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REVIEW OF DOCTORAL THESIS

Thesis title:

pt.: Laboratory analysis of exchange sorption in coal under confining pressure conditions with reference to the description of the processes of underground CO_2 storage with simultaneous capture of CH_4

written by: Letícia Teixeira Palla Braga, MSc

Advisor: Norbert Skoczylas, DSc, PhD, BEng.

Co-advisor: Anna Pajdak, DSc, PhD, BEng.

The formal basis for the preparation of this review is the contract no. 01/08/2023 between the reviewer and the Head of The Strata Mechanics Research Institute of the Polish Academy of Science Przemysław Skotniczny, DSc, PhD, Eng dated July 27th 2023.

1. Content and formal assessment of the thesis

The doctoral dissertation submitted for review by Letícia Teixeira Palla Braga, M.Sc., is entitled "Laboratory analysis of exchange sorption in coal under confining pressure conditions with reference to the description of the processes of underground CO_2 storage with simultaneous capture of CH_4" The dissertation's supervisor is Norbert Skoczylas, DSc, Ph.D, BEng., professor of AGH, and the co-advisor is Anna Pajdak, DSc, Ph.D, BEng., professor of IMG PAN.

The dissertation counts 151 pages, including a reference list of 289 items, table of contents as well as the list of tables and figures. The dissertation consists of 6 main chapters, ends with two chapters i.e. discussion and conclusions.

In Chapter 1, "Introduction," the author points out environmental concerns related to the greenhouse gas (GHG) emissions, namely CO_2 and CH_4, on global warming. She analyzes the

greenhouse effect, presenting the current state-of-art. The general concept of GHG sequestration is discussed as a part of CCS (Carbon Capture and Storage). In particular, the concept of geological storage of CO_2 in coal seams is highlighted. The author presented information on the occurrence of methane in coal seams and the possibilities of its recovery with particular focus on ECBM - Enhanced Coalbed Methane Recovery. The author analyzed previous attempts to implement the ECBM concept in mining practice and projects carried out in Poland. The challenges related to a wider implementation of ECBM technology related to economic issues, geology and sorption processes on coal are outlined.

In Chapter 2, titled "Coal - gas system" the doctoral student included a broad compendium of knowledge on the forms of co-occurrence of gas and coal. The most important information on sorption was presented, including the types of isotherms and the relationship between the degree of coalification, maceral content, temperature, gas pressure, pressure, confining pressure, gas content, and sorption capacity. The author pointed out the differences between CO_2 and CH_4 sorption processes. The exchange sorption process was discussed. The world's literature on the effect of the confining load exerted on coal and the sorption properties was analyzed. The issue of gas transport in coal, including diffusion and filtration processes were discussed. The author meticulously presented the physical parameters describing the coal/gas system, including petrographic, structural and sorption parameters.

She concluded her extensive critical analysis of the state-of-the art by stating the thesis of the dissertation "The confining pressure has a significant influence on the CO_2/CH_4 exchange sorption processes in coal in the aspect of the sorption sweep efficiency and the kinetics of the process." The utilitarian aspect of the dissertation is based on the observation that the literature reports do not indicate studies on the course of the exchange sorption process occurring under controlled confining pressure applied.

Chapter 3 entitled "Research methodology" is an introduction to the research part of the reviewed thesis. The research methods and tools were described. The description begins with the methodology of preparing coal samples for the tests. Following that, the research methods applied were presented i.e. optical microscopy, SEM, porosimetry methods (mercury and gas), sorption tests using a sorption balance and exchange sorption tests using the author's test rig. The most important studies were carried out with the help of in-house made measurement apparatus described in detail in this chapter. The author presented the various functional blocks of the apparatus indicating their role in the research process. Measurement ranges and measurement uncertainties of individual

components of the apparatus were described. The concept of preparing coal samples as Teflon-encased coal briquettes molded in a dedicated briquetting machine was presented. The length of the samples was approximately 145 mm while the diameter was about 30 mm.

Chapter 4 presents the characteristics of coals under the study. The material was acquired from 3 polish coal mines and from an inactive coal mine in France. The coal material was subjected to detailed technical and petrographic analysis. The maceral composition and reflectivity of the vitrinite were determined. Noteworthy is the fact that the selection of coal for the study was broad and covering a wide range of vitrinite reflectance and consequently various degrees of coalification. In this chapter, results of scanning electron microscopy, mercury porosimetry and low-pressure gas adsorption. Based on these measurements, the doctoral student performed a precise analysis of the pore structure of individual coal samples.

Chapter 5 presents sorption experiments on coal free of confining pressure conditions and describes sorption tests performed on a gravimetric setup. These tests provide a starting point for the basic tests, which were performed on samples with confining pressure. An IGA-001 sorption balance was used for sorption tests and the tests were performed for 4 coal samples. As a result sorption isotherms for CH_4 and CO_2 were established. Each isotherm was determined on the basis of 3 sorption points. The test cycle was performed at temperatures of 278K, 313K and 353K. The temperature dependence of sorption capacities was determined and the variation of Langmuir sorption isotherm parameters as a function of temperature was discussed. The values of the effective diffusion coefficient for CH_4 and CO_2 for individual coals were calculated. The doctoral student also took into consideration the effect of temperature on the variation of the values of the effective diffusion coefficient. Performing a full measurement cycle for CH_4 and CO_2 it was possible to determine the preferential sorption of individual coal samples as the ratio of sorption capacities for CO_2 relative to sorption capacities for CH_4 as well as the Langmuir isotherm A-factors for CO_2 relative to CH_4. The doctoral student also examined the variation of preferential sorption as a function of temperature. The kinetics of the process were also analyzed. The author determined the ratio of methane diffusion coefficients in coal for CO_2 relative to CH_4 as a function of temperature.

Chapter 6, entitled Sorption experiments on coal under confining pressure conditions, contains the most important research of the doctoral student directly related to the topic and the thesis of the work. Among the studies conducted, sorption isotherms were determined for the coals analyzed for 4 values of confining pressure i.e. 1.5, 10, 20 and 30 MPa. For all the coals studied, the doctoral student observed a decrease in sorption capacity with an increase of the confining pressure.

CO_2 was injected into the CH_4-saturated coal sample which initiated exchange sorption. The sorption experiments under confining pressure were divided into 3 phases. In the first phase, the injected CO_2 displaced CH_4, thanks to a significant sorption preference taking its place. In this phase, only CH_4 was observed at the sample outlet. In the second phase, the coal was being saturated with CO_2 and the intensity of sorption exchange was decreasing. In this phase, a mixture of CH_4 and CO_2 appeared at the outlet while the concentration of CO_2 was increasing over time. The last phase of the experiment was the stabilization of steady CO_2 flow conditions and the full saturation of coal sample with CO_2. During this phase, the CH_4 concentration at the outlet was dropping to zero. The observations made in this experiment are consistent with similar laboratory experiments and pilot studies. As a consequence, series of graphs illustrating the variation of process kinetics and gas balance in the sample area depending on the confining pressure were presented. This allowed to determine how the confining pressure impacts the exchange sorption process. In particular, the doctoral student presented the results as the dependence of the Sweep efficiency parameter as a function of Displaced volume for individual confining pressures. These parameters efficiently characterize the exchange sorption process, as they allow to assess how much primary CH_4 was removed from the coal sample during sorption exchange, and what is the preferential sorption of coal for CO_2 over CH_4. Results indicate that there is a relationship between these parameters and the confining pressure but the effect of confining pressure is relatively small. A strong relationship, however, relates to the kinetics of the observed processes.

The coal material after sorption exchange was also analyzed from a structural point of view. Small changes were observed with respect to the reference material which was not subjected to the aforementioned experiments.

In the last, eighth chapter, the author of the dissertation summarized the results of the conducted research. The author drew attention to the most important aspects of the work, namely the possibility of applying confining pressure on samples subjected to exchange sorption tests. This reflects conditions of deep coal seams where overburden pressure exerts load on the coal. The doctoral student stressed the novelty of the study and methods applied to perform experiments. Long, cylindrical samples made it possible to conduct sorption analyses taking into account temporal and spatial dependencies.

The dissertation is well written with a proper technical English, yet some of the terms are not properly used (see section Critical comments and remarks). In my opinion, the dissertation is well organized with logical structure and clear statement of the aim of the study. The number and

selection of references is proper and exhaustive. The dissertation has a high scientific value and methodology used in the study can be applied for a rapid, cost-effective initial estimation of CO_2 storage potential of coals and methane recovery.

2. Assessment of the dissertation

The doctoral dissertation of Letícia Teixeira Palla Braga tackles an important issue of the energy transformation era where CO_2 storage is one of the technologies to reduce carbon emissions. At the same it also assesses the methane recovery potential of coalbeds. This may be an added value for projects related to the reduction of methane emissions from mines and brings new knowledge to the field of ECBM (Enhanced Coalbed Methane Recovery). It is worth noting that in the recent 10 years interest in the CO_2 storage in coalbed has decreased. **Nevertheless, the dissertation definitely adds new knowledge to the field. Major conclusions are as follows:**

- the highest sorption capacities were observed for the coal with the lowest vitrinite reflectance value,
- an increase in temperature caused a decrease in sorption capacity with respect to CH_4 and CO_2 while the decrease was exponential with respect to temperature,
- for CH4, a change in temperature from 278 K to 353 K resulted in a decrease in the sorption capacity of the coal of 4.3-6.3 times at 0.1 MPa; for CO2, a change in measurement temperature from 278 K to 353 K caused a decrease in sorption capacity of 3.9-4.6 times at 1.0 MPa, which means that the change in the value of this parameter with CO2 is slightly smaller than for CH4, an increase in temperature caused an increase in the values of effective diffusion coefficients for both CH_4 and CO_2,
- the ratio of the CO_2 coal sorption capacity with respect to the CH_4 sorption capacity of coal was highest in coal with the lowest vitrinite reflectance value and took lower values in coal with a higher vitrinite reflectance,
- the sorption affinity of coal towards CO_2 is higher than toward CH_4, which is most pronounced in coal with a lower degree of carbonization – this conclusion is in line with previous observations found in literature,

The most important conclusions that can be drawn from experiments carried out under confining pressure which were the core part of this dissertation are as follows:

- All sorption tests were carried out by the doctoral student at confining pressures: 1.5 MPa, 10 MPa, 20 MPa and 30 MPa - these values represent overburden pressure conditions at in-situ conditions of deep coal seams (up to about 1100 m depth of deposition),
- the sorption capacity of all tested coals with respect to CH_4 decreased with increasing confining pressure - for CH_4 pressure of 0.8 MPa, an increase in circular pressure by 10 MPa (corresponding to a depth of about 370 meters) resulted in a decrease in sorption capacity for individual tested coals in the range of 0.15 to 0.35 cm^3 CH_4/g,
- the study shows that there is a relationship between the degree of coalification of coals under study and the relative decrease in sorption capacity caused by the increase in confining pressure,
- the sweep efficiency parameter values were in the range of 87-95% which indicates that the CH_4 originally adsorbed in the coal was almost entirely recovered during exchange sorption processes,
- no correlation was found between the degree of coalificiation of coal and the value of sweep efficiency,
- the effect of the value of the confining pressure on the value of sweep efficiency was confirmed, but it is relatively small - the dynamics of the decrease in this parameter ranged from 0.27 to 1.3 percentage points for every 10 MPa increase in the circular pressure,
- an increase in confining pressure causes a decrease in the sorption capacity of the coals with respect to CO_2 - the decrease ranged from 0.27 to 0.39 cm^3 CO2/g for each 10 MPa increase in confining pressure,
- the relative decrease in sorption capacity with increasing confining pressure is more profound for CH_4 than for CO_2,
- Analysis of the changes in the displaced volume parameter, indicates that this parameter is slightly correlated with the confining pressure.

Taking all the above, the thesis stated in the dissertation: "Confining pressure has a significant effect on CO2/CH4 exchange sorption processes in coal in terms of sorption sweep efficiency and process kinetics" has been proven. However, the doctoral student points out that the effect of confining pressure impacts mostly the kinetics of the exchange sorption process. Such a strong effect of confining pressure on process kinetics is due to the strong decrease in permeability and diffusivity of coals that occurs with increasing confining pressure.

A practical conclusion drawn by the doctoral students is that the decrease in sorption capacity with increasing confining pressure is straightforward but not critical for the overall concept of geological CO_2 storage with CH_4 recovery. According to the doctoral student, sorption capacities under confining pressure range up to 30 MPa (corresponding to a seam depth of about 1000 m) do not decrease drastically and therefore coal seams can be considered as a potential sites for CO_2 storage (obviously, if fulfilling other important conditions). The sweep efficiency decreases, depending on the coal type, from about one to several percentage under confining pressure of up to 30 MPa which confirms the assumption that the depth is not a crucial factor for CO_2 storage.

The set of tests performed by the doctoral student, applied methodology and formulated conclusions show that she is able to conduct scientific research independently and prepare a scientific experiment. It also indicates a high level of knowledge of the PhD candidate and ability of critical thinking.

3. Remarks and critical comments

Despite the general positive reception of the thesis content I do have some questions and comments to some of the points of the thesis:

1. The title of the thesis is somehow misleading and does not reflect ideally its content. The second part of the title "(...) description of the processes of underground CO_2 storage with simultaneous capture of CH_4" gives a reader impression that methane is captured in a process. In fact, the thesis mainly deals with Enhanced Coalbed Methane recovery or methane "sweeping" with simultaneous injection of CO_2. I would recommend in rethinking this title in further publications.
2. On page 20 a sentence appears: "Deeper shafts (>750 m) are great because the pressure is higher and the temperature higher, keeping the CO_2 supercritical". The shaft is not the right word as it refers to vertical mine working and the meaning here is supposedly different.
3. Page 21, paragraph 3: „Nucleus experiments showed that a significant decrease in permeability could be caused by coal swelling". What "nucleus experiment" mean?
4. Similarly on page 21 in the same paragraph 3: "fracturation of the coal veins". In oil and gas terminology the term "fracturing" or "fracking" is used. Coal vein in this context is also not a proper phrase.
5. I'm missing a more detailed description and distinction of the excess (Gibbs) and absolute sorption. I'm not sure if the sorption capacity is reported as an excess or absolute sorption.

6. The 'Research methodology' chapter should include a more detailed description of the coal briquette. It is not clear how the briquettes were prepared. Specifically the following would be explained:
    a. What pressure was applied to form a briquette?
    b. Is there any binding agent?
    c. The grain size analysis shown in Figure 4-3 refers to coal before briquetting?
    d. How coal was prepared before briquettes were formed? Was it sieved to a particular fraction?

    These questions are important as the maceral content may change between sieved fractions. It is a common knowledge that in fine coal particles the ash content is usually higher than in coarse particle sizes.
7. What type of flowmeter was used for outlet gas composition measurement? Such flowmeters are often calibrated for a single gas rather than a mixture of gases. If this is not the case this should be clearly stated in order to clarify any ambiguities.
8. In Table 3-1 parameters of coal briquettes are shown. The porosity of briquettes is rather high in comparison to a solid coal cores. On the other hand the permeability of the BUD, ALB, SIL briquettes is rather low (similar to the *in-situ* permeability of coals in Poland). For sample SOB the permeability is relatively high (81.03 mD) whereas the porosity is almost the same as for BUD sample with permeability of 0.13 mD. Such huge differences in permeability are not reflected in the CO_2 breakthrough times during dynamic experiments of CO_2/CH_4 exchange sorption on briquettes in Chapter 6.2. I would like to ask for a more detailed explanation of this phenomena.
9. For low permeability samples such as BUD the swelling effect should be observed and in all cases it is rather negligible. This should be explained and a more detailed discussion would be needed.
10. The second part of the statement in chapter 6.3 that the grains were broken during exchange sorption process is in my opinion too far-reaching. It is difficult to imagine that a physical sorption process could make grain more rounded. I would consider only the process of briquetting or confining pressure as the cause of this phenomena. The table 6-7 where the skeletal density of the samples before and after exchange sorption is shown does not provide a relevant information as the differences are within the experimental error and should be considered as negligible.

4. Review summary and final conclusion

I explicitly state that the dissertation is an original solution of a scientific problem. The doctoral student has demonstrated an excellent ability to formulate scientific problems, conduct research and analyze the results. The doctoral dissertation submitted for review is in the scientific discipline of Environmental Engineering, Mining and Power Engineering, represents an independent solution of the problem, and the Doctoral Student has demonstrated a very high level of theoretical and practical knowledge.

I conclude that the doctoral dissertation of Letícia Teixeira Palla Braga, MSc entitled "Laboratory analysis of exchange sorption in coal under confining pressure conditions with reference to the description of the processes of underground CO_2 storage with simultaneous capture of CH_4" fully meets the conditions specified in art. 187 of the Act of July 20, 2018, Law on Higher Education and Science with Article 179(1) and (2) of the Act of July 3, 2018, provisions introducing the Law on Higher Education and Science (Journal of Laws of 2018, item 1669, as amended) and I request that it be admitted by the Scientific Council of The Strata Mechanics Research Institute of the Polish Academy of Sciences for public defense.

Gliwice 26.09.2023 r.