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**Marcin Kremieniewski*, Stanisław Stryczek**, Rafał Wiśniowski****

# CORRELATION OF PARAMETERS DESCRIBING MICROSTRUCTURE OF HARDENED CEMENT SLURRY FOR THE PURPOSE OF INCREASING TIGHTNESS OF CEMENT MANTLE***

## 1. INTRODUCTION

While sealing the annulus in a wellbore special attention should be paid to preventing microleakages formation in the cement layer. An Auto Pore porosimeter can be used for analyzing the porous microstructure of hardened sealing slurries and also for determining the permeability of the analyzed samples.

On this basis one can modify the recipes and select optimum parameters of slurry, which after bonding will have a compact, low-porosity and low-permeability microstructure. As a result, the unfavorable effect of gas penetration through the hardened sealing slurry can be limited or avoided.

At the Laboratory of Sealing Slurries (Drilling Technology Department INiG PIB in Krosno) there have been conducted experiments and tests aimed at creating new and modifying already existing recipes for sealing slurries. Recently, tests on hardened cement slurries have been also performed.

## 2. POROSITY OF HARDENED CEMENT SLURRIES

Similar to most solids, hardened cement slurries typically have micropores in their structure, varying in size and shape. Such spaces are interconnected forming a large irregular network [6].

Porosity of a given medium is a characteristic phenomenological parameter which neither describes the shape of the pores nor is indicative of their course, but which shows the participation of the porous space in the volume of the analyzed sample. However, apart

* Oil and Gas Institute – National Research Institute, Krakow, Poland

** AGH University of Science and Technology, Faculty of Drilling, Oil and Gas, Krakow, Poland

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from the obvious reason of measurement, i.e. porosity parameter, the porosimetry analyses of sealing slurries are also very useful for other purposes. On this basis many other parameters can be described and lots of precious data derived [2, 3, 5]. Correlation of the obtained results helps one modify the recipes and produce cement mantles of both low porosity and tight matrix of hardened cement slurry [7, 10].

## 3. PORE THROAT SIZE FOR POROSIMETRY ANALYSES INTERPRETATION

Porosity experiments on cement stone with a mercury porosimeter allow for determining the permeability of a given sample while interpreting the cumulative curves of the capillary pressure. Their shape is usually repetitive in the analyzed samples, therefore many elements are similar, e.g. entry pressure point (Fig. 1), entry radius, entry diameter, entry pressure [8, 11]. By indicating such a place when interpreting the cumulative curve one can determine the size of the biggest pores in the analyzed sample [8, 11, 12]. From this point onwards the saturation value increases with the flow of mercury intrusions to the macropores. Basing on the experiments and analyses of saturation curves, the saturation point was assumed to be the displacement pressure (or radius) [4, 8, 11, 12]. Many scientists assume a 10% displacement radius [8, 11, 12], but bearing in mind the how it influences the porosity of the sample, attention should be paid to this parameter when using it in correlation analyses [8, 11, 12].

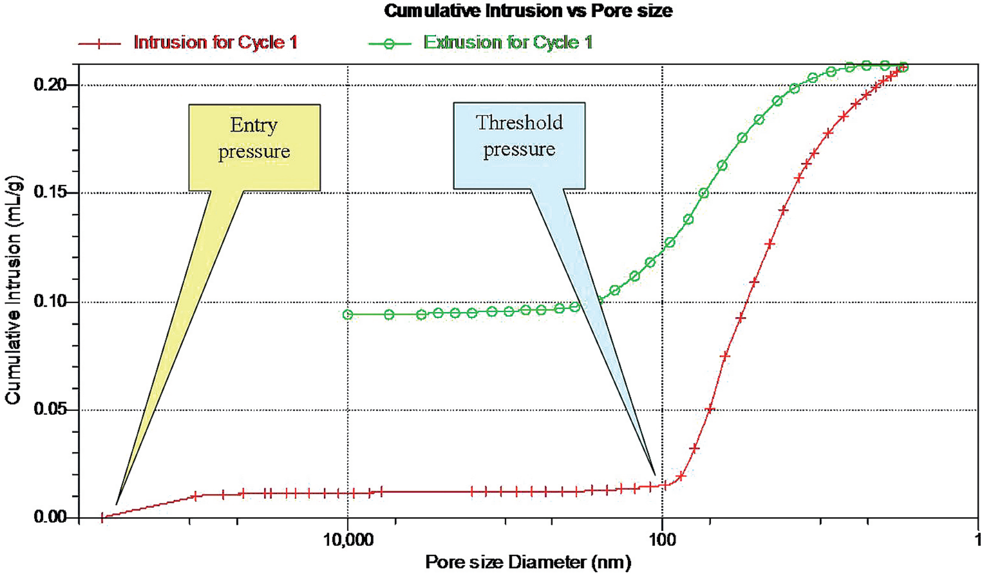



**Fig. 1.** Exemplary cumulative plot with entry and threshold pressures and the corresponding pore size in nanometers

Another characteristic point is the slope of the cumulative curve [9, 12, 15], i.e. a diameter at which mercury saturation of a sample rapidly increases in the low pressure increase conditions. Such a point is called the pore throat size (Fig. 1). This parameter is very important for the interpretation of the tightness of the cement matrix; it allows one to accurately determine the permeability of the hardened cement slurry. At the point of pore throat size a continuous flow of a medium through the sample is originated, i.e. pores of this size provide communication in the analyzed pore structure [8, 12]. The analysis of samples of hardened cement slurries reveals that the better are the filtration properties of samples for sealing purposes (lower permeability), the smaller is the threshold radius (higher threshold pressure). According to the literature [11], if the threshold radius is smaller than 1 micrometer then no flow takes place through the sample in real conditions (limited value of pressure gradients). Initially the saturation curve rapidly increases to later assume a horizontal course and asymptotically tends to maximize saturation for micropores [12].

The listed data are useful for an initial interpretation of the obtained results. The range of porosity formed in pore space > 1 micrometer informs about the magnitude of possible flow.

## 4. BOUNDARY EFFECT VS. SPECIFIC SURFACE

While interpreting the results of porosimetry analyses for low-porosity samples, the "*boundary effect*" has a considerable influence on the results. This is an inaccuracy appearing during mercury intrusion in the low-pressure cup of the porosimeter [8, 12]. The outer surface of the analyzed sample is filled with mercury at some pressure which proportionally grows with the increasing unevenness of sample walls. This effect produces a measurement error (ten parts of percent) and increases the average capillary value [12, 13]. In the case of low-porosity samples this effect can significantly influence the overall result, therefore attention should be also paid to the *specific surface* of the sample in the interpretation. On this basis we can establish if the sample is porous or almost zero-porous [12]. The boundary effect takes place in the latter case. Here, the size of the capillar is described by the size of the unevenness on the surface of the sample and no information about the actual diameter of the capillar is provided. The practical porosity of such samples equals zero and it should be born in mind that the remaining parameters are also zero, regardless of the calculated values [12, 14].

## 5. LABORATORY EXPERIMENTS

Laboratory experiments on fresh sealing slurries were performed at the Laboratory of Sealing Slurries (Drilling Technology Department INiG PIB in Krosno), following the standards: PN-EN 10426-2, *Przemysł naftowy i gazowniczy: Cementy i materiały do cementowania otworów wiertniczych. Część 2: Badania cementów wiertniczych* (*Oil and gas industry. Cements and materials for cementing wellbores. Part 2: Analyses of drilling cements*) and API Spec 10 *Specification for materials and testing for well cements*. The porous microstructure of hardened cement slurries was tested with a mercury intrusion porosimeter Auto Pore IV 9500 (Micrometrics, USA) (Fig. 2).

Four recipes for slurries were selected on the basis of the analysis of compositions applied by cement companies. Their parameters were to maximally resemble those of fresh slurries. Then the slurries were performed according to a definite recipe defined in INiG – PIB, similar to the one used by the cementing services. Network water was used as working fluid. Recipe no. 1 did not include latex or microcement. Recipe no. 2 contained 20% microcement which should seal up the cement matrix. In the third recipe the microcement content was reduced to 10%, and 10% of latex was added. In recipe no. 4 we had only 5% of microcement, and the latex was substituted by 6% counter-migration agent GasSeal. The compositions of cements are listed in Table 1. Tests were performed for the above mentioned slurries, designed for cementing casing pipes in wellbores in temp. 25°C and pressure 3 MPa. Fresh slurries had comparable parameters (see Tab. 2). They were used for making hardened cement slurry samples which were hydrated for 28 days in wellbore-like conditions (temp. 25°C, pressure 3 MPa).


**Fig. 2.** Porosimeter Auto Pore IV 9500

**Table 1**

Composition of slurries used during experiments

| Recipe no. | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| Tap water. | w/c = 0.48 | w/c = 0.54 | w/c = 0.52 | w/c = 0.50 |
| NaCl | – | – | – | – |
| Defoaming agent | 1.0% | 1.0% | 1.0% | 0.2% |
| Liquefier | 0.2% | 0.2% | 0.3% | 0.4% |
| Antifiltration agent | 0.2% | 0.25% | 0.1% | – |
| Latex / *GasSeal | – | – | 10.0% | *6.0% |
| Latex stabilizer | – | – | 2.0% | – |
| Thickening accelerator | 3.5% | 3.5 % | 4.0% | 1.0% |
| Microcement | – | 20.0% | 10.0% | 5.0% |
| Cement Cem 32,5 R | 100.0% | 100.0 % | 100.0% | 100.0% |
| Swelling additive | 0.3% | 0.3% | 0.3% | 0.1% |

Explanations: w/c – water/cement ratio

* Experiment in temp. 25°C, pressure 3 MPa

Next followed tests thanks to which the microstructure of hardened cement slurries could be described (Tab. 3), and the obtained results compared (Tab. 4). The correlation analysis was performed by calculating the coefficient of determination $R^2$, which is one of the basic measures of goodness of fit of the model and is connected with the coefficient of convergence.

**Table 2**

Parameters of fresh slurries

| Parameter | Composition no. | | 1 | 2 | 3 | 4 |
|---|---|---|---|---|---|---|
| Density [g/cm$^3$] | | | 1.78 | 1.78 | 1.79 | 1.80 |
| Spillability [mm] | | | 275 | 260 | 240 | 240 |
| Filtration* [cm$^3$/30 min] | | | 124 | 88 | 56 | 30 |
| Plastic viscosity [MPa·s] | | | 91.5 | 58.5 | 64.5 | 93.0 |
| Yield point [Pa] | | | 9.4 | 5.0 | 6.48 | 9.6 |
| Time of thickening* [h:min] | | 30 Bc | 2–40 | 2–50 | 2–13 | 2–08 |
| | | 100 Bc | 3–58 | 3–20 | 2–40 | 3–20 |

* Experiment in temp. 25°C, pressure 3 MPa

**Table 3**

Parameters describing microstructure of hardened slurries

| Slurry no. | Hydration conditions temp. pressure | Porosity [%] | Permeability [mD] | Threshold pressure [MPa] | [μm]Threshold diameter | Pores bigger than throat size [%] | Specific surface [m$^2$g] | Fractal dimension [-] | Pores [%] | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | >1μm | 1.0–0.1 μm | 0.1–0.05 μm | 0.05–0.01 μm | <0.01 μm |
| 1 | 25°C 3 MPa | 49.9 | 0.26 | 0.0349 | 32.93 | 0.59 | 41.71 | 2.96 | 4.59 | 2.63 | 3.67 | 35.82 | 53.26 |
| 2 | 25°C 3 MPa | 38.3 | 0.22 | 0.0355 | 32.92 | 0.73 | 41.23 | 2.99 | 5.50 | 2.83 | 5.87 | 36.01 | 49.76 |
| 3 | 25°C 3 MPa | 36.2 | 0.15 | 0.0410 | 30.17 | 0.44 | 65.81 | 2.95 | 2.75 | 1.60 | 1.22 | 33.01 | 61.40 |
| 4 | 25°C 3 MPa | 34.0 | 0.03 | 28.4297 | 0.040 | 10.57 | 30.76 | 2.91 | 4.21 | 2.31 | 4.05 | 38.19 | 51.22 |

**Table 4**

Correlations of parameters describing microstructure of hardened cement slurries

| Correlation type | Equation type | Regression equation | $R^2$ |
|---|---|---|---|
| Permeability – porosity | A | $y = 56.263x + 30.358$ | $R^2 = 0.6418$ |
| | **B** | $\mathbf{y = 544.84x^2 - 97.812x + 36.792}$ | $\mathbf{R^2 = 0.8830}$ |
| | C | $y = 50.31x^{0.1207}$ | $R^2 = 0.5007$ |
| | D | $y = 31.222e^{1.3799x}$ | $R^2 = 0.6822$ |
| Total permeability – total specific surface | A | $y = 28.414x + 56.276$ | $R^2 = 0.0276$ |
| | **B** | $\mathbf{y = 2327.2x^2 - 629.7x + 83.76}$ | $\mathbf{R^2 = 0.7689}$ |
| | C | $y = 56.189x^{-0.0254}$ | $R^2 = 0.0083$ |
| | D | $y = 56.702e^{0.2633x}$ | $R^2 = 0.0093$ |
| Permeability – pore throat diameter | A | $y = 146.94x - 0.2272$ | $R^2 = 0.8534$ |
| | **B** | $\mathbf{y = -953.76x^2 + 416.65x - 11.491}$ | $\mathbf{R^2 = 0.9975}$ |
| | C | $y = 5476x^{3.2969}$ | $R^2 = 0.9508$ |
| | D | $y = 0.0447e^{29.725x}$ | $R^2 = 0.8059$ |
| Permeabillity – fractal diemsion | A | $y = 2615x + 2.9156$ | $R^2 = 0.7891$ |
| | **B** | $\mathbf{y = -1.3912^2 + 0.6549x} + 2.8992$ | $\mathbf{R^2 = 0.8786}$ |
| | C | $y = 3.0166x^{0.0094}$ | $R^2 = 0.8519$ |
| | D | $y = 2.9157e^{0.0887x}$ | $R^2 = 0.7909$ |
| Permeability – participation of pores bigger than pore throat diameter | A | $y = -43.848x + 10.317$ | $R^2 = 0.7840$ |
| | **B** | $\mathbf{y = 352.66^2 - 143.57x + 14.482}$ | $\mathbf{R^2 = 0.9873}$ |
| | C | $y = 0.0663x^{-1.3977}$ | $R^2 = 0.8803$ |
| | D | $y = 8.9709e^{-12.244x}$ | $R^2 = 0.7045$ |

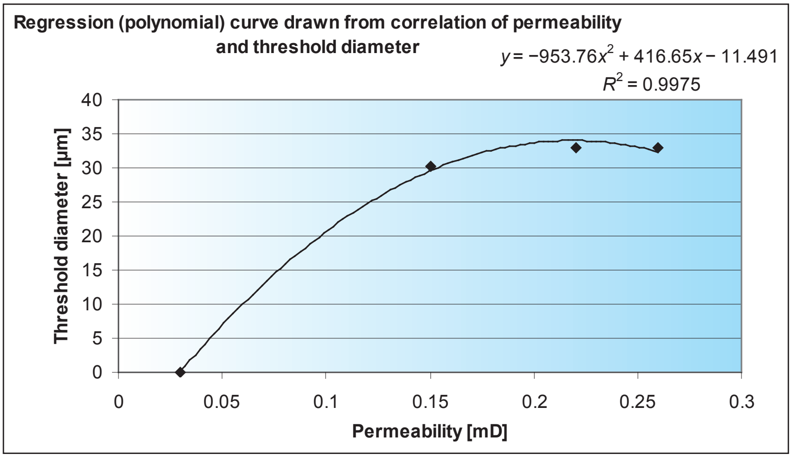
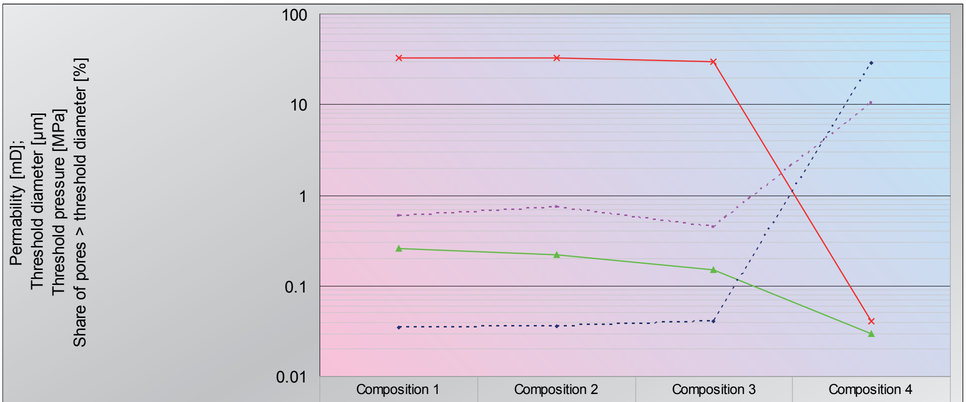



**Fig. 3.** Permeability of hardened cement slurry vs. pore throat size in microstructure of sample




| | Composition 1 | Composition 2 | Composition 3 | Composition 4 |
|---|---|---|---|---|
| Permeability [mD] | 0.26 | 0.22 | 0.15 | 0.03 |
| Threshold diameter [µm] | 32.934 | 32.9267 | 30.1712 | 0.0403 |
| Threshold pressure [MPa] | 0.0349 | 0.0355 | 0.041 | 28.4297 |
| Share of pores > threshold diameter [%] | 0.59 | 0.73 | 0.44 | 10.57 |

**Fig. 4.** Dependence of parameters describing microstructure of hardened cement slurries

The analysis of the experiments reveals that the best fit is obtained for the correlation of permeability and threshold diameter when $R^2$ = 0.9975. The polynomial regression curve in Figure 3 proves that with the increase of the threshold diameter the permeability also grows. The correlation analysis confirms earlier theoretical assumptions that permeability almost does not take place if the pore throat size is below 1 micrometer. Besides, the analysis of Figure 4 reveals that the smaller is the throat size, the higher is the threshold pressure, and the bigger is the share of pores exceeding the throat size, the lower is the porosity.

The correlation analysis shows that the quality of the forming structure of hardened slurry is principally influenced by the parameters described by the permeability measure and the diameter of the pores in the sample. To a lesser degree it is conditioned by total porosity because of the presence of closed pores which do not participate in the flow. The specific surface does not take part in the fluid flow, therefore the coefficients of determination are so low.

## 6. CONCLUSIONS

Thickening of the cement stone matrix by adding microcement and/or macromolecular polymer counteracting the gas migration (Tab. 1, 2) contributed to the lowering of permeability and porosity of cement stone.

The analysis of the results of experiments revealed a dependence between reduction of permeability with the increase of the number of pores bigger than the throat size, and also with the increase of threshold pressure (Fig. 4). This is connected with the lowering pore throat size (Fig. 3). Such behavior of samples is very important while designing recipes of slurries which would be resistant to the conditions in gas wellbores. The analysis of the parameters of fresh slurry and microstructure of hardened cement slurry also adds to better efficiency of sealing of the annulus. The quality of the forming microstructure of the sealing slurry is most influenced by the parameters described by the measures of permeability and porosity.

This knowledge is very useful while designing impermeable, maximally compact and low-permeable hardened cement slurries.

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