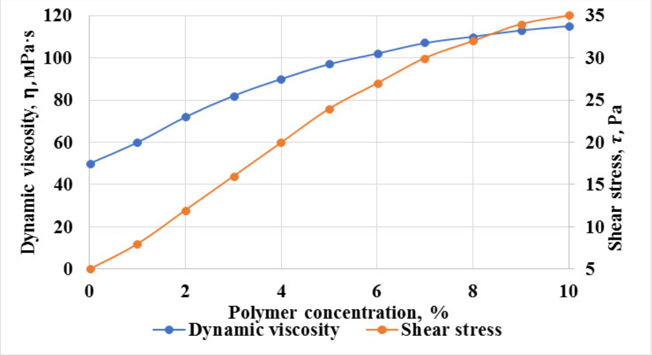

Figure 1: Dynamic viscosity and shear stress of a cementing slurry as functions of polymer concentration.

The dynamic viscosity of the cementing slurry with the addition of PAA is described by the following polynomial model:

$$y = -0{,}584x^2 + 12{,}321x + 49{,}56$$

The model has the form of a quadratic polynomial:

$$\eta(x) = -0{,}584x^2 + 12{,}321x + 49{,}56,$$

where

η- dynamic viscosity of the slurry,

x - concentration of PAA (usually expressed in % or g/L).

The second-degree polynomial indicates that the effect of PAA concentration on viscosity is nonlinear and the influence of the additive either intensifies or diminishes as the concentration increases.

The coefficient of the x^2term is –0.584. The negative value indicates that the dependence has a maximum rather than a monotonically increasing trend. This reflects a phenomenon typical for polymer systems: at low and intermediate concentrations of PAA, viscosity increases, whereas at excessively high concentrations structural over-thickening and subsequent disruption of the formed structure may occur, leading to a decrease in effective viscosity. The coefficient of the linear term x is +12.321. The large positive value indicates a strong increase in viscosity at the initial stage, when even a small amount of PAA significantly enhances the viscosity of the slurry. The constant term is 49.56, which corresponds to the viscosity at zero PAA concentration and represents the base viscosity of the initial cementing slurry without polymer addition.

Since the parabola opens downward, there exists a concentration $x_{\max}$ at which viscosity reaches its maximum. It can be determined as:

$$x_{\max} = -\frac{b}{2a} = -\frac{12.321}{2 \cdot (-0.584)} \approx 10.55$$

This means that:

- Viscosity increases approximately up to a PAA concentration of about 10.5 units (in the same units as used in the model);
- Beyond this maximum, further increases in concentration may lead to structural thinning or polymer oversaturation.

This characteristic:

- Allows determination of the optimal PAA dosage range;
- Helps avoid excessive polymer concentrations that may deteriorate technological properties of the slurry.

The second-order polynomial model:

- Adequately describes smooth nonlinear dependences of rheological properties on concentration;
- May serve as an empirical equation based on laboratory data;
- Is generally applicable only within the investigated concentration range.

Beyond this range, the model may exhibit:

- Physically unrealistic behaviour (e.g., viscosity values below feasible limits);
- Degradation of predictive accuracy.

PAA is a high-molecular-weight polymer that:

- Forms a spatial network in the slurry;
- Increases resistance to shear;
- Induces a transition to a strongly structured state at certain concentrations.

However, at excessively high dosages, polymer aggregation, poor distribution of polymer chains and reduced hydration may occur, explaining the negative quadratic term in the model.

This polynomial model demonstrates that:

- PAA significantly increases slurry viscosity at low and medium concentrations;
- Viscosity reaches a maximum at approximately 10.5 conditional units;
- Further concentration increase may be ineffective or even detrimental.

We analyse dependence of Dynamic Viscosity and Shear Stress on Xanthan Concentration **(Figure 2)**.

The dynamic viscosity of the cementing slurry with xanthan additive is described by the polynomial model:

$$\eta(x) = -0{,}7x^2 + 17{,}6x + 48{,}8$$

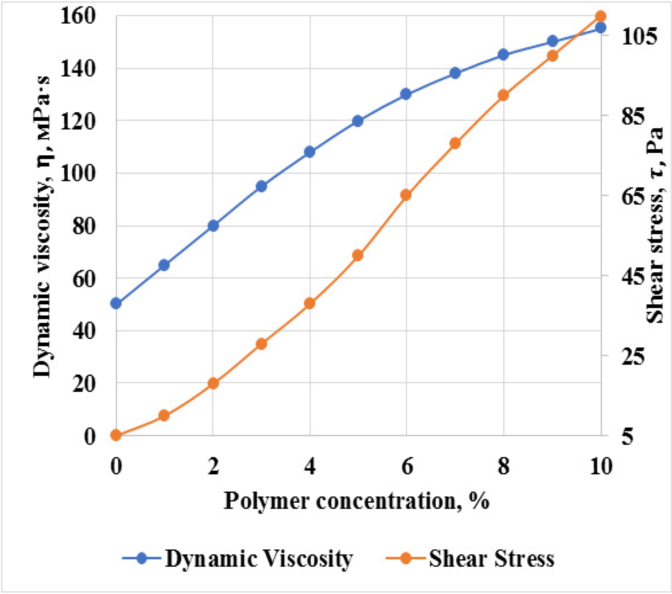

Figure 2: Dependence of Dynamic Viscosity and Shear Stress on Xanthan Concentration.

The shear stress of the cementing slurry with xanthan additive is described by the polynomial model:

$$\tau(x) = 0{,}25x^2 + 8{,}7x + 1{,}74$$

where

x is the xanthan concentration (% or g/L depending on the methodology),

$\eta(x)$ is the dynamic viscosity (mPa·s),

$\tau(x)$ is the shear stress (Pa).

The negative coefficient of the quadratic term (–0.7) in the viscosity model indicates a non-monotonic dependence with a distinct maximum. At low xanthan concentrations, viscosity increases sharply due to slurry structuring. At excessive concentrations, polymer chain agglomeration, solution oversaturation, deterioration of hydration and disruption of the spatial network may occur, resulting in reduced effective viscosity.

–0.7 x^2 – limits the unlimited growth of viscosity. It shows that the model takes into account the saturation effect. +17.6 x – the main contribution of the polymer to increasing the solution's viscosity. +48.8 – the base viscosity without the addition of xanthan.

The maximum viscosity is reached at:

$$x_{\text{опт}} = -\frac{b}{2a} = -\frac{17.6}{2(-0.7)} \approx 12.6$$

Thus, peak viscosity is achieved at a xanthan concentration of approximately 12.6 units.

The model adequately reflects the increase in viscosity with increasing thickener concentration, the presence of an optimal concentration and the decrease in viscosity at excess polymer - a real physico-chemical effect.

Shear stress model equation

$$\tau(x) = 0.25x^2 + 8.7x + 1.74$$

where $\tau(x)$ is the shear stress, characterizing the ability of the solution's structure to resist the onset of flow. High values of indicate pronounced structural and mechanical properties.

The coefficient x^2 of is positive; therefore, the shear stress monotonically increases with increasing xanthan concentration. The solution structure becomes stronger. This corresponds to the well-known properties of xanthan. Xanthan forms a networked, highly elastic structure and with increasing concentration, a denser spatial network is formed. The resistance to shear increases faster than the dynamic viscosity.

0.25 x^2 - accelerated growth of shear stress at high concentrations, reflecting nonlinear structuring. 8.7 x – the main contribution of the polymer to the strength of the structure. 1.74 - the shear stress of the initial solution without xanthan.

Unlike viscosity, which shows a maximum, shear stress does not have a peak and does not decrease, because increasing the number of polymer chains always enhances structural strength. During agglomeration or saturation, viscosity may decline, but the structure (yield stress) continues to grow. The model confirms that increasing xanthan concentration always enhances structuring, raises the yield stress and improves the solution's rheological stability.

Viscosity depends on the effective hydraulic resistance, which reaches a maximum and then decreases. Shear stress depends on the structural strength, which is maintained even at oversaturation. These models allow for determining the optimal xanthan concentration to obtain a stable yet workable solution.

We study the dependence of dynamic viscosity and shear stress of the cementing slurry on the concentration of AM/AMPS (**Figure 3**).

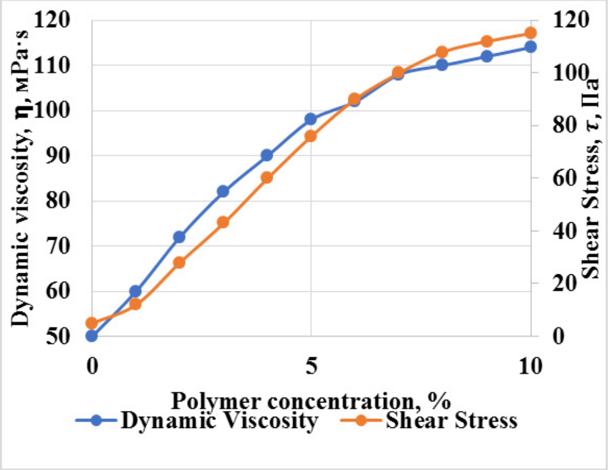

Figure 3: Dependence of Dynamic Viscosity and Shear Stress on AM/AMPS Concentration.

The dynamic viscosity of the cementing slurry with AM/AMPS additive is described by the polynomial model:

$$\eta(x) = -0{,}63x^2 + 12{,}7x + 49{,}2$$

The shear stress of the cementing slurry with xanthan additive is described by the polynomial model:

$$\tau(x) = -0{,}653x^2 + 18{,}7x - 2{,}34$$

where

x is the AM/AMPS concentration (%),

$\eta(x)$ is the dynamic viscosity (mPa·s),

$\tau(x)$ is the shear stress (Pa).

The model represents a quadratic parabola with downward-opening branches, indicating that at low concentrations of AM/AMPS, the polymer's growth causes an increase in viscosity - the system becomes more structured. At high concentrations, viscosity decreases, reflecting possible oversaturation of the system with polymer, disruption of the spatial macromolecular network, charge screening and a reduction in interchain interactions - the manifestation of a "shear-thinning" effect at excess polymer. This type of dependence is typical for solutions of water-soluble copolymers.

Since the coefficient of x^2 is negative, the function has a maximum:

$$x_{\max} = \frac{-b}{2a} = \frac{-12.7}{2(-0.63)} \approx 10.1$$

Thus, the maximum viscosity is achieved at approximately 10% AM/AMPS (conditionally, the actual value depends on the units). At concentrations above this value, viscosity begins to decrease, reflecting the optimal modification range.

Model**:**

$$\tau(x) = -0.653x^2 + 18.7x - 2.34$$

Where:

- τ - shear stress (Pa)
- x - AM/AMPS concentration

This is also a quadratic model with negative curvature, similarly indicating the presence of a limiting value. At low concentrations of AM/AMPS, shear stress increases. At high concentrations, shear stress decreases.

Calculating the function's maximum:

$$x_{\max} = \frac{-b}{2a} = \frac{-18.7}{2(-0.653)} \approx 14.3$$

Thus, the maximum shear stress is achieved at around 14% concentration. Compared to viscosity, the maximum occurs at a slightly higher concentration, indicating different sensitivities of these parameters to the polymer system structure.

At the early stages of copolymer addition, the polymer induces the formation of a spatial network of polymer chains, increasing structural strength and resistance to shear.

Polynomial models show that modifying the cementing solution with AM/AMPS copolymer has a nonlinear effect: a small increase in concentration improves rheological properties, but excess leads to deterioration of both viscosity and shear stress. This reflects the typical behavior of polymer solutions, where there exists an optimal dosage range that ensures improved solution stability, enhanced structural-mechanical properties and optimized transport and pumping.

Results

The conducted mathematical modeling showed that for all studied polymeric modifiers (PAA, xanthan and AM/AMPS copolymer), the dependence of dynamic viscosity and shear stress of the cementing solution on polymer concentration is strongly nonlinear and is adequately described by second-order polynomial models. The obtained empirical relationships allow not only a quantitative assessment of the effect of additives but also identification of optimal concentration ranges where maximum improvement of rheological properties is achieved[7-10].

For systems with PAA and AM/AMPS, dynamic viscosity exhibits a pronounced maximum. In both cases, the coefficient of x^2 is negative, indicating saturation of the system at higher polymer concentrations. At the initial stage (low and medium concentrations), there is a significant increase in viscosity due to the formation of a spatial network of polymer chains, enhanced intermolecular interactions and increased hydration of macromolecules. Further increases in polymer concentration lead to a deterioration of the structural organization: possible formation of agglomerates, disruption of uniform polymer distribution, reduced degree of hydration and increased packing density of macromolecules. These processes result in a decrease in effective viscosity, which is well reflected by the negative quadratic term of the model[11-15].

In the case of PAA, the maximum dynamic viscosity is reached at a concentration of approximately 10.5 units, indicating the optimal dosage range for this polymer. Since PAA has a high molecular weight and tends to form highly interconnected structures, exceeding the optimal concentration can lead to excessive densification and uneven polymer distribution, reducing pumpability and workability of the solution.

For the AM/AMPS copolymer, the maximum viscosity occurs at around 10.1%, close to the value for PAA; however, its effect on shear stress differs. Unlike viscosity, AM/AMPS shows a maximum shear stress at approximately 14.3% concentration. This indicates that the structural strength of the system (yield stress) continues to increase at higher concentrations than viscosity. This effect may be explained by the fact that yield stress depends more strongly on the strength of interchain bonds and the formation of a three-dimensional network rather than solely on hydrodynamic resistance. Therefore, optimizing AM/AMPS dosage must take into account the different behaviors of these parameters: the concentration that provides maximum viscosity does not always coincide with the concentration of maximum shear stress[16-21].

For xanthan systems, dynamic viscosity is also described by a parabolic model with a negative quadratic term, indicating an optimal concentration at which maximum viscosity is achieved (approximately 12.6 units). Unlike PAA and AM/AMPS, xanthan exhibits a more pronounced increase in shear stress with increasing concentration and the corresponding model has a positive coefficient for . This means that the structural strength of the solution monotonically increases with increasing xanthan concentration and no saturation is observed in the studied range. This effect corresponds to the known properties of xanthan as a strong structure-former: even at high concentrations, it retains the ability to form an elastic network, increasing resistance to shear.

Comparative analysis of the models shows that xanthan most effectively increases shear stress and structural stability, which is important for preventing sedimentation and ensuring suspension stability during transport. However, high concentrations can lead to excessive viscosity, reducing pumpability; therefore, the optimal concentration must balance structural stability and workability. For PAA and AM/AMPS, the presence of a pronounced viscosity maximum makes adherence to the correct dosage critical, as both deficiency and excess of polymer can reduce modification efficiency.

It is important to note that second-order polynomial models are empirical and are valid only within the studied concentration ranges. Beyond the experimental range, they may produce physically unrealistic values (e.g., negative viscosity), which limits their applicability. Nevertheless, within the defined conditions, these models allow the determination of optimal additive concentrations, prediction of rheological behavior and assessment of the impact of modifiers on technological parameters[22].

Thus, the study results confirm that optimization of rheological properties of cementing solutions using polymer additives requires consideration of nonlinear dependencies and optimal concentration ranges. The obtained models not only describe experimental data but also serve as a practical tool for selecting rational formulations that provide the required stability and pumpability of the solution under oil and gas field conditions.

Conclusions

The study established that modification of cementing slurry with water-soluble polymers - polyacrylamide (PAA), xanthan and the AM/AMPS copolymer - has a **pronounced nonlinear effect** on key rheological characteristics of cement systems, particularly dynamic viscosity and shear stress. The obtained quadratic models not only describe the patterns of change in these parameters but also allow the determination of concentrations at which optimal rheological performance is achieved.

Modeling results confirmed that at low and medium polymer concentrations, there is a significant increase in viscosity and structural strength of the solution, caused by the formation of a spatial network of macromolecules and an increase in shear resistance. However, exceeding a certain threshold leads to a decrease in viscosity due to system oversaturation, formation of agglomerates and deterioration of uniform polymer chain distribution. This behavior is typical of complex dispersed systems and is supported by recent studies, which also note the existence of optimal concentration ranges for any organic or inorganic additives to improve the rheological properties of cement suspensions.

An important feature of modified systems is the different sensitivity of rheological parameters to polymer concentration: while dynamic viscosity reaches a maximum at one concentration, maximum shear stress may occur at a different value (e.g., for AM/AMPS, the maxima of viscosity and shear stress differ). This reflects the difference in mechanisms affecting hydrodynamic resistance versus structural strength, consistent with modern research highlighting the significant role of additives and dispersion in forming viscosity gradients and yield stress in cement suspensions.

4.For xanthan systems, shear stress increases markedly with increasing polymer concentration, without obvious saturation in the studied range, indicating xanthan's strong ability to form stable structural networks. This is also supported by experimental studies showing that polysaccharide additives improve resistance to segregation and enhance deformation resistance under high loads.

The constructed second-order empirical models adequately describe experimental data only within the studied concentration ranges. Outside these ranges, polynomial approximations may produce unrealistic values (e.g., negative viscosities), requiring either limitation of the applicability range or replacement of the polynomial with more complex models (e.g., Herschel–Bulkley models or spectral approaches) when considering a wider range of operating conditions for cement slurries.

The results are consistent with current trends in cement rheology research: modern publications emphasize the importance of accurate modeling and experimental calibration of rheological parameters, taking into account additive type, temperature, pressure and suspension composition. This confirms the relevance of mathematical modeling as a tool for optimizing cementing solution formulations.

The practical significance of this work lies in the fact that the proposed mathematical models and identified optimal polymer concentration ranges can be applied in the development of cementing formulations, ensuring enhanced technological reliability of cement systems under oil and gas well conditions with varying operational parameters (temperature, pressure and geochemistry of formation fluids).

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