Abstract

The doctoral dissertation was intended to investigate the influence of clay and carbonate minerals on the sorption capacity of methane and carbon dioxide of shales. The thesis was that clay minerals were influencing the sorption capacity of Silurian – Ordovician shale. The research was preceded by a literature review . The shale samples was excavated form basin Baltic – Podlasie – Lublin and were characterized by extremely low organic content (approx. 5%), while the considered mineral matter were varied and fluctuated within limits 50% – 65%.

The influence of mineral groups: illite, montmorillonite, chlorite and kaolinite was tested with in-house projected and built high pressure volumetric setup. The tests were carried out at two temperature values: 50° C and 80° C. Sorption isotherms from experimental data were computed with usage of an accurate equations of state: Wagner & Setzmann for methane and Span & Wagner for CO2 were used. Obtained valued varied in range $10,54 - 26,84m^3$ /Mg in 50° C for CO₂, $2,53 - 16,11 m^3$ /Mg in 80° C for CO₂, $2,12 - 9,55 m^3$ /Mg in 50° C for CH₄ and $2,24 - 8,21 m^3$ /Mg for 80° C for CH₄. The analyzed data was subjected to qualitative analysis in accordance with the published guide by the Główny Urząd Miar on the basis of ISO recommendations. Experimental results were fitted with Langmuir model, with an additional factor in the equation linking gas density to sorption capacity.

The possibility of carbon dioxide storage in the studied rocks was tested using two methods: conventional and Ambrose. Used two values of porosity: 4,5% and 9,5% and two values of moisture: 35% and 70%. Obtained results varied from $4 - 14m^3/Mg$ for lower porosity and higher moisture to $8 - 23m^3/Mg$ for higher porosity and low moisture.

The linearity correlation was checked with Pearson coefficient method to determine relation of the sorption capacity to the content of individual groups of minerals which allowed for drawing preliminary conclusions about their impact on sorption capacity. Then descriptive statistics were created and the differences in mean sorption for particular groups of minerals were checked. Due to the differences in the means, it was decided to conduct Student's t-test in order to test the statistical significance of these differences. It has been proved that the differences in the means are statistically significant and thus the thesis has been proved.