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MICROSTRUCTURE OF POROUS SPACE IN CEMENT SHEATH USED FOR SEALING OIL WELLS

Abstract: The effect of cement slurry modification on the microstructure of the annular space in a wellbore is presented in this paper. An admixture of macromolecular copolymer GS was used, which is usually applied in cement slurry technology to counteract gas migration by the binding cement slurry. The copolymer addition also results in sealing up the cement matrix at the stage of the binding and formation of hardened cement slurry. The modification of a slurry composition with this admixture results in the fact that the cement matrix has low porosity and is strongly compact. Consequently, a significantly higher number of micropores with small diameters are formed than those with larger micropores in the analyzed hardened cement slurry sample. An admixture of a macromolecular copolymer (7 wt.% of the cement) was added and 10% of the latex was removed from the recipe to show the influence of the modified recipe on the microstructure of the cement sheath. Thanks to this modification, the microcement participation could be reduced by 50% with the simultaneously improved quality of the most important technological parameters of fresh and hardened cement slurry. The basic and modified recipes were analyzed. The following parameters of the slurry were determined: rheology, filtration, water settlement, and time of densification. The influence of the modified slurry on the parameters describing the microstructure of the hardened slurry was analyzed for the hardened slurry (i.e., porosimetric porosity and microtomographic porosity). The microstructure of a sample fracture was also investigated. The analyses were conducted for recipes of slurries to be used for sealing wells at a temperature of 40°C and pressure of 10 MPa.

Keywords: cement slurry, drilling, oil wells

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1. INTRODUCTION

The sealing of the annular space in wellbores lies in forming a cement sheath with a maximally compact and impervious microstructure. This contributes to the elimination of microleaks in the hardened cement slurry. For designing such a gas-impermeable structure of a hardened cement slurry characterized by the proper mechanical properties, the Oil and Gas Institute – National Research Institute, Faculty of Drilling, Oil, and Gas started to cooperate with the Faculty of Materials Science and Ceramics AGH UST on the modification of the technological parameters of fresh and hardened sealing slurries. Determining the parameters that describe the pore microstructure of a cement sheath as well as its changes during the life of a wellbore (i.e., during long-lasting deposition in borehole-like conditions) creates the bases for working out the correct recipes of sealing slurries that possess low porosity and permeability after hardening. This is especially important for eliminating unfavorable gas migration through the hardened sealing slurry.

2. MICROSTRUCTURE OF HARDENED CEMENT SLURRY

Most solids have free spaces in their structures (i.e., pores). Sometimes, these spaces can be interconnected, forming a vast irregular network of microcanals. In some cases, this structure is favorable; e.g., in cellular concrete (insulation) (Fig. 1). However, when sealing a wellbore, the lowest possible porosity is required for hardened cement slurry (Fig. 2). To obtain the demanded structure of the cement sheath in the annularspace of the wellbore, various additives and admixtures are applied. Such sealing materials affect the porous structure and lower the porosity of the cement sheath [1, 2].

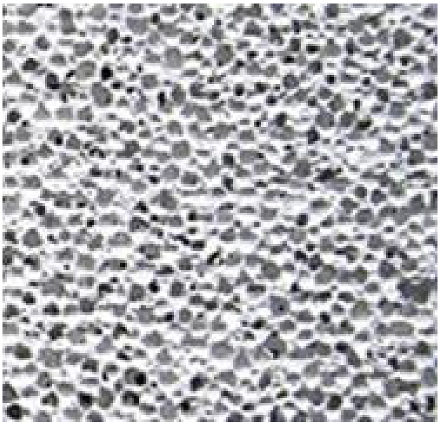

Fig. 1. Porous structure of cellular concrete

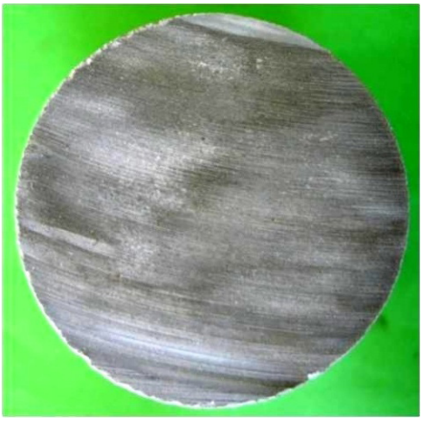

Fig. 2. Porous structure of low-porosity cement sheath

The use of filling materials is only one of the aspects of designing appropriate cement slurries. Among other important technological parameters of a slurry are the remaining properties of fresh and hardened cement slurries. When working out a slurry recipe, all of its parameters are controlled and modified from the beginning (preparation of the slurry) to the final stage (i.e., gas-impervious low-porosity structure of hardened cement slurry). For doing this, scientific and research institutions make use of professional research and measuring apparatuses, and they also rely on the opinions of qualified specialists.

3. ANALYSIS OF MICROSTRUCTURE OF HARDENED CEMENT SLURRY

Our laboratory experiments on the cement slurries were conducted on the basis of the following standards:

- PN-85/G-02320 “Cements and cement slurries for cementing wellbores”;
- PN-EN 10426-2 “Oil and gas industry. Cements and materials for cementing wellbores. Part 2: Analysis of drilling cements”;
- API SPEC 10 “Specification for materials and testing for well cements”.

The analysis of the porous structure of the hardened cement was performed with the following apparatuses:

- Auto Pore IV 9500 mercury porosimeter (Micrometrics, USA) (Fig. 3);
- Benchtop 160 CT x-ray microtomograph (Fig. 4);
- Nova Nano SEM 200 scanning electron microscope (Fig. 5).

Fig. 3. Auto-Pore IV mercury porosimeter (OGI-NRI)

Knowledge of the physicochemical parameters that describe the porous structure allows for modifying sealing slurries to maximally thicken the matrix of the cement slurry as well as counteract the microcracking and corrosion of the cement sheath in a wellbore [3, 4, 5]. The porosity analyses with the Auto-Pore mercury porosimeter (Fig. 3) allow us to describe the number of free spaces in a given sample. The analysis of the remaining parameters obtained from the other measurements can be used for defining the durability of the hardened slurry, the permeability and density of the sample matrix, and many other parameters on the basis of which the recipe of the slurry can be modified to obtain the required effect. However, due to the lack of data on the spatial distribution of the pores, parameters such as the hydraulic permeability of a fluid cannot be measured; this is unfavorable, as this information is very important for the interpretation of the gas flow in a hardened cement slurry. For this reason, the porosity measurements with the mercury porosimetry methods are sometimes supplemented with the indication of the Benchtop x-ray microtomograph (Fig. 4), which visualizes the porous structure of the cement sheath (picture of cracks and fractures) [6, 7]. X-ray microtomography is one of the most advanced analytical methods; thanks to this, a hardened cement sample can be x-rayed. On this basis, a 3D image of the empty spaces inside a sample can be obtained. The 3D image is processed, bringing about information describing the microstructure of the analyzed sample (both graphically and empirically) [8].

Fig. 4. Benchtop 160CT x-ray microtomograph (OGI-NRI)

If a more detailed description of the cement sheath microstructure is required, scanning electron microscopy analyses (SEM) can be performed at the Faculty of Materials Sciences and Ceramics AGH-UST. The analyses of the microstructures of the sample fractures are realized with the Nova Nano SEM 200 (Fig. 5). Additionally, the elemental composition analysis is also performed with an EDX probe; thanks to this, the chemical composition of hardened cement can be directly observed in the microareas [10].

Fig. 5. Nova Nano SEM 200 scanning electron microscope (AGH-UST) [9]

4. COMPARATIVE ANALYSIS OF TECHNOLOGICAL PARAMETERS OF HARDENED CEMENT SLURRY BEFORE AND AFTER MODIFICATION

For making a comparative analysis of the structure of a cement slurry before modification (Slurry R1) and after modification (Slurry R2), a recipe for cement slurry was selected for borehole conditions (a temperature of 40°C and pressure of 10 MPa). The slurries were based on tap water with CEM I 32.5R Portland cement as a hydraulic binder.

The basic recipe (R1) included the following:
– 10% latex admixture,
– 20% microcement [wt. % as related to the mass of the cement] for sealing the cement matrix.

The modification of the basic recipe lied in lowering the water-to-cement ratio from 0.52 to 0.50. During the modification, the latex and latex stabilizer were eliminated in lieu of a 7% admixture of a GS macromolecular copolymer. The amount of microcement was lowered to 10%, whereas the remaining additives and admixtures were used in quantities that allowed us to obtain the parameters required under the given geological-technical conditions of a wellbore. The recipes of the slurries are presented in Table 1.

Table 1
Compositions of slurries before and after modification
(for given temperature 40°C and pressure15 MPa)

Composition [%]	R1	R2
Tap water	w/c =0.52	w/c = 0.50
Defoamer	1.00	0.20
Liquefier	0.10	0.40
Antifiltration agent	0.20	–
Latex	10.0	–
Latex stabilizer	2.00	–
Macromolecular copolymer GS	–	7.00
Density accelerator	1.50	–
Microcement	20.0	10.0
Cement CEM I 32,5 R	100.0	100.0
Swelling agent	0.30	0.10

Denotations: w/c – water-to-cement ratio

The modification mainly had an effect on the filtration (a reduction from 68 cm^3/30 min to 10 cm^3/30 min), improvement of the rheological parameters, and elimination of water settling. Moreover, the thickening time changed from 30 Bc to 100 Bc (for comparable thickening times of both slurries). The transition from 30 Bc to 100 Bc in Slurry R1 was 43 minutes, and in the modified R2 – 16 minutes. The technological parameters of the slurries are presented in Table 2.

Table 2
Parameters of slurries before and after modification

Parameter		R1	R2
Density [g/cm^3]		1.79	1.80
Spillability [mm]		260	300
Filtration [cm^3/30 min]*		68.0	10.0
Plastic viscosity [mPa·s]		70.0	64.5
Yield point [Pa]		6.18	3.1
Structural strength [Pa]		11.5	4.8
Settling of water [%]		0.4	0.0
Thickening time [hrs:min] *	30 Bc	2:04	2:42
	100 Bc	2:47	2:58

* Time to reach measurement temperature was 20 minutes

Owing to the fact that the experiments were mainly aimed at finding the changes in the microstructure of the pores of a hardened cement sheath in the annular space of a wellbore, the most important technological parameters were presented in Table 3. The analysis of the obtained results revealed the presence of pores belonging to particular volume classes characterized in microtomographic analyses; i.e., 1 to 6 (Class 1 – smallest pores; Class 6 – largest pores). The results obtained for the microstructure of the cement sheaths of the hardened cement slurries showed the dominance of the smallest pores belonging to Classes 1 through 3 in modified Sample R2 (marked in orange in Table 3). A considerably smaller number of the biggest pores belonging to Classes 4 through 6 can be observed in the same sample. A reverse tendency was noted in Sample R1. This characteristic of the hardened slurry samples was also confirmed by plots visualizing the % participation of the pore volume (Figs. 6, 7). Larger-sized pores prevailed in Sample R1 before modification (marked in Figure 6), whereas smaller pores dominated in the modified sample (marked in Figure 7).

Figures 8 and 9 visualize the porous structure analyzed with the x-ray microtomography methods. Figures 8 and 9 reveal a stronger densification of the green color, which represents the greater presence of free spaces in the sample before modification (Fig. 8) than in the modified sample (Fig. 9). The photos visualizing the participation of microspaces depending on their sizes (Figs. 10, 11) allow for an interpretation of the presence of pores belonging to a given volume class. The prevalence of a given color provides qualitative and quantitative information about a given class of pores; the data corresponds to the values presented in Table 3.The microstructure of the sample fracture was additionally analyzed for visualizing the microstructure of the cement sheath (Figs. 12, 13). The cement sheath before modification (Fig. 12) showed a less homogeneous structure than after modification (Fig. 13).

The interpretation of these results confirmed the modification; as a result, a compact and impervious structure of the cement sheath was obtained. This was also proven by the porosity results (Tab. 3), where both the coefficient of the microtomographic porosity and porosimetric porosity had lower values for Sample R2 (after slurry modification).

Table 3

Results of analyses of cement stones after 28 days of hydration

No	Temp./pressure of hardened sample (± 0.1%)	No. of sample	No. of pores in class						Coefficient of microtomographic porosity K_p [%]	Porosimetric porosity [%]
			$2 \cdot 10^2$–$2 \cdot 10^3$ [μm³]	$2 \cdot 10^3$–$2 \cdot 10^4$ [μm³]	$2 \cdot 10^4$–$2 \cdot 10^5$ [μm³]	$2 \cdot 10^5$–$2 \cdot 10^6$ [μm³]	$2 \cdot 10^6$–$2 \cdot 10^7$ [μm³]	$>2 \cdot 10^7$ [μm³]		
			I	**II**	**III**	**IV**	**V**	**VI**		
1	40°C/ 10 MPa	R1	8495	63,588	5825	390	17	1	7.8	37.97
2		R2	49,340	81,017	6459	319	7	0	4.5	32.23

* Uncertainty of measured physical parameters in Table 3 evaluated after accuracy class of Benchtop 160CT at level of 0.0001%

– smaller number of pores – greater number of pores

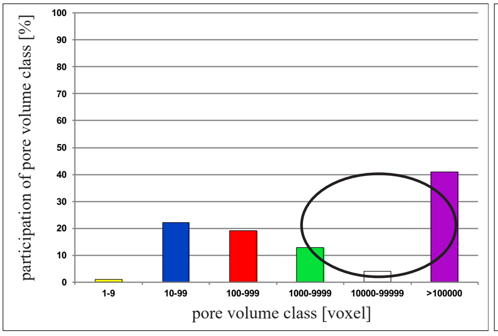

Fig. 6. Participation [%] of pore volume classes in Sample R1 (10 MPa/40°C)

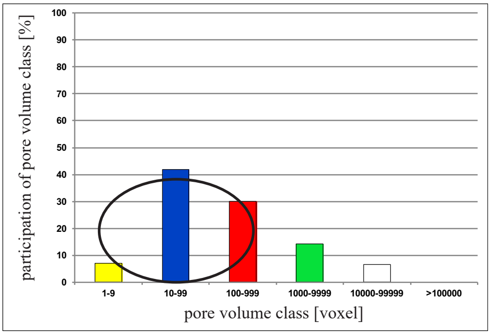

Fig. 7. Participation [%] of pore volume classes in Sample R2 (10 MPa/40°C)

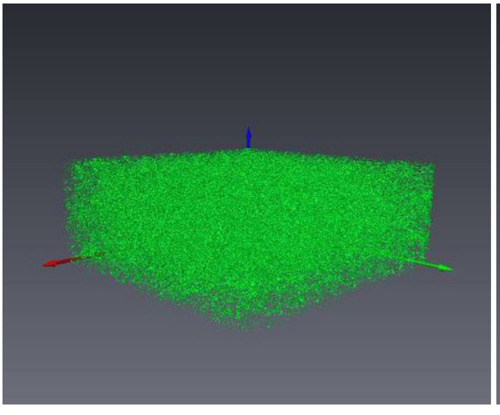

Fig. 8. Number of pores in Sample R1 (10 MPa/40°C)

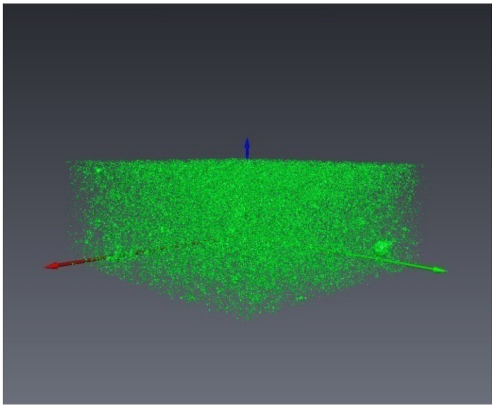

Fig. 9. Number of pores in Sample R2 (10 MPa/40°C)

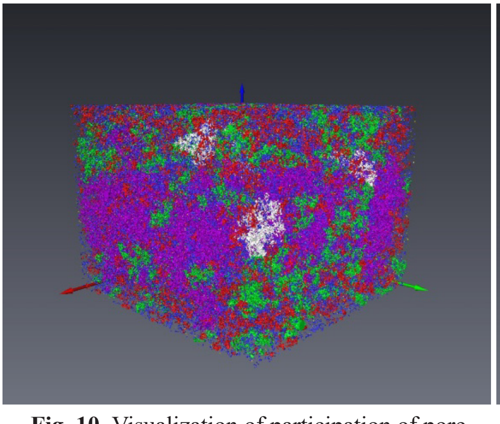

Fig. 10. Visualization of participation of pore volume classes in Sample R1 (10 MPa/40°C)

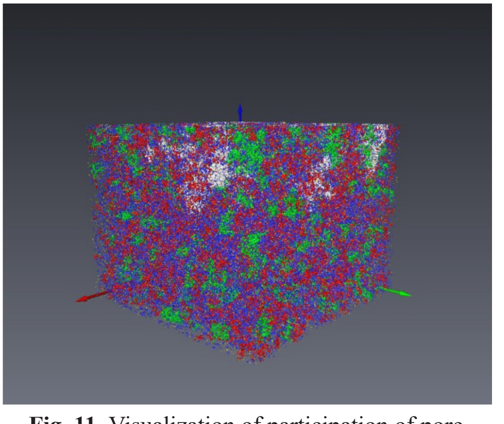

Fig. 11. Visualization of participation of pore volume classes in Sample R2 (10 MPa/40°C)

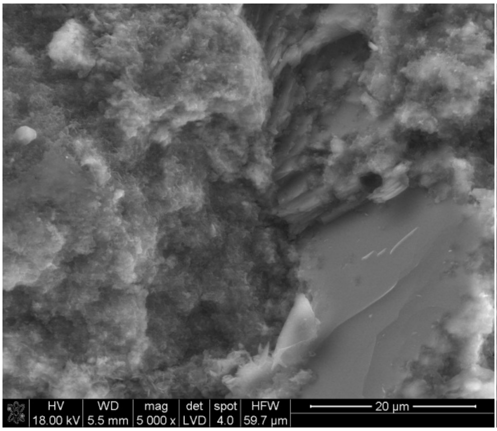

Fig. 12. Microstructure of Sample R1 fracture after 28 days of hydration (10 MPa/40°C)

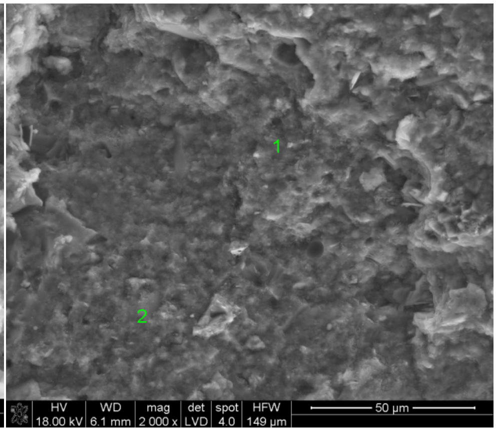

Fig. 13. Microstructure of Sample R2 fracture after 28 days of hydration (10 MPa/40°C)

The analysis of the microstructures of the hardened cement slurries considerably contributed to the improvement of the tightness of the cement sheath as well as its durability during the long exploitation of the reservoir. This is connected with the fact that the knowledge of the microstructure and processes taking place in it allow for the correct qualitative and quantitative selection of geological and technical conditions. The scope of information on the microstructure of hardened cement slurries and correct interpretation of the parameters describing it are crucial for the investor as well as cementing services. In many cases, this knowledge may protect against future sealing-up jobs and allow for safe exploitation without the danger of premature corrosion of the hardened cement stone. Accordingly, scientific and research institutions should carry out analyses on the microstructure of cement sheaths and undertake measures at designing gas-impermeable and maximally compact cement sheaths.

5. CONCLUSIONS

- Knowledge of the microstructure of the cement sheath in a wellbore after laboratory analyses and interpretation of the obtained results allows us to design an optimal recipe for sealing slurry for the given geological and technical conditions.
- The designed sealing slurries should be modified to lower the porosity and permeability of the hardened sealing slurries to ultimately obtain a homogeneous structure in the cement sheath.

  The experience gained during the experiments prompted the following conclusions:
  - the coefficient of microtomographic porosity of the hardened cement slurry should not exceed 25.0%;
  - the resultant cement sheath should have the lowest number of pores from the higher classes (VI, V, and IV) and greatest number of pores from the lower classes (I, II, and III) (Tab. 3);
  - the microstructure of a sample skeleton in 3D visualization should be uniform and have the lowest possible number of macropores (Fig. 9);

- the homogeneity of the homogeneous structure of the cement slurry should be established by an SEM analysis of the fracture(s).

– The modification of the cement slurry allowed us to obtain a low-porosity, impervious, and structurally uniform hardened cement slurry that can be successfully used for cementing casings in gas wellbores.

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