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# ELABORATION OF MENDING ADDITIVES FOR THE CEMENT SHEATH REPAIR

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The dynamic loads and internal stresses applied onto a well during its operation period, gradually leads to deterioration of the cement sheath that usually exists behind the casings. Such mechanical and chemical exposure causes the cement to develop severe cracks that enables cross feeds behind casings and uncontrollable flow between formations leading to oil-gas mixture and migration of hydrocarbons into freshwater aquifers causing immediate harm to local water sources [1], affecting the zonation capability of the cement itself behind the casings.

This issue has been in the industry of oil and gas for ages, leading us to investigate the possibility of maintaining the integrity of the cement stone behind the casings through the principle of "self-healing" materials, through this principle a self-healing cement was formulated adding secret agents into the ordinary cement powder which will be able to cure cracks in the cement stone under special conditions without human intervention. This can be an effective measure for loss of well integrity prophylaxis and eliminates well shutdowns for well workover operations.

Keywords: "self-healing" cement, well support integrity, modifying additives, hydraulic sealing, cement sheath, cracks.

#### Introduction

In the Oil and gas business, the wells are subjected through various mechanical, chemical or natural stresses such as perforations, side tracks leading to drilling through casings shoes, formations integrity testings, fractures, deepening etc, such activities hinder the integrity of the well, where the annulus integrity (cement barriers) or zonal isolations are most affected with such operations.

It is known that destruction of the cement stone occurs under the influence of large shear stresses resulting from static and dynamic loads. Modelling and simulations has proven that most of the shear stresses that are applied on the casings demonstrate the greatest stresses fall under the zone of the applied dynamic load and are insignificant on the periphery. However, the statistics depicts that in most cases of wells lining, cement stone made of the neat cement does not withstand even a minor load [2].

However, not only the neat cement demonstrates failure in tight hydraulic sealing but also the use of modern water influx control technologies meant to cure problematic water zonation is timely restricted. At first the

usage of them may lead to an increase in oil production, but all of them require significant expenses for conducting water-shutoff works, and are often temporary [1]. Early breakthrough of water production impacts the field economics where water disposal facilities and water treatments evacuations are needed, while keeping in consideration a decrease in hydrocarbon productivity. Many more problems can occur if such isolation was not maintained such that the formation water can be extremely corrosive due to high sulphates and CO<sub>2</sub> that exceeds the partial pressure regime of the casings causing it to corrode much faster, altering the lifespan of the well and endangering the integrity of the completion.

One of the prospective ways to solve the problem of untight hydraulic sealing could be through the usage of "self-healing" cements [3].

The concept of self-healing polymeric materials has been known since the 1980s. It highlights the opportunities for healing microcracks in various set of materials for much more sustainability and safety of the polymeric components [4]. Self-healing science accounts almost 35 years of study. However, the biggest breakthrough has been done over less than 15 years. This has been the steer towards the introduction of nanotechnology, which exfoliates the manipulation of atomic structure and size in order to create a new or maintain a regenerative product. The most fundamental studies were carried out and successfully implemented in construction engineering. However, self-healing cement system is a new delicacy for petroleum industry, thus requires more tailored study of healing agent, coating and chemical mechanism, as the system is exposed to well conditions with various temperatures, pressures, humidity and periodical dynamic loads imposed on the support of the well.

We found out the "self-healing" cement for oil wells cementing is a specially designed and manufactured grouting material, mainly based on the regular cement powder and mending additives, which is able to cure cracks in the cement stone under special conditions without human intervention. The authors substantiate a formulation of the "self-healing" cements displaying the ability of an autonomous healing by the modifying additives integrated into the cement powder where the introduction of water in the mixture becomes the activating element of the healing substance. The core of the modifying additive is represented by water-swellable core coated with a water-soluble shell that is fabricated using a special technology [5].

# The experimental set up and model framework

This experiment consists of a series of tests to identify and evaluate the ability for the modifying agent to heal the cracks in a sample of well cement stone, governed under down hole conditions, inclusively to studying the cement slurry and the resulting cement stone technological characteristics.

The experimental set up represents a number of phases: checking the active core swelling kinetics; cooking a solution for the coating layer; coating the active core with a shell; preparation of the "self-healing" cements slurry using the Portland cement and the fabricated Modifying Additives; fabrication of the "self-healing" cements specimens for checking the filtering and mechanical properties.

Initially, the main requirements to the healing additives were delineated as following: the additives should not affect the general characteristics of the cement slurry and the resulting stone, as well as sustaining the repeatability of the healing process.

It is considered the modifying additives can be represented by the core of a water swellable polymer surrounded by a solid shell (Figure 1), which temporarily prevents a contact of the polymer with water. Besides, the shell must prevent hydration within a cementing time – a time after injecting cement slurry into the well and it's setting [6].

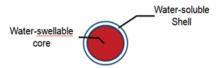


Figure 1. Modifying additive pattern

Preparation of self-healing cement slurry involves a base of Portland cement powder class G and 1% of coated Modifying Agent, which must be added into the cement powder and properly distributed whereupon the whole composition is mixed up with water within 0.5 WCR [7].

As a core of the modifying agents (MA) insoluble crosslinked copolymers of acrylamide was chosen, which contain polymer chains set parallel to each other with the average amount of cross-linking agent. At the moment, when water is in contact with one of these chains, it is drawn into the polymer molecule by osmosis effect. Thus, the water rapidly accumulates in the polymer network, enabling the MA to increase its size tenfold. The property of the MA to increase in the size repeatedly eliminates the possibility of the biggest crack blockage failure.

The coating procedure is a main process of the capsule creation as the rational coating technique provides the appropriate stability and solubility of the shell. The principal method of the coat making is done through the weighted layer technique, where a polymer complex composed of several components of natural polymers is a solution for the coating, which is based on alkaline water. Following to the understanding of the coating procedure the core granules are to be in the tank, the shell solution is to be injected from the upper nozzles while hot air is blown from the bottom nozzles thus drying up the covered granules in suspension avoiding any side contacts.

In order to maintain the integrity of the procedure, the granular size is to be examined through the Raman microscope. As seen below, the diameter of one taken particle ranges between 0.15 up to 0.3 mm where the uniformity of the shell as well as perception of the coating layer thickness was inspected using Jeol Scanning Electron Microscope. The thickness of the coating layer was established due to the fact, that boundaries between the shell and polymer were clearly identified (Figure 2).

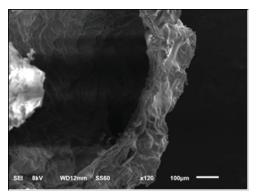


Figure 2. Sliced Modifiying Agent

Accordingly, the Modifying Agent was fully prepared for the demo test of its accuracy, which outlined the 'solubleswellable' mechanism operability. The degree of dissolving-swelling was also determined applying the method of Zhigacha-Yarova, which depicts the additives swelling after 2 days at the time of the shell fully dissolution in alkaline water. The swelling lasted for 9 days with the volume incrementing up to 3000% comparing to the initial volume of the additives (Figure 3).

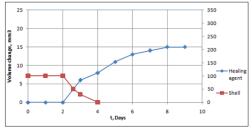


Figure 3. The kinetics of the polymer core swelling-polymer shell dissolution

Since the dissolution of the MA shell and the core swelling starts only two days after the beginning of the cement slurry hydration, 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 which is facilitated by the equality (comparability) of the sizes of the additive and grains of cement.

The cooked cement specimens with the integrated polymer were tested according to API standards. The filtering properties of the resultant cement stone were tested using the Permeameter device and a special designed technique of a visual observation. The modifying agent distribution in the cement stone was identified applying non-destructive scanning inspection.

It is highly important to pay special attention to the technology and methodology of the cement slurry preparation, as it proximately simulates a process of the well cementing. The more time the stirring – the more products of hardening are formed in the cement slurry, better passing through the stages of cement powder hydration, besides in the forming cement mortar crystalline structure the additives are being kept suspended in the solution, as while mixing the coagulation connecting structures starting to interact.

The cooked cement samples were set in the special cylinders for 24 hours hardening after which a test for permeability was conducted with water passage through the formed stone. The obtained and processed inlet and outlet parameters of the tested cement samples were plot on a graph to determine a coefficient of permeability, which can be seen in the Figure 4. The y-axis reflects the force with which the gas moves along a cylindrical sample of cement stone, the x-axis shows the values of the phase permeability obtained from the extended Darcy equation for filtering compressible gas under steady state flow and isothermal condition, where the volume flow rate of the gas Q (cm3/s), the viscosity u (cP), the length L (cm) and the cross-sectional area A (cm2) of the sample, the initial pressure at system start-up Po (atm) and the final discharge pressure are known as Pi (atm). Thus, the obtained results of the investigations shows that at 1% of the MA the permeability of the tested cement stone decreases multiply. This fact indicates an ability of the integrated modifying agent to expand it's volume controllably thus filling the gaps and cracks.

Usually cement stone defects are 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. However, open through cracks are the most dangerous defects in terms of wellbore integrity, therefore, water breaking through the channels (lower, upper, bottom) should be a trigger of a swelling additive mechanism for "self-healing" cements activation [2].

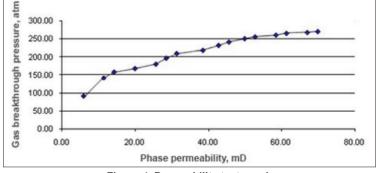


Figure 4. Permeability test graph

The C.T. Scanner was applied to study the polymer distribution and the cement stone characteristics after the self-healing cement hardening. The resultant stone sample was examined by producing computer-processed combinations of many X-ray images taken from different angles to construct crosssectional images (virtual 'slices') of specific areas of a scanned object. These tomographic functions allow the user to see inside the object without cutting in details.

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 was detected 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 homogeneity of the structure improved, what lead to announce that the optimal values of specific gravity and density of the additive were found to allow the additive in suspension until the cement slurry set.

It is known, that there is a relationship between the cement stone strength and dispersion of additives. A large particle will experience a greater internal and external pressure, and will tend to discharge on its contact [2].

At last the final water test was applied. It was a specially designed test, which was aimed to check visually an ability of the modifying agent to block cracks thus determining a stop of the water passage through the flushed zones.

A system of micro cracks was artificially created by the application the excessive load at the cement sample. Whereupon the prepared cement sample was installed in a vessel and tightened with a rubber. Finally, water was poured on the top of the inserted sample and was left to pass through. After 6 days the sample stopped passing water through, it was taken to be gently split into several parts. Following splitting into parts, it was clearly seen that the sizes of cracks were considerably smaller than the sizes of polymer particles, which affected the phenomenon of liquid pass blockage. From the Figure 5 below, it can be seen the way a swelled particle of the polymer shut down a crack through which water that was passing by gravity. The shut down crack is clearly seen in the figure made by scanning the cracked cement sample after the water filtering test.

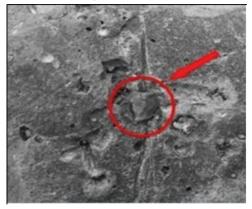


Figure 5. Final water test scan

It is concluded the filtering test revealed an ability of the additive to response repeatedly on the presence of water and to retain its mending properties to block the channel passages at a fixed flow rate of water without decomposing the agent's structure. After the presented test results the summing up denotes: no water seeping detected after almost a week, what substantiated that the stated objective of the development additives for autonomous restoration of the oil well support mending the filtering channels in the cement stone.

Finally, the wet cement sample after the filtering test was placed back to the C.T. Scanner for making the final findings, which lead us to improve the early assumptions. The image of the scanning test is demonstrated by the Figure 6, which indicates three active zones painted with the characteristic colours.

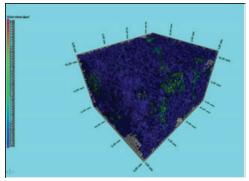


Figure 6. The scanned sample after the filtering test

The green colour indicates the polymer location in the cement stone after interaction with water; the cracks created in the sample pass through this location. The blue colour shows the homogeneity of the initial medium, which was not affected by the approaching water, i.e. equidimensional grains of cement and polymer are in the matrix. The transition colour which goes from navy blue-to-blue and -gray indicates the place of the polymer particles accumulation that formed a clot, i.e. showing the heterogeneity of the stone by the size of the pores filled with the polymer particles during the hydration of the cement. As it is seen the cracks are vertically oriented due to the fact that the pores pressure disengage have a spread in the horizontal plane, since the lines of the concentrators tension go vertically, condensing at the particle boundaries.

The final non-destructive test of the cement sample made it possible to study

an effect of the modifying additives optimal dispersity and their adequate distribution in a total volume of the cement stone as well as to evaluate their qualitative characteristics.

## Conclusion

The represented study covers elaboration of uniform modifying additives distribution in a cement matrix: determination of the optimal density of the modifying agent with respect to the density of the cement powder; determination of the effective amount of the additive, the effect of the additive concentration in the channel shutting down efficiency, study of the effect of the additives dispersion; assessment of the relationship between the concentration of additives and the size of cracks. Moreover, a technology of the modifying agent coating is substantiated. The requirements to the shell and the core were defined. The shell and core active compounds were designed. As a result the approach of well cement autonomous healing is represented by the modifying agent integrated into the cement, the healing agent is a water-swellable polymer which is allowed to burst out of the water-soluble shell due to the water-shell interaction coming through the cracks immerging in the cement sheath, thus causing a healing effect. However, the modifying agent should only be activated after the secondary interaction with water in order to withstand cement slurry preparation and to suit deep well exceeding pressures avoiding material decomposition.

The given technology is a new environmental friendly well cementing approach, alternative to the traditional technology of oil and gas wells cementing using cement with additives or pure cement slurry. "Self-healing" cements is not only restoration but also prophylactic action. The optimal formula of the cement powder and accurately integrated coated additives composition, which is able to improve well support durability and to restore the integrity of the failed well owing to a system of cracks emerged in the cement sheath thereby letting water passage through. The results of the study, which are in line with the aim of the study, proves the ability of the devised technique to prevent loss of the cement sheath integrity thus preventing behind-the casing flows.

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# ҰҢҒЫМАЛАРДЫҢ ЦЕМЕНТ БЕКІТПЕСІН ҚАЛПЫНА КЕЛТІРУ ҮШІН ЕМДІК ҚОСПАЛАРДЫ ӘЗІРЛЕУ

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Ұңғыманы пайдалану кезінде оған әсер ететін динамикалық жүктемелер мен ішкі кернеулер біртіндеп цемент тасының тозуына әкеледі, әдетте шегендеу құбыры артында болады.

Осындай механикалық және химиялық әсермен цементте қатты жарықтар пайда болады, бұл шегендеу құбыры артындағы қабат аралық ағынға және қабаттар арасындағы бақыланбайтын ағынға әкеледі, бұл мұнай-газ қоспасының пайда болуына және көмірсутектердің тұщы су сулы қабаттарына ауысуына әкеліп соғады, жергілікті су көздеріне тікелей зиян келтіреді [1], шегендеу құбырлар артындағы цементтің өзі аймақтарға бөлу қабілетіне әсер етеді.

Бұл мәселе ғасырлар бойы мұнай-газ саласында болды, бұл материалдарды «өз-өзінен қалпына келу» қағидаты арқылы шегендеу құбыры артындағы цемент тасының тұтастығын сақтау мүмкіндігін зерттеуге итермеледі. Осы қағидаттың көмегімен адамның араласуынсыз ерекше жағдайларда цемент тастарындағы жарықтарды жоя алатын құпия қоспалар қосылған өз-өзінен қалпына келетін цемент жасалды. Бұл ұңғыманың депрессиясының алдын-алудың тиімді шарасы болуы мүмкін және күрделі жөндеу үшін ұңғыманың тоқтап қалуын болдырмауға көмектеседі.

Негізгі сөздер: «өз-өзінен қалпына келетін» цемент, бекітпенің герметикалығы, түрлендіретін қоспалар, гидрооқшаулағыш, цемент сақинасы, жарықтар.

# РАЗРАБОТКА ЗАЛЕЧИВАЮЩИХ ДОБАВОК ДЛЯ ВОССТАНОВЛЕНИЯ ЦЕМЕНТНОЙ КРЕПИ СКВАЖИН

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Динамические нагрузки и внутренние напряжения, действующие на скважину в период её эксплуатации, постепенно приводят к износу цементного камня, обычно имеющегося за обсадными трубами. При таком механическом и химическом воздействии в цементе образуются сильные трещины, что приводит к межпластовому перетоку за обсадными трубами и неконтролируемому перетоку между пластами, что влечет за собой образование нефтегазовой смеси и миграцию углеводородов в пресноводные водоносные горизонты, нанося непосредственный ущерб местным источникам воды [1], влияя на способность распределения на зоны самого цемента за обсадными трубами.

Эта проблема существовала в нефтегазовой отрасли на протяжении веков, что побудило нас исследовать возможность сохранения целостности цементного камня за обсадными трубами с помощью принципа «самовосстановления» материалов. При помощи этого принципа был разработан самовосстанавливающийся цемент с добавлением секретных добавок, которые смогут устранить трещины в цементном камне в особых условиях без вмешательства человека. Это может быть эффективной мерой профилактики разгерметизации скважины и поможет исключить остановки скважины на капитальный ремонт.

Ключевые слова: "самовосстанавливающийся" цемент, герметичность крепи скважины, модифицирующие добавки, гидроизоляция, цементное кольцо, трещины.

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