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**Review of a PhD dissertation entitled "Laboratory analysis of exchange sorption in coal under confining pressure condition with reference to the description of the processes of underground CO<sub>2</sub> storage with capture of CH<sub>4</sub>"**  
**written by Leticia Teixeira Palla Braga, MSc;**  
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## **1. Introduction**

The investigation of the relationships concerning the sorption capacity of hard coals with regard to methane and carbon dioxide, the transport of these sorbates in the coal structure, and the influence of the chemical and petrographic composition of coal on sorption capacity are the subject of many studies. Due to the high heterogeneity in the structure of the coal material, these relationships are still not fully clarified. The research being carried out at a number of universities is both basic and applied, much of it aimed at the CO<sub>2</sub> sequestration process or the exploitation of coal seams and the safety of miners. The wide-ranging literature review performed by the doctoral student clearly shows that undertaking research in the field of exchangeable sorption of methane and carbon dioxide is justified. The need to reduce CO<sub>2</sub> emissions and the development of technologies to eliminate this gas by storing it in geological structures is raised in many policy initiatives, research projects and also climatic scenarios. Therefore, undertaking such a research topic is fully justified, and the experimental nature of the work, complemented by rich mathematical analysis, emphasizes the utilitarian goals outlined in the dissertation.



## 2. Content of the dissertation

The dissertation has a 151 pages, including a reference list of 289 items, table of contents, tables and figures. The dissertation consists of 6 main chapters, ending with a discussion and conclusion. The **Introduction** section of the dissertation is very well written, providing the information required to understand the goal of the thesis and including the state of knowledge regarding the the occurrence of CO<sub>2</sub> and CH<sub>4</sub> in the atmosphere and coal seams. The concept of ECBM is described, as well as the research experience to date with attempts to locate CO<sub>2</sub> in coal seams. Challenges facing ECBM technology are discussed, in particular the exchange sorption issues associated with simultaneous CH<sub>4</sub> recovery and the effects associated with coal swelling during sorption. It is well balanced' not too long' and well supported by many scientific sources

The second chapter of the dissertation "Coal - gas system" organizes the current state of knowledge regarding the occurrence of CO<sub>2</sub> and CH<sub>4</sub> in coal and the interaction of these gases with the surface of the coal material. It discusses the phenomenon of adsorption and the influence of a number of parameters on the behavior of the coal-gas system. The differences between the sorption of CH<sub>4</sub> and CO<sub>2</sub> were also presented. The world literature has been analyzed in terms of describing the phenomenon of CO<sub>2</sub>/CH<sub>4</sub> exchange sorption and sorption in coal material subjected to confining load. Similarly, the phenomena of CO<sub>2</sub> and CH<sub>4</sub> transport in coal was showed. The analysis of the state of knowledge carried out allowed clarify the research direction on the study of the coal-gas system taking into account the analysis of the course of exchange sorption under confining loading conditions. The recognized research niche became the reason for planning and carrying out experimental studies aimed at achieving results that fill the gap in this area of knowledge. The thesis of the work was formulated: "The confining pressure has a significant influence on the CO<sub>2</sub>/CH<sub>4</sub> exchange sorption processes in coal in the aspect of the sorption sweep efficiency and the kinetics of the proces ". This thesis clearly signals that confining pressure exerted on the coal sample should have a clear effect on a number of processes involved in exchange sorption.

In Chapter 3, "Research methodology," the doctoral student described the research methodology. The coal samples that were later subjected to sorption tests were in the form of coal briquettes. The author described the procedure for preparing the briquettes. The research

that was carried out on the initial coal samples was described: petrographic analysis, scanning electron microscopy, structural analyses and sorption tests. Also described in detail was the author's experimental system, which was used to achieve the main research objective-analysis of the course of exchange sorption in a sample subjected to confining loading.

Chapter 4 describes the test material. Four coal samples were selected, three of which came from Polish mines while the fourth came from the Lorraine Basin in France. The material was subjected to elemental, technical and petrographic analysis. The selected samples varied in their degree of carbonization from about 76%, to 87% elemental C content. Microscopic analyses (optical and SEM), porosimetry and low-pressure gas adsorption were also performed.

In Chapter 5, the doctoral student presented the results of an extensive sorption study of the coal samples under relaxed conditions. The studies included the determination of sorption capacities for CH<sub>4</sub> and CO<sub>2</sub> at several points, resulting in the determination of sorption isotherms. The studies were conducted at three different temperatures. The research cycle thus planned made it possible to determine changes in sorption capacities and isotherm parameters as a function of temperature for CO<sub>2</sub> and CH<sub>4</sub>. Studies of the variation of diffusion coefficient values for CO<sub>2</sub> and CH<sub>4</sub> as a function of temperature were also analyzed.

In Chapter 6, the author describes the most important research from the point of view of the thesis statement. It should be noted that the idea of the experiment was an attempt to map the concept of underground geological storage of CO<sub>2</sub> in coal seams with CH<sub>4</sub> recovery. An important parameter of the conducted research is the confining pressure to which the coal material was subjected during the study. The author's measuring equipment used in the study allowed the confining pressure to reach a controlled level of up to 30MPa, which corresponds to the depth of the deposit below 1100 m. The author conducted studies of changes in the sorption parameters of coal relative to CH<sub>4</sub> with increasing confining pressure. A decrease in sorption capacity accompanying an increase in confining pressure values was found. Coal material in sorption equilibrium against CH<sub>4</sub> at a pressure of 0.8 MPa was the starting point for exchange sorption experiments. The beginning of the experiment involved changing the gas at the inlet of the coal sample to CO<sub>2</sub> and generating a pressure gradient on the sample by lowering the pressure at its outlet, which started the transport of the gas. Directly observed during the

experiments were the gas pressure in the reference vessel at the sample inlet, the gas output, pressure and composition at the sample outlet. The confining pressure exerted on the sample was stabilized by one of the functional systems of the apparatus. The measured parameters allowed precise balancing of the amount of gas injected into the sample, as well as leaving the sample. The experiments were conducted at 4 confining pressures. The results of the experiments were presented as a set of graphs showing the gas balance for each confining pressure. In the course of further analysis, the parameters displaced volume and sweep efficiency, which are key to the interpretation of the course of exchange sorption, were also determined. The author showed that there is a relationship between the confining pressure and the course of exchange sorption. The quantitative effect of confining pressure on exchange sorption is noticeable, but negligible. However, a very significant effect of confining pressure on the kinetics of the course of the studied processes was observed. The structure of the pore space and the surface topography of the carbonaceous material before and after the processes of exchange sorption under confining loading changed little as a result of the experiments at confining pressure.

The substantive part of the dissertation ends with Chapters 7 and 8, in which the Doctoral Student conducted an extensive discussion of the results and presented a summary of her research. It should be emphasized that the most important goals of the dissertation were achieved. The previously stated thesis of the work was proven, demonstrating the effect of confining loading on the sorption capacity of the analyzed coals with respect to  $\text{CH}_4$  and  $\text{CO}_2$ . A significant effect of confining loading on the kinetics of exchange sorption processes was also found. The parameters displaced volume and sweep efficiency show a relationship with the value of confining load, but the quantitative correlation is relatively low.

### **Evaluation of the dissertation**

The reviewed dissertation is an original study. The idea is coherent, the doctoral student defined the objectives, the method of realization, chose the research methods and carried out the research process. On the basis of the results achieved, she correctly formulated conclusions. The strength of the work is the very original concept of the experiment, especially since

the reproduction of the real conditions that prevail in the coal seam is not easy. The constructed apparatus provides an opportunity for innovative research. The author proved that the confining pressure affects the parameters describing exchange sorption, especially the kinetics of the process. It was also found that an increase in the confining pressure decreases the sorption capacity of coal samples relative to dioxide. This is important for underground storage of this gas in coal deposits. The editorial aspect of the paper is also a strong point. In addition to some comments, which will appear later in the review, it is important to emphasize the good editorial level, the quality of the photographs and the readability of the figure, as this facilitated the proper perception of the results. Also notable is the very large number of bibliographic items, most of them from recent years, which demonstrates the acquisition of a broad spectrum of knowledge in the subject matter in which the doctoral student is active.

#### **Critical comments on the substantive side of the dissertation**

The paper contains several formal and factual inaccuracies:

- In subsection 3.4, in the section describing mercury porosimetry, equation number 13 is given for determining the pore size distribution. At the same time, the dissertation does not present the results of this analysis, why?
- The Langmuir isotherm equation is fitted to equilibrium sorption points in structural studies conducted by low-pressure gas adsorption and gravimetric sorption studies. It is described in two places, as Equation 14 and Equation 19. The duplication of the equation was not necessary.
- In the chapter describing the results of sorption tests without confining loading conditions (Chapter 5) and in subsequent chapters, the author presents graphs of the dependence of selected parameters and fits curves to them to determine the trend of their changes. At the same time, tables with equations of fitting these curves are provided below the graphs, which in my opinion would be much more readable if they were placed directly next to the graphs.

- Chapter 6, which constitutes the results of the study, begins with a literature review. I think the introductory section of this chapter would have been worth including in the Introduction section.
- Section 6.1.1 describes the relationships of exchange sorption as a function of time for each of the tested coals. The results of the experiments are extremely valuable, but the presentation of these values taking into account the mass of the sample is missing. Moreover, what would the course of the exchange sorption process look like as a function not of time, but of the volume of CO<sub>2</sub> injected?

In addition to the comments and observations presented above, there is also the question of what the author was motivated by when preparing the samples for testing. Wouldn't the use of a solid coal sample give a more complete representation of the actual conditions in the coal seam?

#### **Final conclusion**

The presented dissertation is well described, meets the criteria of good scientific practice, and contains results that can be considered as scientific novelty. Based on reviewing this dissertation, I conclude that MSc. Letica Teixeira Palla Braga has extensive theoretical and experimental knowledge in the area of research related to the dissertation and demonstrates the ability to conduct scientific work independently, and the dissertation presented for evaluation represents an original solution to a scientific problem. In light of the above, I believe that the dissertation by MSc. Letica Teixeira Palla Braga submitted for evaluation meets the criteria for a PhD degree (Article 187 of the Act of July 20, 2018, The Law on Higher Education and Science and requests that the Scientific Council at the Strata Mechanics Research Institute of the Polish Academy of Science accept MSc. Letica Teixeira Palla Braga for further stages of doctoral proceedings.

*Ja niżej podpisany stwierdzam, że recenzowana rozprawa doktorska Pani Letica Teixeira Palla Braga spełnia warunki określone w art. 187 ustawy z dnia 20 lipca 2018 r. Prawo o szkolnictwie Wyższym i Nauce i wnioskuję do Rady Naukowej Instytutu Mechaniki Górotworu Polskiej Akademii Nauk o dopuszczenie Pani MSc. Letica Teixeira Palla Braga do dalszych etapów postępowania w sprawie nadania stopnia doktora.*

