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## Development of mathematical models to control the technological properties of cement slurries

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Oil and gas producing enterprises are making increasingly high demands on well casing quality, including the actual process of injection and displacement of cement slurry, taking into account requirements for the annular cement level, eliminating possible hydraulic fracturing, with developing a hydraulic cementing program. It is necessary to prevent deep invasion of cement slurry filtrate into the formation to exclude bridging of productive layers. It is impossible to fulfill all these requirements at the same time without application of modifying additives; complex cement compositions are being developed and applied more often. Furthermore, need to adjust cement slurries recipes appears for almost every particular well.

In order to select and justify cement slurries recipes and their prompt adjustment, taking into account requirements of well construction project, as well as geological and technical conditions for cementing casing strings, mathematical models of the main technological properties of cement slurries for cementing production casing strings in the Perm Region were developed. Analysis of the effect of polycarboxylic plasticizer (PI) and a filtration reducer (fluid loss additive) based on hydroxyethyl cellulose (FR) on plastic viscosity (V), spreadability (S) and filtration (F) of cement slurries is conducted. Development of mathematical models is performed according to more than 90 measurements.

**Key words:** production well; casing cementing; technological properties of cement slurry; modeling the properties of cement slurries; cementing technology; well casing quality

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**Introduction.** Recipes of cement slurries for casing of well are subject to frequent adjustments due to the need to simultaneously comply with following requirements: slurries must be easily pumped, have rheological properties that can prevent the occurrence of hydraulic fracturing during cementing, have reduced filtration rate, and meet all requirements for the main technological properties [1, 5-7].

Many researchers are studying the effect of various modifying additives on main technological properties of cement slurries. As a result, recipes are developed taking into account the specifics of cementing process conditions on the field and requirements well construction project, including fluid loss additives, plasticizers, defoamers, expanding additives, etc. [1, 4, 6, 7, 9, 12, 20]. Requirements for modern cement slurries are determined by applied technology for well casing, and precise control of their main technological properties determines the possibility of implementing selected cementing method [8, 10, 11, 29].

Much attention of Russian and foreign researchers is paid to rheological properties that determine hydraulic cementing program with regard to high bottomhole temperatures and pressures [5, 13, 15, 21, 22]. Therefore, in addition to actual development of cement slurries recipes, various methods for investigation of properties are proposed, which bring the conditions of laboratory tests closer to real field tests [14, 24, 27].

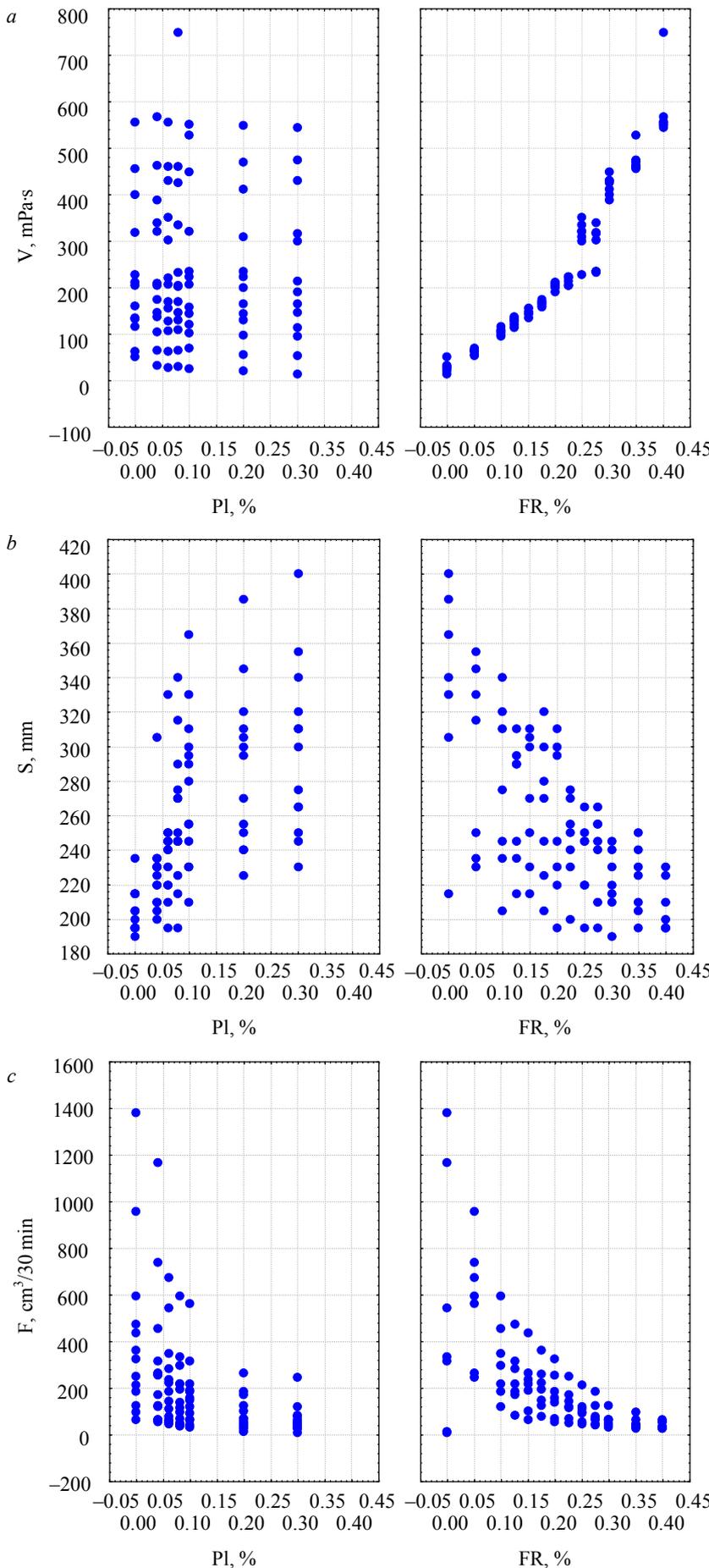


Fig. 1. Correlation fields between V and PI, FR (a); S and PI, FR (b); F and PI, FR (c)

Large amount of laboratory test results allows the application of mathematical modeling methods to reduce the number of experiments and to use resulting models for operational management of the main technological properties [17, 18, 23, 26, 30]. However, these models describe one of the technological properties indicators and influence of only one component on any basic composition and are incomplete.

#### Statement of the problem.

The task was to develop mathematical models that describe the change in the parameters of cement slurries depending on the amount of modifying additives introduced. That would allow operational adjustment of cement slurries recipes taking into account the requirements of well construction projects for the main technological properties, as well as geological and technical conditions for casing string cementing.

The following cement slurry recipe was adopted as the basis: Portland cement of PCT-I-G-CC brand; defoamer (DF) based on polyols and esters of fatty acids – 0.2 %; water-cement ratio – 0.46. In this recipe, modifying additives were introduced to obtain required indicators of the main technological properties [1, 11].

According to the results of laboratory study, it was noted that defoamer additive does not affect considered and simulated technological properties. Let us introduce restrictions on applicability of the developed mathematical models: temperature conditions  $25 \pm 4 \text{ }^\circ\text{C}$ ; cement slurry density  $1.87 \pm 0.02 \text{ g/cm}^3$ .

**Methodology.** At the first stage of research, correlation fields



between V and Pl, FR; S and Pl, FR; F and Pl, FR were constructed (Fig.1) and pair correlation coefficients  $r$  between considered modifying additives and studied parameters of technological properties of cement slurries are calculated [3, 16].

Analysis of constructed correlation fields shows that the ratios and strength of the correlation between V, S, F and Pl, FR have different forms.

Configuration of the correlation fields indicates that the plasticizer has a very insignificant effect on the plastic viscosity, while the effect of the filtration reducer on same parameter is significant. Moreover, in concentration range for FR 0-0.225 %, plastic viscosity mainly depends on FR, and at a higher concentration ( $\geq 0.250$  %), Pl also begins to make some contribution to value of V, without demonstrating a linear relationship and indicating the complexity and possible interdependence of Pl and FR influence on V. Layout of correlation fields indicates an antagonism of Pl and FR by their influence on S and joint unidirectional effect on F.

Calculation of regression coefficients in the developed models was performed with the least squares method. Possibilities of using statistical methods to solve similar problems are given in [3, 16]. Note that the models are built separately for F, S and V.

Let us compare average values of actual F and model  $F^M$  in the selected intervals by calculating the criterion  $t_p$  according to following formula

$$t_p = \frac{|X_1 - X_2|}{\sqrt{\frac{1}{n_1} + \frac{1}{n_2} \left( \frac{(n_1 - 1)S_1^2 + (n_2 - 1)S_2^2}{n_1 + n_2 - 2} \right)}}$$

where  $X_1, X_2$  – average values of F and  $F^M$  respectively;  $S_1^2, S_2^2$  – dispersions.

Difference in average values is considered statistically significant if  $t_p > t_t$ . Values  $t_t$  were determined depending on amount of compared data and significance level ( $\alpha = 0.05$ ).

Comparison of the average values showed that for F and  $F^M$  they are not statistically different in both cases at  $p < 0.05$ . For a deeper statistical analysis of the values of F and  $F^M$ , their distribution was studied. Optimal magnitudes of values intervals for indicators are calculated according to Sturgess formula:

$$\Delta X = \frac{X_{\max} - X_{\min}}{1 + 3,32 \lg N}$$

where  $X_{\max}$  – maximum indicator value;  $X_{\min}$  – minimum indicator value;  $N$  – amount of data.

In each interval, frequencies are determined:

$$P(X) = N_k / N_g,$$

where  $P(X)$  – frequency in  $k$  interval for F group ( $q = 1$ );  $q = 2$  corresponds to  $F^M$  group;  $N_k$  – number of cases for indicator content  $P(X)$  in  $k$  interval;  $N_g$  – sample size for classes 1 and 2.

When comparing the density of distribution for indicators in the studied classes, Pearson statistics were used:

$$\chi^2 = N_1 N_2 \sum_{i=1}^e \frac{1}{M_1 + M_2} \left( \frac{M_1}{N_1} - \frac{M_2}{N_2} \right)^2,$$

where  $N_1, N_2$  – number of values of F and  $F^M$  respectively (classes 1, 2);  $M_1, M_2$  – number of values that fall within a given interval, respectively, for two classes studied;  $e$  – number of intervals [3, 16].

**Discussion.** To build filtration models in different ranges, studied sample was formed according to the principle from minimum ( $F_{\min} = 10 \text{ cm}^3/30 \text{ min}$ ) to maximum ( $F_{\max} = 1381 \text{ cm}^3/30 \text{ min}$ )

values. Number of indicators studied is equal to two, so the first model is built on three data. Next model will be built at  $n = 4$  and so on until  $n = 91$ .

As a result, three groups of values were distinguished according to influence of reagents PI and FR on property F. For the first group, an updated nonlinear model (range  $F < 80 \text{ cm}^3/30 \text{ min}$ ):

$$F^{M1} = 388 - 1479.9FR - 920.1PI + 1600.1PI \cdot FR + 1599.9FR^2 + 1000.1PI^2,$$

at  $R = 0.999$ ,  $p < 0$  forecast error equals  $0.002 \text{ cm}^3/30 \text{ min}$ .

Following model is obtained for the second group of values ( $80 < F < 380 \text{ cm}^3/30 \text{ min}$ ):

$$F^{M2} = 440.81 - 1022.38FR - 757.82PI,$$

at  $R = 0.982$ ,  $p < 0$  forecast error equals  $34.015 \text{ cm}^3/30 \text{ min}$ .

For the third group model is as follows ( $F > 380 \text{ cm}^3/30 \text{ min}$ ):

$$F^{M3} = 1221.67 - 5309.76 FR - 5149.04PI,$$

at  $R = 0.893$ ,  $p < 0$  forecast error equals  $149.87 \text{ cm}^3/30 \text{ min}$ .

Using the above formulas, values  $F^{M1}$ ,  $F^{M2}$ ,  $F^{M3}$  were calculated and compared to actual values F.

From a practical point of view, interval of F values corresponding to the first class (the smallest values of the filtration rate) is of more interest, since it reflects the requirements of vast majority of regulatory documents on casing cementing for the most critical sections of oil and gas wells. Forecast error is also minimal, which will allow very accurately calculate  $F^M$  values by known values of PI and FR. In this case, necessary range of F values can be achieved in the entire range of PI concentration due to varying the content of FR.

To graphically solve the question on choice of cement slurries recipe, taking into account the requirements for the main technological properties, a graph of  $F^{MM}$  dependence on PI and FR is constructed (Fig.2). Similar graphical solutions were obtained for other technological properties of cement slurries. According to graph (Fig.2), it is possible to determine the concentration values of PI and FR at which  $F^{MM}$  values are minimal and have values that satisfy the requirements of well construction projects.

Analysis of the comparison of model and actual values showed that the non-linear model in selected range of PI, FR values works much better than other developed models. It should be noted

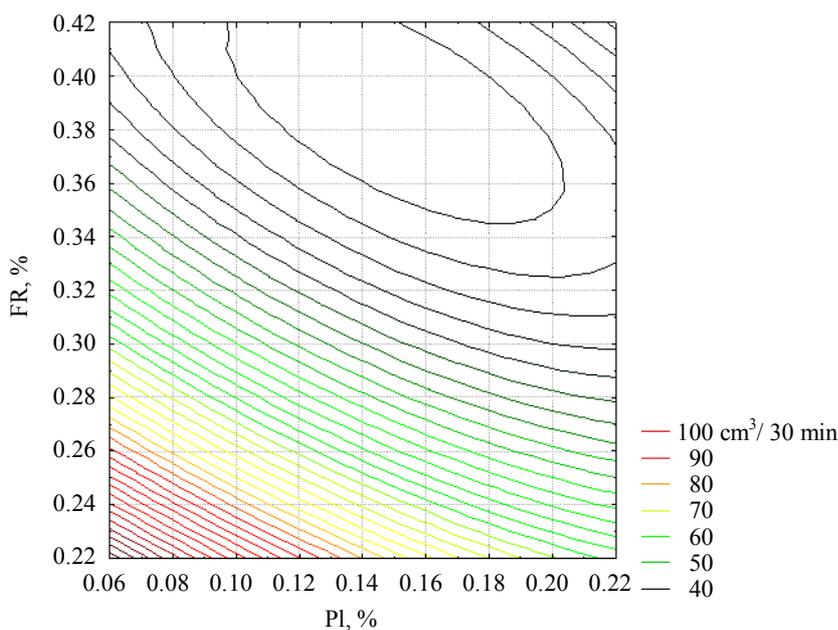


Fig.2. Graph of  $F^{MM}$  dependence on PI and FR

that even in this case, five values are observed when the values of F and  $F^{MM}$  do not significantly coincide. It was found that these discrepancies occur in cases where a zero concentration of FR is used in range of plasticizer concentrations of more than 0.06 %. Identified phenomenon is associated with process of measuring this parameter.

Filtration index is a direct reflection of system ability for filtrate loss additive, implemented in a specific instrument situation – procedure for measuring the parameter. Potential ability of the system for filtrate



loss directly depends on amount of free dispersion medium that can be sediment on a filter of a certain diameter at a given pressure drop. Dispersion medium is predominantly solvent molecules (in this case, water), free from participation in formation of solvate shells around cement grains. When measuring the parameter, cement slurry, loaded into the chamber of the filter press, which is a vertical cylinder, undergoes a pressure drop at which the dispersion medium begins to filter out through the filter located below. During the measurement, due to lack of mixing, the system is subject to sedimentation separation, as a result of which heavy particles of cement are lowered towards the filter and, being compressed, form a physical barrier that prevents free filtering of the dispersion medium. Plasticizer molecules adsorbed on surface of cement grains increase mobility of cement particles, especially in conditions of low viscosity of liquid phase, surrounding the particles. Such an increase in mobility directly depends on concentration of the plasticizer and, starting with a certain concentration (in this case, from 0.06 %), it has a significant effect on the process of measuring the filtration index. This effect is compensated if there is a minimum amount of filtration reducer in the system, input of which ensures thickening of aqueous phase in cement slurry that significantly slows down sedimentation process. Mentioned above shows that satisfactory sedimentation stability is achieved at a concentration of  $FR \geq 0.05$  %.

Thus, the data obtained for a zero concentration of FR should not be used in construction of models, since they do not reflect real state of the system by its ability for filtrate loss and are the result of distortion due to noticeable influence of sedimentation.

Then, using the same methodology, models were built on technological properties of cement slurries S and V.

Comparison of S and  $S^M$  ratios, in contrast to F and  $F^M$  ratios, shows that significant non-linearity between them is not observed. According to the principle that was stated above, 83 multidimensional models were built. Analysis of S and  $S^M$  ratios showed that there are three types of relationships. In the first section there is a significant increase in R values from 0.177 to 0.810 in the range of 190-250 mm. The second section is in the range of 250-300 mm, an insignificant change in the values of R occurs here. In the third section in the range of  $S > 300$  mm, a slight increase in the values of R is observed. Analysis of spreadability models allowed to reveal three types of influence. At values of  $S < 240$  mm, influence of PI and FR values is almost the same, with S in the range of 240-340 mm, a higher influence of PI is observed, then inversion of the influence for PI and FR values is observed, i.e. the influence of FR becomes more significant than PI.

Thus, according to the influence of PI and FR reagents on property S, three groups of values were distinguished. A non-linear model is obtained for the first group (range  $S < 240$  mm):

$$S^{MM} = 220.079 + 594.23PI - 54.7803FR - 661.3888PI^2 - 644.0422FR \cdot PI - 81.8865FR^2,$$

at  $R = 0.885$ ,  $p < 0$  forecast error equals 7.29 mm.

Following model is obtained for the second group ( $240 < S < 350$  mm):

$$S^{MM} = 271.124 + 836.3447PI - 464.8676FR - 1326.5561PI^2 - 905.5659FR \cdot PI + 803.4287FR^2,$$

at  $R = 0.889$ ,  $p < 0$  forecast error equals 14.66 mm.

For the third group model is as follows ( $S > 350$  mm):

$$S^{MM} = 348.333 - 916.667FR + 175.000PI,$$

at  $R = 0.998$ ,  $p < 0$  forecast error equals 2.04 mm.

From a practical point of view, interval of S values corresponding to the first class ( $S < 240$  mm) is of more interest, since it reflects the requirements of well construction projects.



Forecast error for this interval of S values (180-240 mm) is 2-4 %, which will make it possible to accurately calculate  $S^M$  values with known values of PI and FR. In this case, necessary range of S values can be achieved over the entire range of FR concentrations by varying the content of PI.

When developing models of plastic viscosity, it was found that formation of V values occurs depending on PI and FR for two models. At values of  $V < 240$  mPa·s, FR and PI are involved in formation of values. In other cases, value of V is formed only by FR.

Total of 84 multidimensional models were built. According to influence of PI and FR on V, two groups of values were distinguished, division into groups occurs mainly in terms of FR reagent concentration.

A model is obtained for the first group ( $V < 240$  mPa·s)

$$V^{M1} = 29.294 + 819.8383FR - 32.8641PI,$$

at  $R = 0.989$ ,  $p < 0$  forecast error equals 9.409 mPa·s.

For the second group of values in order to identify areas where non-linearities can be observed, a non-linear model of FR and PI influence on plastic viscosity was constructed. Results of study are compared with the description of physical and chemical processes occurring during the mixing of cement slurry according to analyzed recipes.

It is known that molecules of cellulose ethers are moderately rigidly chained, and independent position of each molecule (their free orientation) is possible only in relatively dilute solutions. As the number of rigid macromolecules in a given volume of the solution increases, probability of their arbitrary orientation will be less, and when a certain critical concentration is reached, further increase in the number of macromolecules in this volume will be impossible without mutual ordering of their part. Therefore, starting from a certain critical polymer concentration, an additional phase appears in the system, which is represented by ordered macromolecules. With an even greater increase in polymer concentration, fraction of ordered phase will increase until all macromolecules are mutually ordered [2].

For solutions of rigid-chain polymers, following concentration dependence of viscosity is characteristic. First, with an increase in the polymer concentration, curve passes through a maximum corresponding to critical concentration at which the formation of anisotropic (liquid-crystal)

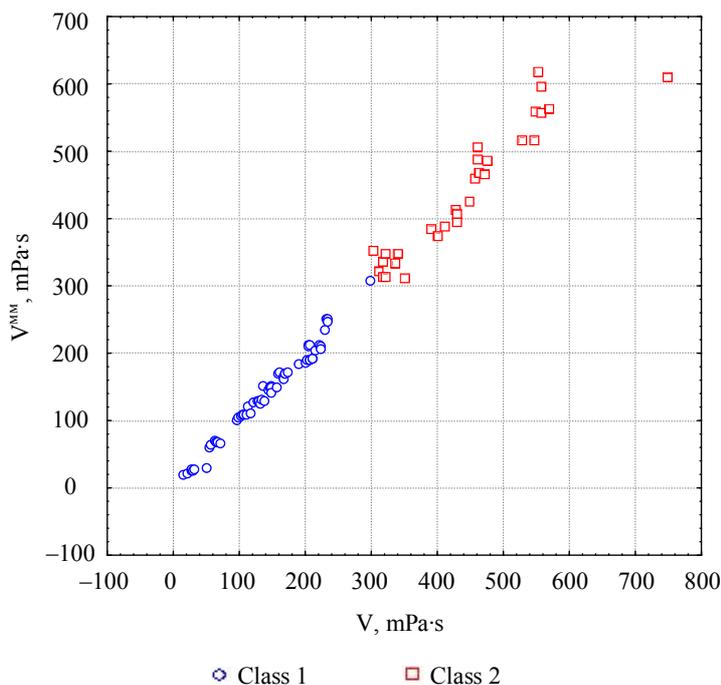


Fig.3. Correlation field between  $V^{MM1}$ ,  $V^{M1}$  and V

phase begins. Then the curve passes through a minimum corresponding to transition of the system to a fully ordered anisotropic state. Decrease in viscosity is due to layered flow of anisotropic solutions, which has a lower resistance to flow than the mesh network of molecules in isotropic solutions [25].

With a further increase in the polymer concentration, viscosity begins to increase again due to formation of a fluctuation network between the liquid-crystal domains of anisotropic phase [19], as well as a decrease in fraction of free solvent. This character of dependence is also present in cellulose derivatives solutions filled with fine-dispersion particles [28].

Thus, a refined non-linear model is obtained for the second group of values ( $V > 240$  mPa·s):



$$V^{MM1} = -43.621 + 2811.9621PI + 365.5409FR - 8351.5551PI^2 - 2275.8001FR \cdot PI + 2564.79FR^2,$$

at  $R = 0.991$ ,  $p < 0$  forecast error equals 12.964 mPa·s.

Model values of plastic viscosity were calculated and compared with actual values (Fig.3) using mentioned above formulas. It can be seen that values of  $V^{MM1}$ ,  $V^{M1}$  and  $V$  coincide well over the entire range of values. Results of mathematical modeling are confirmed by peculiarities of rheological behavior of cement slurries with different concentrations of FR and PI reagents.

Analysis of experimental data obtained during the study shows that rheological behavior is preserved in the range of plasticizer concentrations of 0-0.200 % (Fig.4). In this case, maximum, corresponding to beginning of anisotropic phase appearance in the HEC solution, and minimum, corre-

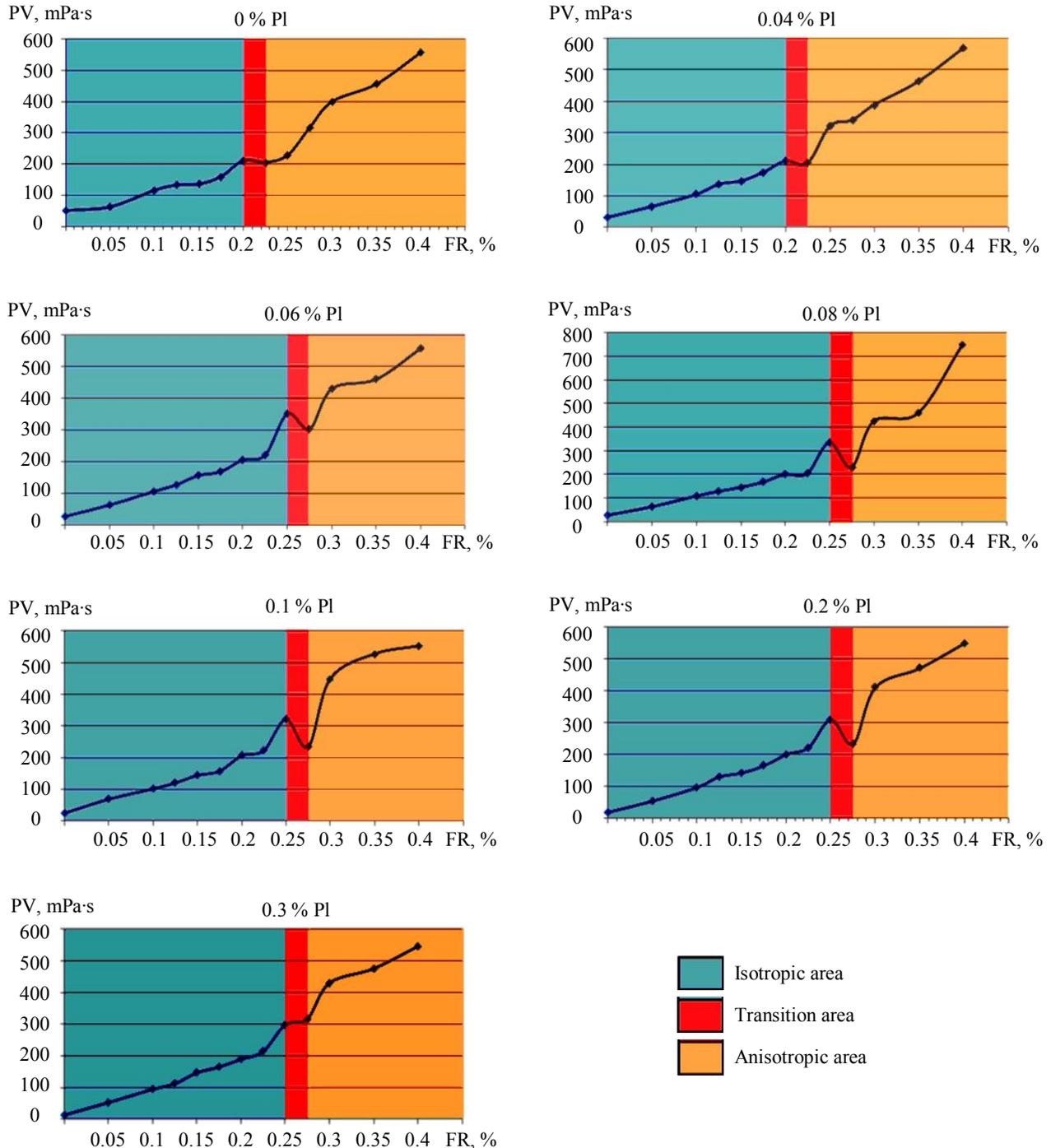


Fig.4. Dependence of cement slurry plastic viscosity (PV) on FR concentration at various PI concentrations



sponding to complete anisotropization of the solution, shift from 0.200 and 0.225 % HEC at plasticizer concentrations  $< 0.06$  % towards increasing concentrations of HEC (0.250 and 0.275 %) at plasticizer concentrations  $\geq 0.06$  %.

This feature is in good agreement with effecting mechanism of plasticizer, which is that when adsorbed on cement grains, it displaces a certain amount of water from their surface, which was bound in hydration shell of the grain, thereby increasing the concentration of free water molecules in the system, which can be involved in hydration and dissolution of HEC molecules. Given that specific surface of cement remains constant, it can be expected that amount of water that can be released from the hydration shell composition during chemisorption of plasticizer molecules on the grain surface is also finite. At plasticizer concentrations  $\geq 0.06$  %, a certain saturation of cement grain surface is achieved, after which the amount of released water does not change so significantly.

For rheological model, three areas can be arbitrarily distinguished: a completely isotropic area (HEC concentrations of 0-0.200 % at any plasticizer concentration), a two-phase transition area (HEC concentrations from 0.200-0.250 to 0.225-0.275 % depending on plasticizer concentration) and a completely anisotropic area (concentration of HEC 0.275-0.400 % at any concentration of plasticizer), which clearly correlates with results of mathematical modeling.

At a plasticizer concentration of 0.3 %, characteristic maximum and minimum are not identified on the graph. This is probably the result of a noticeable decrease in amount of free solvent – free water becomes involved in hydration of an additional number of plasticizer molecules, which doesn't allow friction between layers to be lowered with increasing anisotropization of solution due to “lubricating” effect of the water interlayer. Poor distinction of maximum and minimum in the graphs for plasticizer concentrations of 0-0.04 % is caused by the same reason, although in this case, free water is involved in formation of hydration layers on the surface of cement grains free of plasticizer.

Noting this remark, in the range of plasticizer concentrations of 0.06-0.2 %, within which the number of free water molecules in the system capable of participating in hydration and dissolution of HEC molecules varies insignificantly, for rheological model, three areas with distinct boundaries can be arbitrary set: a completely isotropic area (HEC concentrations  $< 0.250$  %), a two-phase transition area of appearance and accumulation of a liquid-crystal phase (0.250-0.275 %) and a completely anisotropic area (HEC concentrations  $> 0.275$  %).

In the range of an isotropic HEC solution existence ( $< 0.250$  %), plastic viscosity of the system does not show a dependence on concentration of plasticizer and remains approximately constant. In the range of HEC solution existence in an anisotropic form ( $> 0.275$  %), effect of a plasticizer on viscosity of the system already exists and is difficult to describe.

Presence of free plasticizer molecules that are not associated with the surface of cement grains can cause strengthening in the mesh network between moving layers of anisotropic phase by forming a “bridge” bond mediated by the plasticizer molecule, connected simultaneously with both layers. To realize such a “bridge” bond, one segment of the plasticizer molecule must form a chain of hydrogen bonds with one layer of anisotropic phase, and its other segment with vacant region of other layer. Furthermore, for one plasticizer molecule to be associated simultaneously with two different layers of anisotropic phase, certain conditions must be met. In order to be able to realize the bridging, it is necessary that the region of potential fixation within another layer is not yet occupied by another similar plasticizer molecule and is at an accessible distance.

For example, with an increase in concentration of plasticizer, probability for a site, vacant for attachment within another layer, will be less. Therefore, bridging can be realized at plasticizer concentrations not exceeding a certain critical value. In the field of very low concentrations, such bonds will also be realized, but due to their small numbers, they cannot be identified by increasing the vis-



cosity of the system. On the other hand, with a decrease in the distance between layers of anisotropic phase (i.e., with an increase in HEC concentration), such a bond is easier to realize, and, therefore, this occurs at lower concentrations of plasticizer molecules. Starting at some critical distance, formation of such bonds becomes very unlikely.

It can be expected that described strengthening in the interaction between layers of anisotropic phase will be identified in the form of an increase in viscosity of the system in a rather narrow range of concentrations that are free from interaction of plasticizer molecules with cement. With an increase in HEC concentration, such an increase in viscosity will occur at lower concentrations of plasticizer.

Since the distance between anisotropic layers is a function of HEC concentration, region of bridge bonds' existence will be limited by a certain balance of HEC concentrations and free plasticizer molecules and can be described by their ratio, which will actually require additional study outside the scope of the objectives of this work.

From a practical point of view, range of  $V$  values corresponding to the first class ( $V < 240$  mPa·s) is of more interest, since it meets the requirements of most hydraulic well cementing programs. Forecast error is not more than 9.5 mPa·s, which will make it possible to quite accurately calculate  $V^M$  values by known PI and FR values.

In this case, necessary range of  $V$  values can be achieved over the entire range of PI concentrations at FR concentrations not exceeding 0.225 %. It is positive that in this case it is necessary to deal with the range of FR concentrations within which there is only an isotropic HEC solution, when plastic viscosity of the system does not show a sensitive dependence on PI presence, which will allow varying the FR concentration relatively freely and independently.

With a higher FR content, achieved values of plastic viscosity are undesirable or unacceptably high.

**Conclusion.** Summarizing the simulation results from standpoint of the developed models' applicability, it should be noted that overlapping concentration range of PI and FR in the area of working values for parameters  $S$  and  $F$  (class 1 in both cases) is quite wide, but when the area of required values for parameter  $V$  is applied, it decreases sharply.

Expansion of the overlapping field for PI and FR concentration ranges in the area of operating values for all three parameters at once ( $S$ ,  $F$ , and  $V$ ) can be achieved by reducing the degree of HEC polymerization incorporated in the recipe. Despite the fact that interaction features for components of the system by objective reasons should be preserved, adjustment of models or, at least, refinement of the boundaries of the selected classes will be required.

Comparing the results of laboratory investigation and mathematical modeling of the main technological properties with a description of physical and chemical processes that occur during mixing of cement slurries compositions in accordance with the developed recipes, as well as proposed methods for analyzing available data used for correlation and regression analyzes, analysis of constructed multidimensional statistical models, both linear and non-linear, allowed quantifying the effect of various modifying additives' values of PI, FR in recipes of cement slurries and their combinations on filtration index, spreadability and plastic viscosity.

Constructed models can be used in predicting the values of  $F$ ,  $S$ ,  $V$  taking into account requirements of well construction project, conditions for cementing, estimated values of hydraulic fracturing pressures and absorption when developing a hydraulic program for cementing of wells. Model values of the main technological properties will reduce the number of probable concentrations of modifying additives during development of recipes, which will lead to time and cost savings at the stage of preparatory work for well casing.

Developed mathematical models were used to optimize cement slurries recipes to develop a work program for cementing the production casing of an oil production well at one of the fields in

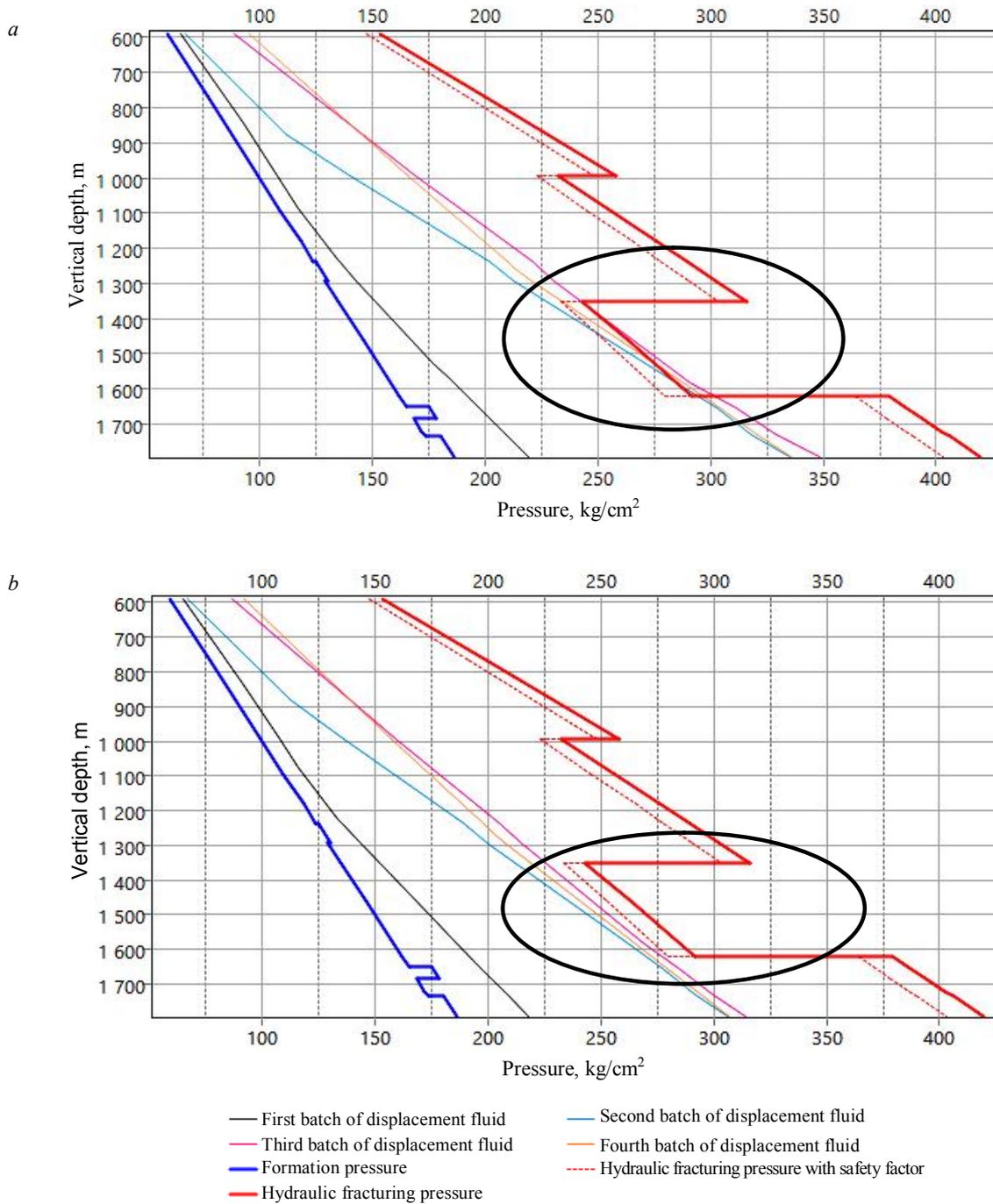


Fig.5. Calculation of open borehole pressures for injection of displacement fluid taking into account values of plastic viscosity for cement slurry made according to design recipe with probable hydraulic fracturing (a), adjusted model formulation without exceeding of fracturing pressure (b)

the Perm Region (Fig.5). Cement slurry was made on the basis of the design recipe, and it turned out that obtained rheological properties can lead to appearance of hydraulic fracturing during implementation of specified modes of cement slurry injection and jet-in (Fig.5, a). In addition, value of filtration rate was higher than required.

Using developed mathematical models, a correction of cement slurry was performed. In fact, defined filtration index of cement slurry, recipe of which was optimized based on obtained model values, did not exceed required design value, and rheological properties corresponded to requirements of the work program and excluded the likelihood of hydraulic fracturing during injection and displacement of cement slurry (Fig.5, b).



Recipe obtained on the basis of developed mathematical models is recommended for use. Laboratory analysis of cement slurry showed the correspondence of model and actual values of the main technological properties for cement slurry. Difference in values of the indicators for simulated technological properties did not exceed 3 %.

The obtained results made it possible to identify peculiarities of physical and chemical interaction of considered modifying additives and their mutual influence in composition of the base cement slurry and determine the limits of their concentrations, beyond which it is not possible or difficult to control the main technological properties of the resulting cement slurries.

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