## Optimization of self-healing additives dispersity in cement

Ismagilova, ER, Agzamov, FA and Abbas, AJ

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Abstract. The article reflects results of the experimental studies on the modifying agent’s dispersion to affect the nature of its distribution in the total volume of cement stone. An attempt was made to evaluate the strength and filtration properties of the cement stone with respect to the heterogeneity of its structure.

The effect of a character of the modifying additive distribution on the permeability and strength of the cement stone was investigated, as a result it was clarified that the zone of influence of the applied dynamic load does not depend on the heterogeneity of the plugging material, and the values of deformation in the cement stone depend on the dispersion, the nature of the distribution of the additive in the volume of the cement stone, the period of the modifying agent activation.

The dynamic loads, which most strongly provoke the destruction of cement stone under the influence of high stresses, are considered. Using the finite element method (FEM), the ANSYS application program evaluated stresses in a cemented column, describes the process of deformation of cement stone, taking into account the heterogeneity of its structure.

Based on the variability of the additive location, channel models for the most preferred localization of the modifying additive have been determined as open through cracks.

The application of the mathematical model, which was elaborated, demonstrates a possibility of the maximum reduction of the water conductivity if the optimal distribution of the modifying additive in the matrix of the cement stone provided.

Keywords: modifying additive, crack, “self-healing” cement, dynamic loads, shear stresses, cement stone bending strength

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Well cementing is a final process in the well completion procedure, aimed at a provision of a hermetic isolation of the well construction elements by sealing them with cement. Consequently, the functions of the well cement: casing hanging on the well’s walls, sealing the space between the wall and a casing string, thus ensuring the casing protection from external influences (Ovchinnikov et al., 2011).

However, the history of uneven-aged wells exploitation demonstrates that the cement stone is the most vulnerable link and can be easily destroyed under the influence of high dynamic loads and inner pressures as well as from the impact of aggressive formation water seepage (Agzamov et al., 2005).

The stresses arising in the cement stone during various operations were calculated in the study (Agzamov et al., 2011) which showed that in many cases they exceed the cement stone ultimate tensile strength. At the same time, at a distance of several meters from the perforation zone, the cement sheath deformation makes up to 0.3-0.7 mm, which makes it possible to maintain the casing integrity as long as an appropriate modification of the cement is chosen.

A disperse reinforcement for plugging materials can be the most preferable direction for increasing the resistance of a cementing stone (Agzamov et al., 2013; Rabinovich, 1998; Brautman et al., 1978), while evenly distributed in a matrix and having a different direction, fiber reinforcing agent (fiber) can perceive loads in any direction, thus preventing the formation and development of cracks in the composition.

The breach of a cement sheath may occur due to the incompatibility of cement setting time to a cement slurry formulation, of a casing hardware, of a cementing technology to mining and geological conditions, and be also a result of thermal impacts on the column during the development and well operation (Ovchinnikov et al., 2011; Agzamov And others, 2011). Micro-gaps at the contact cement stone – casing string, can also be formed as a result of a mechanical action on the string during the borehole deepening, i.e. while drilling from under the shoe of the previous string, pressure testing, well shooting, hydraulic fracturing or other technological operations.

Perforation, hydraulic fracturing, pressure testing and any mechanical actions in combination with an
aggressive corrosive environment can cause the hardest destruction of a cement stone under the influence of large shear stresses resulting from static and dynamic loads. At the same time, statistics depicts in most cases the non-additive formulation of oil well cement does not justify the cement sheath integrity expectations.

The use of modern water influx control technologies can lead to an increase in oil production, but all of them require significant costs for conducting water-shutoff works, and are often temporary.

One of the prospective ways to solve this problem could be the usage of “self-healing” cements (Bhavsar et al., 2008, FUTUR Self-Healing Cement System, 2013). We have substantiated the formulation of the cements which displays ability to autonomous healing by modifying additives integrated into the cement slurry subsequently activated after the secondary interaction with water thus blocking emerged cracks. The core of the modifying additive is represented by water-swellable polymer coated with a water-soluble shell prepared using a special technology (Ismagilova et al., 2016).

In the laboratory of the University of Salford (UK), using a scanning equipment called CT Scanner (computer tomograph), which allows to conduct a non-destructive testing of a cement sample, we investigated a distribution of the modifying additive (MA) in a total volume of the cement stone and quantified their characteristics. Herewith, samples of a cylindrical shape were made using a solution of 0.5 water-cement ratio, where Portland cement powder contained 1.0% of the modifying agent.

The results of the first experiments on the cement stone scanning showed the necessity to regulate the additive dispersion, as well as to improve an interaction between the MA granules and the cement slurry. It has been shown that the coarse particles of the modifying additive are less effective than those that are finely dispersed, which are better suspended in the solution. As a result the sedimentation stability of the solution was increased, the stratification into phases eliminated, the rheological properties of the cement slurry. The additive demonstrated the uniformity of the MA distribution, carried out with the integrated additives of smaller size facilitating by the equality (comparability) of the sizes of the additive and grains of cement.

It is known that the size of water channels is about 100 microns (according to Schlumberger (Bellabarba et al., 2008)), so the size of the swollen particles should exceed these values.

Since the predominant Portland cement particle’s size is 5-40 µm, and their hydration is accompanied by an increase in volume of 20-30% occurring due to the cement gelation, it is possible to expect the pores formation in the hardening cement stone which have substantially smaller sizes that are not capable of passing liquids and gases through themselves. However, the situation is not typical for cementing slurries which originally have an elevated initial water content (WCR = 0.44-0.50). Therefore, when hardening a large volume of capillary pores inevitably forms in cementing slurries, the size of which exceeds the sizes of the water-passing channels, which significantly reduces the insulation properties of the resulting stone. This may indicate that even without external influences impairing the integrity of the stone, the cement matrix is not waterproof for formation fluids hence requires it’s modification.

In order to cut off the channel with a size of 100 µm, it is necessary to integrate a modifying additive with a density which will be approximately equal to the density of the cement slurry and the size within the size of the clinker grains, thus preventing the subsiding or emergence of the additive. If the density of the additive and cement slurry will be different, a stabilization of the solution can be achieved by adding fiber (Agzamov et al., 2013).

When activated (interaction with water), the modifying additive (MA) should be able to increase the initial size by a factor of tens. In particular, the additive with a size of 5 µm must have a swelling degree of 2000%, and at a size of 40 µm it must have a 250% swelling degree.

The evaluation of the swelling kinetics showed that the MA swells for 9 days, increasing the initial volume to 3000% that confirms the ability of the selected modifying agent to block the maximum possible water-passing cracks.

Since the dissolution of the MA shell and the core swelling starts only two days after the beginning of the cement slurry hydration (Ismagilova et al., 2016), there is no negative effect of the integrable additive on the rheological properties of the cement slurry. The additive also does not affect the solution during it’s thickening, setting and the cement stone strengthening. This is facilitated by the equality (comparability) of the sizes of the additive and grains of cement.

The results of the next cement stone samples scanning carried out with the integrated additives of smaller size demonstrated the uniformity of the MA distribution, which let to announce that the optimal values of specific gravity and density of the additive is found what allows to keep the additive in suspension until the cement slurry set (Fig. 1).

In the next stage we assessed how nature of the modifying additive distribution affects the permeability and strength of the cement stone. Using the finite element method (FEM) of the application program ANSYS, the strain and stress in the cement stone were estimated, taking into account the heterogeneity of its structure.

Simulation of shear stresses on the well supports showed that the greatest stresses fall on the zone of the applied dynamic load and are insignificant on the periphery, regardless the heterogeneity of the cementing stone material.
The Figure 2 (a) demonstrates the load applied to the cement stone sample, where the stress grows linearly along with the deformation until the development of microcracks and ruptures begins, passing from a linearly proportional relationship to a nonlinear law near the point of the failure. The red colour in the figure denotes the location of the greatest stress concentration, when the cracks coalesce among themselves and reach a critical size, in this case the sample have a crack, the nature of which is the mechanism that incorporates the stress at the interface with the geometric shape of the sample.

The Figure 2 (b) displays the amount of energy absorbed by the sample at the point of the most heterogeneous structure of the stone. We assume that the red dot in the figure indicates the location of the precipitated additive. This picture is also synchronized with the strength test, during which initially the sample resists an initiation and expansion of cracks, then elastically deformed absorbing the energy of rupture.

On further increase in stresses the sample ceases to absorb the energy of rupture, an expansion and growth of cracks starts, the load exceeds the limit of the mechanical strength achieving irreversible deformation changes, as a result the beam breaks.

However, the values of deformation in a cement stone depend not only on the zone, type and amount of the applied dynamic load, but also on the distribution, the pattern of the additive distribution in the volume of the cement stone, that was also supported by the results of laboratory tests for determination of the cement stone ultimate strength for bending. Thereby, with the uneven distribution of the additive in the total volume of the cement stone, in particular its thickening during it’s sedimentation, the testing of the samples for bending strength demonstrated the lowest results (2.35 MPa). On the edge of the sample breach, joined together pores are visualized at the bottom of the sample which are filled with the polymer grains, as it can be seen the stone has a heterogeneous structure, cavities are detected (Fig. 3).

As soon as the additive is uniformly distributed in the total volume of the cement stone, the 3D filtration theory works, when regardless the location of the water approach, the passing channel will be blocked. On the permeability measuring devices gas/water working agents (API 10B-2 / ISO 10426-2, 1997) are brought to the end edge of the sample, usually from the bottom up, so it is possible to test only a linear filtration through the cement stone. In the case of the modifying additive sedimentation, the device does not show a real picture with a possible linking of water channels up, for example, overflows from overlying layers. However, an option with the additive sedimentation is acceptable for modeling the cracks “healing” in the bottomhole formation zone, which may be formed during the perforation as a result of the uncontrolled capillary defects overgrowth.

Having carefully studied the processes of the MA autonomous operation inside the cement matrix, we tuned the properties of the modifying additives up taking into account their effect on the resulting properties of the cement stone. Thus, for the optimal
distribution, the concept of a matrix system is adopted, the polymer particles of which are located at nodes of the regular lattice, the state of which is reached when a cement stone forming. Thus, neglecting the randomness of motion in a viscoplastic flow, we assume that at the indicated density and concentration of the additive, it will occupy the optimal positions when transforming to the stone-like state.

Based on the above-described problems and the variation in the location of the additive, the task was set to determine the channel model, for which the use of “self-healing” additives would be most preferable.

Capillary defects aroused in a cement stone because of technological operations inside casing strings or cement stone corrosion can be conditionally divided into the following types: pores which have a cross section close to the circumference; cracks with parallel walls in the form of a slit; cracks with non-parallel walls of a conic section; cracks having an arbitrary geometry (Fig. 4) (Matvienko, 2006).

As it is known, the formation of any channel, characterized by length, width (opening of the discontinuity) and depth, indicates a crack. Herewith, deadlock (closed) and through cracks can be distinguished (Fig. 5). Figure 5a the left one indicates a deadlock crack that has only one outlet to the surface, a through-crack is shown on the right site, which has two outlets to the surface.

However, usually cement stone defects in the form of cracks, resulting from fatigue failure of a cement stone, perforation, excessive filter loss or volumetric shrinkage, do represent a mixture of different models of channels that are interconnected and not interconnected.

Moreover, through pores and capillaries are the most dangerous defects in terms of wellbore integrity, therefore, water (lower, upper, bottom) should be a trigger of a swelling additive mechanism for “self-healing” cements activation which breaks through the channels and may lead to a water cuttings of well production.

Thus, it is assumed that open through cracks are the most preferable channels for the modifying additive local placing and subsequent pore blocking. Naturally, this does not exclude an effective operation of the additive in the other channels, and we believe that there is no restriction on its applicability in terms of the well cement support leakage types which are shown in Figure 6, borrowed from the work (LeNeveu et al., 2006).

To check the optimal amount, the properties of the manufactured MA and its distribution in a predetermined water-cement ratio in the cement slurry, a mathematical model was designed. The following assumptions were made:

1) The mixing liquid is a Newtonian liquid, water.
2) The resulting cement slurry relates to viscoplastic fluids.
3) The hygrometric processes during the transition of the viscoplastic cement gel into the stone-like state are not taken into account.
4) We take into account the distribution of the polymer particles in the cement stone.
5) The influence of time is not considered.
6) As a basis we took results obtained from the permeability measurements, which showed that when 1% of the modifying additive integrated, the filtration in the sample decreased by an average of 82%.
7) The gradient of the water breakthrough pressure according to the cavernous space is assumed equal to 2.8 MPa/m.

Let’s imagine that formula 1 demonstrates the matrix of cement stone, cooked from neat cement slurry with a standardized water-cement ratio, which does not contain any modifying additives. From practice, we know that such a stone is absolutely water permeable, allowing the filtration of formation water through itself. The following formula (1) describes the complete water filtration (value \( B \)) through the cement stone (\( M_o \), value) containing no modifying additives (value of \( C \):

\[
M_o = C = B, = C – B = 0.
\]

(1)

Fig. 4. The main types of capillary defects in the cement stone: a) cylindrical pore; b) conical pore; c) crack with parallel walls; d) crack with non-parallel walls; e) crack of an arbitrary geometry

Fig. 5. Characteristics of cracks: a) deadlock and through cracks, side view; b) deadlock and through cracks, top view
Let $M_0$ be a viscoplastic cement slurry, and $M_1$ – a gel that transforms into a stone-like state:

$$M_1 = P + 0.01C = 0.18B,$$

$$M_0 = M_1,$$

$$C - B = 0.01P + C - 0.18B = 0,$$

$$0.01P = -0.82B => B = (0.01/(-0.82)) \cdot P.$$

Previously, we have experimentally shown that by adding 0.01 parts of polymer to 1 part of cement, the filtration decreased by 82%. Equation (1) shows that without the polymer addition, complete filtration of the water takes place, but after addition of the polymer, the filtration is reduced by a fraction (-0.18).

If we assume that both liquids of the model participate in the transition to the solid phase, then it is possible to equate the initial and final values of the models:

$$M_0 = M_1,$$

$$C - B = 0.01P + C - 0.18B,$$

$$0.01P = -0.82B => B = (0.01/(-0.82)) \cdot P.$$

From this it follows that the polymer particles optimally distributed (the main condition), both in the viscoplastic cement slurry and in the cement stone, can give a filtration reduction of 99.82% (the minus sign shows a reduction) by blocking the water-passing channels. In Table 1, the first column indicates the parts of the polymer component content, one of each is equal to 0.2%, added to the cement slurry up to a maximum concentration of 1%. In the second column, the value of the reduction in permeability in the cement stone corresponding to the polymer content can be seen.

To illustrate the model, we present the result in a graphical form, which shows the maximum reduction in the water conductivity of the channels when 1% of the evenly distributed polymer additive is integrated into the cement slurry (Fig. 7).

### Conclusion

Experiments using a device for non-destructive testing of the cement sample made it possible to thoroughly study a distribution of the modifying additive (MA) in a total volume of the cement stone and to evaluate their quantitative characteristics. The use of a finely dispersed additive demonstrated an improved sedimentation stability of the solution, an increased homogeneity of the stone structure.

Based on the variability of the additive location, channel models for the most preferred localization of the modifying additive have been determined in order to most effectively demonstrate the “self-healing” effect, which are open through cracks.

The application of the mathematical model demonstrated the possibility of maximum reduction of the channels water conductivity to 90.82%, under the condition of optimal distribution of the 1% polymer additive.

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