Likar and Tajnik: Analysis of CO₂ Adsorption in Different Lytotypes of Lignite

Abstract

The problem of reducing CO₂ emissions in the atmosphere is indirectly related to the potential storage options in different environments in the earth’s crust. One of the promising possibilities for reducing emissions of carbon dioxide (CO₂) into the atmosphere is the geological storage of CO₂ in deep, unminable coal seams. Measurements of the CO₂ adsorption of 10 lignite samples from the Velenje Coal Mine and different rocks and soils from surrounding areas were carried out using Langmuir isotherm principles. Adsorption measurements were taken using the gravimetric method, where exposed samples at a selected temperature to different CO₂ pressures were done. Also, the measures of mass changes in the measuring and reference cells were the basis of calculations for the mass and volume of the adsorbed CO₂. Measurements were taken at a temperature of 23 °C and at CO₂ pressures varying from 18 to 38 bars. The results of laboratory investigations of the lignite from the Velenje Coal Mine have shown the capacity adsorption from 9 to 14 m³ CO₂/ton (at measuring pressures up to 4 MPa) of coal in the given conditions, which cannot compare with other rocks and soils.

Keywords: Lignite, rock, carbon dioxide, adsorption, geological storage, Langmuir isotherm

1. Introduction

Many new possibilities exist how to store the increasing amounts of carbon dioxide (CO₂) and other gases in the atmosphere in different ground and seawater environments. Many scientific reports conclude that it will be necessary to reduce the quantity of CO₂ emissions into the atmosphere.

One of the promising possibilities for reducing CO₂ emissions is its storage in deep, unminable coal seams. CO₂ injection in unminable coal seams could be one interesting option for both the storage and methane recovery processes¹. These deep coal seas, situated at 300 to 1500 m below the surface, are known for their ability to retain enormous quantities of gas, primarily methane (CH₄), which may be replaced with CO₂ or other gases (Figure 1). In comparison with the acquired methane a larger volume of CO₂ may be stored.

For measurement of the adsorption isotherms, the gravimetric method was used. In this method, the increasing mass of an empty reference cell and a cell containing lignite or other tested rocks and soils is measured while both cells are connected to a gas supply at the same temperature and CO₂ pressure. The data obtained in this way are used to calculate the mass of adsorbed gas at different pressures.

The subsurface earth layers are the largest carbon reservoir, which stores a great majority of the world’s carbon stocks in coal, oil, gas, organic-rich shale, and carbonate rocks. The geological storage of CO₂ in the Earth’s crust is a natural process that has developed over hundreds of millions of years. CO₂ was formed through biological and volcanic processes by chemical reactions between rocks and liquids accumulating in the subsurface layers. It was released from carbonate minerals as a gas, in supercritical form, as a gas mixture, or as pure CO₂. For the
purposes of geological storage, CO₂ should be initially compressed, usually up to a dense, compact, liquid phase called the "supercritical phase." The temperature of earth layers increases with depth depending on the geothermal gradient. CO₂ density also increases in depths up to approximately 800 m or more, while injected (i.e., gas forced under pressure) CO₂ is in the supercritical phase. The possibilities of geological storage of CO₂ are diverse and depend on the geological composition and structure of rocks. Storage is therefore possible in the interiors of basins or caverns, emptied oil and gas fields, deep coal seams, and deep-lying sedimentary layers saturated with saltwater (Figure 1).

Unmined coal seams allow storage, which involves trapping, in which the injected CO₂ is adsorbed onto the pores’ surface filled by other gases (such as methane), which can be displaced with proper technology. One important condition is the effectiveness of the technique of injections which depends on the gas permeability of the coal seam. It is generally accepted that coal seam storage is most likely to be feasible when undertaken in conjunction with enhanced coalbed methane recovery (ECBM) in which the commercial production of coal seam methane is assisted by the displacement effect of the CO₂. Coal is in principle an attractive storage medium for CO₂ because it adsorbs strongly to the coal locking it firmly in place.

In reality geological storage involves potential risks for humans and ecosystems, as there is the possibility of CO₂ leakage from operational and abandoned boreholes, and leakage through defects and cracks in the ground layers. Gas leakage may also reduce the quality of ground water, damage sources of hydrocarbons or minerals, and have fatal effects on plants and subterranean animals. The release of CO₂ back into the atmosphere would also affect the health of surrounding inhabitants or threaten their safety. To mitigate or prevent the consequences of any possible gas leakage would require a carefully selected location, efficiently organised supervision, adequate monitoring programmes providing early warnings that the storage area is not functioning as expected, and plans of rehabilitation procedures for stopping or controlling CO₂ emissions.

2. Storage Formations

A great many sedimentary layers throughout the world are suitable for CO₂ storage. Generally speaking, storage areas should have an adequate storing capacity and injection possibilities, a satisfactory protective cover layer or adequate barriers, and a sufficiently stable geological environment to ensure the necessary stability of the storage area. The criteria for the adequacy of storage formations include: characteristics of formations (tectonic activity, type of sediments, and geothermal and hydrodynamic regimes); composition of formations (hydrocarbons, coals, salt); industrial development and infrastructure; and socially disputable issues (stage of development, economy, environmental issues, public education, and public opinion). Poor storage possibilities can be found in geological formations that are thin (below 1000m), have an insufficient reservoir capacity, poor protective cover layers, intensive tectonic damage and fractures, folds within layers, highly discordant layers, or too high pressure in reservoirs. The efficiency of CO₂ storage in geological formations is defined as the quantity of CO₂ that can be stored per unit of rock volume. The efficiency increases with increasing density of CO₂. Storage safety also increases with increasing density, as the cover pressure results in upward migration, which is naturally greater with lighter liquids. CO₂ density increases intensively with depth. After the transition from a gaseous to a liquid state, the density increases minimally and may even decline with continuing depth, which depends on the temperature gradient. "Cold" sedimentary layers with small temperature gradients are more suitable for storage, because CO₂ attains a higher density at a smaller depth (700–1000 m) than “hot” sedimentary layers, which have large temperature gradients where similar densities occur at greater depths (1000-1500 m).

Most important in the selection of a location are porosity and layer thickness (for storage capacity), as well as its permeability (for injection). Porosity normally decreases with depth due to compressing and cementing, which reduces storage possibilities and efficiency. The storage formation must be covered with an extensive barrier layer like shale, salt, or anhydrite, which prevents the CO₂ from escaping into higher lying, shallower rocks and then onto the surface. Storage areas in non-transparently fractured and otherwise tectonically damaged sedimentary rocks or their parts, particularly in seismically active areas, should be carefully selected, unless the damaged
rocks have been rehabilitated and made impermeable to CO₂.

2. 1. Coal Seams

Coal seams contain gas, which is mainly comprised of CH₄ and smaller quantities of CO₂. Nitrogen (N₂) is also present in certain areas, but only in small quantities (<10% of total gas volume). Other higher hydrocarbons (C₂⁺) can also be present in some deeper coals, yet these generally do not exceed 12% of the total gas. The gas contained in deep coal seams is usually of thermogenetic origin, which means that it was formed in the process of organic metamorphism (chemical and physical changes in material at high temperatures and pressures). For shallow coals, gas is generally a by-product of anaerobic biological activity. Different coals contain various micro, mezzo, and macro pores. Usually micro pores are characterized with diameters less than 2 nm, the macro pores are pores with a diameter of 50 nm. Pores of intermediate size are called mezzo pores. Although coal is a rock for gas collection, they are markedly different from conventional reservoirs for oil. The volume of pores in coal is small and the majority of gas in coal consists of adsorbed gases, which cover the surface of the micro pores. A coal micro-pore surface area can reach several hundreds of square meters per gram of solid, making large areas available for gas adsorption.

The micropore surface area has been shown to be in the order of 20 to 200 m²/g, therefore making large areas available for adsorption of gases. The measured size depends on the type of sorbent, for example CO₂ cover a larger surface area than N₂ because it has better access to micro pores of coal⁵.

The amount of adsorbed gases phase in coal depends not only on the free surfaces, but also on the state of equilibrium between the attractive and reflective surface forces - Van der Waals' forces⁶. Balance is achieved when the total surface potential energy of gas and solids is at its minimum. Gas adsorption on coal is a long and weak interaction, and physiological phenomenon known as „sorption“ or „physical adsorption.“ The physiological process of sorption of gas molecules lose kinetic energy and adhere to the surface of coal. The amount of energy released is an indicator of adsorption intensity, and is generally less than half the enthalpy of condensation of methane and also by condensation of CO₂. The order of magnitude of energy released in physic sorption is 20 kJ mol⁻¹, while the gas molecules chemo sorption form a covalent chemical bond with the molecules of a solid surface, and the released energy is much higher; usually order 200 kJ mol⁻¹.⁷

As already mentioned, the volume of surface pore system in coal greatly exceeds the volume of pores, so the majority of the gas stored in the adsorbed phase. This is particularly true at low pressures, where almost all the gas in the coal in the adsorbed phase. The potential volume of gas that can be adsorbed onto the coal can be assessed according to its inner surface.⁵

Coal contains various fractures and cracks, which contribute to the permeability of the system. Although coal is a collecting material for gas, it differs distinctly from ordinary oil collectors because the quantity of stored gas may exceed the volume of open pores in the coal’s surface. The volume of pores in coal is small and the majority of gas in coal is adsorbed gas.

Gaseous CO₂, injected through boreholes, will pass through cracks in coal, spread across coal seams, and adsorb on the surface of coal micropores. At this point, gases with lower affinity (e.g., methane) will escape from the coal.

3. Measurement of CO₂ Adsorption Using Langumuir’s Isotherm⁵

The surface of a solid shows a strong affinity to gas molecules that come into contact with a surface. Adsorption is the process of capturing or bonding molecules on a surface. The opposite process is „desorption,“ which means the removal of gas molecules from a surface. The molecules of the adsorbate and adsorbent or substrate (base) may react physically or chemically, which is called physical or chemical adsorption. In contrast to adsorption, absorption is the penetration or passing into the interior of another phase.

Langmuir’s isotherm is the simplest physically probable isotherm that is based on the following assumptions:

1) Adsorption does not occur beyond monolayer coverage (θ = 1);
2) There is no interaction between adsorbed atoms or molecules;
3) All sites on the surface are equivalent and can adapt. There is maximally one adsorbed molecule per one surface site;
4) The ability or possibility of a molecule to get adsorbed at a particular site is independent of the occupation of neighbouring sites;
5) Thermodynamic equilibrium is established between adsorption (k_ads) and desorption (k_d). The rate of adsorption is proportional to the pressure, while the rate of desorption is not.

3. 1. Expression for Gas Storage in Coal

The adsorbed quantity of gas depends on the energy of free gas and, consequently, on temperature and pressure. At a given temperature and pressure and after a sufficient period of time, the adsorbed phase and the free phase are in kinetic equilibrium, namely the levels of adsorption and desorption on the surface of coal pores are equivalent. The kinetic equilibrium of adsorbed gas may be expressed as...
using Langmuir’s equation: 5

\[ c_{\text{ads}} = \frac{V_L \cdot p}{p + p_L}, \]  

(1)

where \( c_{\text{ads}} \) represents the concentration of adsorbed gas (volume of gas per unit of coal mass), \( p \) is the gas pressure, while \( V_L \) and \( p_L \) are the experimentally determined coefficients. The \( V_L \) coefficient represents the maximum storage capacity of gas and is called “Langmuir’s volume parameter,” whereas \( p_L \) is “Langmuir’s pressure parameter” and represents the pressure of gas at which coal adsorbs the gas volume, which is equal to half of its maximum capacity, or \( c = V_L / 2 \), when \( p = p_L \).

At small pressures, Langmuir’s equation is simplified into a linear equation of pressure (Henry’s law) with linearity coefficient \( V_L / p_L \). Such small \( p_L \) values indicate a steeper adsorption curve which limits more quickly towards the final value \( V_L \). This means that coal with small \( p_L \) values attain its full storage capacity at lower gas pressures compared to coal with high \( p_L \) values.

Because Langmuir’s equation is based on a monolayer adsorption mechanism (isotherm of the first type), it is useful in measurements at small pressures (below 60 bars), as well as for gases in which the size of molecules and the diameter of coal pores are approximately of the same size.

3. 2. Gas Concentrations in Coal

Coal in-situ contains gas in the adsorbed phase on the surface of micropores, and as a free phase compressed into macropores. The concentration of free gas \( c_f \) (volume of gas per unit of coal mass captured at atmospheric pressures) may be expressed as:

\[ c_f = \frac{\varepsilon \cdot p}{\rho \cdot p_{\text{atm}}}, \]  

(2)

where \( p \) is the gas pressure, \( \varepsilon \) is the porosity of coal, \( \rho \) is its density, and \( p_{\text{atm}} \) is the atmospheric pressure.

The concentration of the adsorbed phase \( c_{\text{ads}} \) is normally larger than the concentration of the free gas \( c_f \). Theoretically, one may conclude, by a comparison of equations (5) and (6), that at pressures which are the same or greater than a certain pressure \( p_c \), the density of free gas is so high that the mass of free gas could become comparable to the mass of the adsorbed phase:

\[ p \geq p_c = \rho \cdot p_{\text{atm}} \cdot \frac{V_L}{\varepsilon} - p_L \Rightarrow c_f \geq c_{\text{ads}} \]  

(3)

As shown in the equation above, in case of high \( p_L \) values and the high porosity (\( \varepsilon \)) of coal, the concentration of coal gas may be the same or larger than the concentration of adsorbed gas.

3. 3. Method of Determining CO₂ adsorption

The gravimetric method measures the growing mass of coal, which becomes saturated with gas at increased pressure. The method was explained in details by Saghafi et al. 5 An equation of this state is derived from the density of free gas. Density is measured simultaneously in an empty reference cell, which is kept at the same pressure and temperature as that of the cell containing coal.

4. Measurements and Results

The lignite sample was first placed into a pressure pipe whose internal diameter matched the diameter of lignite core (\( l = 29 \text{ cm} \); \( r = 10 \text{ cm} \)). If necessary, the sample was forced into the pipe with a press. The lignite sample remaining at the ends of the pressure pipe was removed by cutting and planning. Thus prepared, the sample was inserted into the measuring apparatus for the gravimetric measurement of CO₂ adsorption in lignite. Tests were performed at a constant temperature and at varying pressures of CO₂.

In this research the disposal of 10 samples of lignite from the Velenje Coal Mine were prepared. Five of them were from the same location, so that the degree of adsorption of coal from various locations was also compared. Measurements of the CO₂ adsorption of different geological materials to compare CO₂ adsorption capacity between lignite and other materials were also completed. Special attention was paid to sandstone, marl, claystone, clay with sand (or sandstone), and limestone. Our results were represented as amount of adsorbed CO₂ (\( m_{\text{ads}} \), \( V_{\text{ads}} \) and \( c_{\text{ads}} \)) in g, dm³ and m³ per tonne of material.

Figure 2. Adsorbed CO₂ mass as a function of pressure.

Lignite can absorb more CO₂ at higher pressures (Figure 2).

The relative error was determined from the difference between the maximum and final mass in the reference cell. The difference in masses occurred due to less than ideal
sealing, as there were minimal gas leakages at the contacts of different surfaces. The average relative error was 13.1%. The gas pressure during measurement was constant, because the valve allowed for continuous gas inflow.

It is evident that Langmuir’s adsorption isotherm is obtained in the same lignite, and described by equation (5) (Figure 5). The influence of adsorbed gas volume depends on its pressure, the coefficients $V_L = 20.8 \text{ cm}^3/\text{g}$ and $p_L = 34.0 \text{ bar}$ were determined for the first coal, and $V_L = 14.2 \text{ cm}^3/\text{g}$ and $p_L = 32.0 \text{ bar}$ for the second coal (Figure 5).

The CO$_2$ volume that can be adsorbed per ton of lignite at a specific pressure was also calculated. These results are shown in Figure 6, where Langmuir’s isotherm is also obtained as a solution (Figure 7). The coefficients obtained from the equation are $V_L = 32.6 \text{ m}^3$ and $p_L = 51.8 \text{ bar}$ for the first coal, and $V_L = 16.5 \text{ m}^3$ and $p_L = 29.6 \text{ bar}$ for the second coal.

Figure 8 shows the dependence of gas pressure on the adsorbed volume dependent on gas pressure. Such dependence is selected because obtained line with an incli-
nation of $1/V_L$ and a $p_L/V_L$ segment on the ordinate has a physical base. The coefficient values $V_L = 20.1$ cm$^3$ and $p_L = 32.1$ bar for the first coal, and $V_L = 15.2$ cm$^3$ and $p_L = 35.9$ bar for the second coal can be obtained from the line equation.

Figure 9 shows the dependence of gas pressure on the adsorbed mass per ton of lignite dependent on gas pressure. From the line equation it’s clear that the coefficient values $V_L = 32.2$ m$^3$ and $p_L = 50.8$ bars for the first coal, and $V_L = 17.2$ m$^3$ and $p_L = 31.6$ bar for the second coal.

The difference in the values of parameters obtained from the line equation and the adsorption curve equation ranges from 1 to 6% for the first lignite lithotype, and from 4 to 11% for the second lignite lithotype.

In past decade a few sorption tests were done on coal dust and flotation waste from coal processing in abandoned coal mines, but did not find more different results compared with geological materials.

When analyses results of other geological materials (i.e., sandstone compared with lignite) it showed the largest adsorption capacity among the other geological materials but no higher adsorption was noticed than in lignite. The injected CO$_2$ content into the measured samples ranged up to 10.9 m$^3$/t (sandstone at 20 bar; Figure 10). Other materials did not show impressive CO$_2$ sorption (clay with sand or sandstone, marl, claystone, limestone). Only sandstone sorption can be compared to the sorption of lignite samples. The measurements performed indicate that lignite from the Velenje Coal Mine can adsorb from 9 to 14 m$^3$/ton of lignite. Just to be clearer, the comparison between these results on two litho types of lignite with results from Turkey, Australia, United States, and Canada. Coal from Turkey can adsorb from 2 to 48 m$^3$/ton of coal; coal from Australia can adsorb from 40 to 80 m$^3$/ton of coal (pressures up to 7.38 MPa); and coal from the United States can adsorb from 12 to 16 m$^3$/ton of coal (pressures up to 25 MPa was done).

5. Conclusion

One of the promising possibilities of reducing CO$_2$ emissions into the atmosphere is geological storage. Geological storage is possible if there is a geological layer lying at a suitable depth, with high porosity and permeability, which is capable of accepting larger quantities of CO$_2$, and when there is an impermeable cover above this layer preventing the migration of CO$_2$ towards the surface. The possibilities of CO$_2$ storage are therefore in the interior of basins or caverns, emptied oil and gas fields, deep
layers of coal, and in deep-lying sedimentary layers saturated with saltwater.

Hence, the possibility of storing CO₂ also exists in coal seams. For this purpose we conducted tests using lignite samples from two different locations in the Velenje Coal Mine. Using the gravimetric method, samples of two different lignite lithotypes were exposed to different CO₂ pressures at the same temperature. The change of mass in the measuring and reference cells was measured, and the measurements used to calculate the mass and volume of adsorbed CO₂. Measurements were conducted at a temperature of 23 °C and at pressures ranging from 18 to 38 bars. Using Langmuir’s isotherm, the adsorption properties of both types of lignite were presented. The results of measurements indicate that lignite from the Velenje Coal Mine can adsorb from 9 to 14 m³ CO₂/ton of lignite, which is comparable to the results which were carried out on coals from Turkey, Australia, and the United States. Comparison with other geological materials which were also tested clearly showed that the adsorption capacity of CO₂ was lower than in lignite.

6. References


Povzetek

Naraščanje koncentracije ogljikovega dioksida (CO₂) in drugih plinov v ozračju je glavni vzrok globalnega segrevanja. Strokovnjaki se strinjajo, da bo treba zmanjšati količino izpustov CO₂ v atmosfero. Ena izmed obstoječih možnosti zmanjševanja emisij CO₂ je skladiščenje v globokih nahajališčih premoga, ki v bližini in daljini prihodnosti ne bodo odkopani. Te globobe plasti premoga, ki se nahajajo od 300 m do 1500 m pod površjem zemlji, so znane po tem, da lahko zadržujejo ogromne količine plina, primarno metana (CH₄), ki se ga lahko nadomesti s CO₂ ali katerim drugim plinom. V primerjavi s pridobljenim metanom se lahko shranji v te premoge sloje približno dvakrat večjo prostornino CO₂.

Postopek, ki je bil razvit za merjenje adsorpcijskih izoterm, temelji na gravimetrični metodi. Pri tej metodi se meri naraščanje mase prazne referenčne posode in posode, ki vsebuje premog, medtem ko sta obe posodi povezani z dovodom plina pri enaki temperaturi in tlaku. Iz tako pridobljenih podatkov izračunamo maso adsorbiranega plina pri različnih tlakih.

Preizkusi, ki so bili izvedeni v Laboratoriju za mehaniko hribin na Naravoslovnotehniški fakulteti, Univerze v Ljubljani, na deseti vzorcih lignita, odveženi v Premogovniku Velenje, so pokazali, da je navedeno metodo možno uspešno uporabiti za določanje adsorpcijskih lastnosti geoloških materialov. Meritve adsorpcijskih izoterm so bile izvedene pri temperaturi 23 °C in pri tlaku CO₂ od 18 bar do 38 bar. Rezultati meritev so omogočili predstavitev adsorpcijskih lastnosti obeh litotipov lignita z Langmuirovo izotermo.

Lignit, katerega vzorci so bili odvzeti na prvi lokaciji, lahko adsorbiše do okrog 13,6 m³ CO₂/t premoga pri tlaku 38 bar, medtem ko ima lignit z druge lokacije lastnost da pri 37 barih adsorbiše 9,0 m³ CO₂/t premoga.