A SOLUTION FOR CARBON DIOXIDE STORAGE AND COAL BED METHANE BENEFICIATION IN JIU VALLEY COALFIELD

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Abstract: The paper deals with a proposal of an integrated project for CO2 storage coming from the coal burning power plants and a joint CH4 (so called CBM) recovery and its valorization in energetic applications which will lead to a substantial reduction of the delivering price for the produced energy. Coal deposits considered to be non-exploitable for technical or economic reasons are proven to be of major importance for the storage of CO2 captured from industrial burning installations because coal is characterized by the existence of large volumes of micro-pores inside which are able to physically absorb various gases, one tonne of coal containing even more than 25 m3 of absorbed methane, and at the same time it being characterized by higher affinity for carbon dioxide gas than for methane. Because the capture, processing and transport of carbon dioxide are technically resolved, the paper is focused mainly in the issue of storage, and the joint process of methane gas replacement and its boosted delivery from coal seams. In both these processes, the main issue is the adsorption/desorption capability of the coal versus CO2 and CH4, on which basis the in place methane amount and the carbon dioxide storing capacity can be calculated. The main outcome of the study is the proof of feasibility of this technology in the Jiu Valley coal basin, which will contribute to the revitalization of coal mining and energy production activity in the area.

Keywords: carbon dioxide, Greenhouse Gas, beneficiation, Jiu Valley

1. INTRODUCTION

Among the large range of clean coal technologies, the Carbon Capture and Storage (CCS) technology seems to be the most promising option, because of its high potential of reducing carbon dioxide emissions, coming from the fossil fuel burning. Apart from other emission mitigation technologies, the CCS can beneficiate from existing research results regarding capture, sequestration, liquefaction and transportation already demonstrated in pilot projects, proving its technical, technological and economic feasibility.

As the Intergovernmental Panel on Climate Change Special Report states, „Carbon dioxide (CO2) capture and storage (CCS) is a process consisting of the separation of CO2 from industrial and energy-related sources, transport to a storage location and long-term isolation from the atmosphere” is considered „as an option in the portfolio of mitigation actions for stabilization of atmospheric greenhouse gas concentrations”. Nevertheless, at the moment they are a lot of unsolved financial, commercial, social and legal and also technical problems, related mainly on the storage issues, which may have a strong influence on the global implementation and development of this technology.

As a result of the coal mining downsizing in Jiul Valley coalfield, the extraction activity is concentrated only in the perimeters which allowed optimal geologic-mining conditions to apply mining methods leading to best economical results.

This downsizing of mining perimeters and the closure of non-performing mine plants led to the situation in which only 30% of reserves are considered in concessions, and only 5% are considered as industrial reserves.
The coal deposits considered to be non-exploitable by technical or economic reasons can be used as storage environments for large volumes of the captured carbon dioxide resulted from the burning in coal fired power plants, and, in plus, the injection of the carbon dioxide in the virgin coal seams can be used as a stimulant of the contained methane gas, which produces a double benefit: an environmental one, avoiding the emission of a GHG namely the methane, and an economic one, by using it as a secondary energy resource or raw material for chemical industry.

2. SEQUESTRATION OF CO₂ IN GEOLOGIC FORMATIONS

In order to be stored in geologic formations, the carbon dioxide must be compressed until the supercritical (liquid) state, which is maintained as is in depths over 800 m, as a result of the geothermal gradient and strata pressure joint action. As storage media, can be used exhausted gas and oil reservoirs, coal seams, and deep saline continental or off-shore aquifers.

The storage media must satisfy many criteria, among which the most important are: porosity, permeability and storage capacity; the presence of an impermeable rock overburden, or a catching structure which avoid the vertical migration of the sequestrated CO₂; location at a depth over 600 meters, where the strata pressure is high enough for maintaining the supercritical state of the dioxide, maximizing the storage capacity.

The un-exploitable coal seams represent appropriate storage media for CCS technology. The coal is characterized by the existence of a huge number of micro-pores in which different gases are absorbed or adsorbed physically, mainly methane, e.g. one ton of coal can contain about 25 m³ of methane.

Meanwhile, the coal presents a higher affinity for the carbon dioxide than for the methane (figure 1), so the ratio of volumes absorbed in the coal matrix (VolumeCO₂/ VolumeCH₄), can vary from 1 (the case of anthracite), until 10 or more for other sorts of coal.

While injecting carbon dioxide in coal seams the methane will be released, so by CCS the recovery rate of CBM can reach 90 % in comparison with the usual 50 % of CBM drainage.

Only the virgin coal seams can be candidates for CCS but it must be avoided a possible future conflict between CCS and an eventual demand of mining out the coal seam considered.

3. POTENTIAL STORING CAPACITY ASSESSMENT

It exists many methods to establish the storing capacity, in general based on the content of gas in place, to be replaced with CO₂, and the geometry of the reservoir (strata).

A method largely accepted in Canada, Australia and UK [2], is used for many type of reservoirs such as coal seams, exhausted oil/gas reservoirs, salt formations. For the non-exploited coal seams, which are interesting for our study, one determines the initial gas volume, IGIP (Initial Gas In Place) using the formula (1):

\[
IGIP = A \cdot h \cdot \bar{n}_c \cdot G_c \cdot (1 - f_w - f_m), \quad m^3
\]

where:
A and \( h \) – surface, respectively the thickness of the seam (in m², respectively m);
\( n_c \) – coal density (in t/m³).
$G_c$ – gas content factor (m$^3$/t);

$f_a$ and $f_m$ – ash and respectively moisture content of the coal.

Nevertheless, while calculating the potential storage volume of a reservoir, one must distinguish between. In this respect, the theoretical volume is based on theoretical models and includes economically non-viable hypotheses, the effective volume take into account the technical and technological limitations and the particularities of the strata, and the real volume penalize the last one with economic restrictions.

4. DETERMINING THE CARBON DIOXIDE STORING CAPACITY IN COAL

In comparison with other storing media, e.g. exhausted oil/gas reservoirs, salt aquifers etc., for which the research is somewhat advanced enough, the research regarding the storage of CO$_2$ in coal seams is relatively recent, the results validating only partially the theoretical assumptions.

For the assessment of storing capacity of carbon dioxide in Jiul Valley’s coal seams, we may use the results obtained till now regarding the methane absorption in hard-coal.

While in natural gas reservoirs where the methane under pressure fills the pores of host rock, in coal seams this is only in a small amount in free state in the rock’s pores, the main part being physically adsorbed by Van der Waals bonds.

In coal seams, mainly in deep ones, the amount of trapped methane gas is about 30-60 m$^3$/t.

From point of view of the storage mechanism, at present three forms are accepted: free gas, physically or chemically bonded [3, 5].

The quantity of free gas when the methane fills all the voids (pores, fractures, cleats) represents only 5 to 10 % of total gas content, depending on porosity, pressure and temperature.

The gas pressure may reach 30-40 bar, while the volume of pores able to store gas depending on pressure and moisture content vary from 0,01 to 0,11 m$^3$/t for coal and from 0,004 to 0,04 m$^3$/t for sandstone.

The largest share of gas in coal is stored in the form of physically or chemically bonded in adsorbed, absorbed and chemosorbed state reaching in many cases 90 % of total amount.

In adsorbed state (in which we find about $\frac{3}{4}$ of total stored gas volume) the bond between gas molecules and the surface of solid matrix micropores walls is realized by the intermolecular attraction forces, called Van der Waals forces, and the gas is forming a thin layer around the coal molecules.

The most important aspect of this kind of bond is represented by its reversibility, the stored gas being easily released by the coal matrix facilitating its extraction.

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In bonded state, the gas is present also in absorbed state, in which case, the molecules of gas penetrate among coal molecules, without chemically react with, forming a solid solution. The desorption of this quantity of gas is possible only if the coal is highly grinded.

In chemosorbed state, between the gas molecules and the coal molecules a chemical bond take place, and the release of the gas is possible only by special procedures, but because of the reduced share of the gas existing in this state (less than 3 %), it is not interesting in any aspect.

![Fig. 2. Adsorption isotherms for dry coal as a function of pressure and volatile material content.](image-url)
In order to have a correlation between the adsorption capacity of coal for methane and carbon dioxide, we can refer to the results of lab researches for these two gases as a function of volatile material content and absolute pressure (figure 2).[3]

Analyzing the two graphs above, we can notice that:
- regardless the content of volatile materials, in the same conditions of pressure and temperature the adsorption capacity is 1.5 times greater for carbon dioxide than for methane;
- increasing content of volatile materials produces the decrease of the adsorption capacity regardless the type of gas in question.

The storing capacity, i.e. the adsorbed gas volume is dependent on pressure at a given temperature and can be described by the Langmuir’s law [4] which states that when a gas is in contact with a solid an equilibrium state occurs between the gas and solid molecules, which is dependent on relative stability of the adsorbed (bonded) gas related to free state, the gas-solid system’s temperature at the separation level and the pressure of the gas at same location.

The last two factors, i.e. the pressure and the temperature has contradictory effects, regardless the kind of gas, so we can increase the adsorbed volume by increasing the pressure and we can reduce it by increasing the temperature. (figure 3).

At a given temperature, the adsorption capacity depends on the pressure according to Langmuir’s law, as in formula (2):

\[
C_p = C_{p00} \frac{K_c P}{1 + K_c P} \tag{2}
\]

In which:
- \(C_p\) – represents the adsorbed gas quantity (m³/t);
- \(C_{p00}\) and \(K_c\) – coefficients depending on the nature of gas, temperature and the characteristics of the adsorbing surface;
- \(P\) – is the gas pressure (bar).

For this form of the Langmuir’s law mathematical expression, the constants \(C_{p00}\) and \(K_c\) can be determined as a function of volatile material content, dependence which is presented in figures 4 and 5.

Apart from these two parameters, i.e. the pressure and the temperature, the researches revealed the existence of other parameters influencing the storing capacity, such as the nature of the gas, the content of volatile materials (the rank of coal), the petrographic composition of the coal, the moisture and the ash content.
**Nature of the gas** – from this point of view the coal presents a higher affinity for the carbon dioxide than for the methane or nitrogen (figure 2).

**Content of volatile materials** (rank of coal) – the minimal volume of adsorbed gas occurs when the content of volatile materials is in range of 20-40% (figures 6 and 7) regardless the temperature and pressure.

**Moisture content** – the moisture content has an influence on the adsorption/desorption capacity of coal, in the sense of its decreasing with the increase of moisture content, this influence being illustrated in figure 8;

**Ash content** – ash content influence negatively the adsorption capacity, in the sense of its reduction with the ash content increase, because only organic material contributes to gas adsorption;

**Petrographic composition** – it influence the adsorption capacity, but it is difficult to be quantified, however it is known that higher exinite, resinite and fusite contents increases the adsorption capacity.

### 5. METHODS OF DETERMINING THE METHANE GAS CONTENT OF COAL SEAMS

Two category of methods are actually used for measuring or assessing the gas content of coal seams, as follows:

- direct methods, which are based on the measurement of the gas volume released by coal samples collected in sealed containers, in the process of forced desorption;
- indirect methods, based on empirical relations which correlates the storage capacity with sorption isotherms determined in laboratory.

While using direct method, the desorption is realized in special containers on coal samples as fresh as possible. During the desorption, the samples are maintained in the same temperature as in place, and the measured desorption rate allows the assessment of the initial quantity of gas in the sample. Periodically, the released gas is conducted to a measuring cylinder (figure 9) and eventually chemically analyzed. The remaining quantity of gas in the sample is determined after its grinding until the particle size is under 1 mm (usually 20 μm).

The overall gas content is composed by many partial contents, which determination is made by different procedures. The gas lost during the sample collection ($Q_1$) is assessed from the free gas remaining in the container ($Q_2$), based on the necessary time for sample collection and container...
sealing, until the moment of measurement, period in which a quantity \( Q_2 \), has been released, and the quantity \( Q_3 \) is determined by collecting and measuring the gas released after grinding process.

Fig. 9. Echipament de măsurare a conținutului de gaz (standardul Australian).

In this way, the desorbed gas quantity from pure coal is given by the formula (3):

\[
Q = \left( \frac{Q_1}{M} + \frac{Q_2}{M'} \right) \frac{1}{1 - 1.1c} \quad [cm^3/g], \text{ or } [m^3/t] \tag{3}
\]

In which:
- \( M \) – mass of collected sample (g);
- \( M' \) – mass of grinded sample (g);
- \( c \) – ash content (%)

In the case of lack of data related to the gas content of a coal seam, obtained by direct methods, which are difficult to be performed, we can use alternative methods, such as the method proposed by Kim [4], based on the analysis of adsorption capacity of different kinds of coal in seams located at different depths (figure 10).

In this respect, Kim proposes an empirical formula (4) in which the main parameters are the moisture content, volatile material content, the absorbed gas volume by the wet coal, the fixed carbon, seam thickness, and the temperature.

\[
V = \frac{(100 - M - A)}{100} \times \left[ \frac{V_w}{V_d} \right] \left[ K(P)^N - (b \times T) \right] \tag{4}
\]

Where, \( V \) - Volume of methane gas adsorbed (cm\(^3\)/g)
- \( M \) - Moisture content (%)
- \( A \) - Ash content (%)
- \( V_w/V_d = 1/(0.25 \times M + 1) \)
- \( V_w \) - Volume of gas adsorbed on wet coal (cm\(^3\)/g)
- \( V_d \) - Volume of gas adsorbed on dry coal (cm\(^3\)/g)

The values of \( K \) and \( N \) depend on the rank of the coal and can be expressed in terms of ratio of fixed carbon (FC) to Volatile matter (VM)

\[
K = 0.8 \times F.C \div V.M + 5.6
\]

where, \( F.C \) - Fixed carbon (%)
- \( V.M \) - Volatile matter (%)
- \( N \) - Composition of coal (for most bituminous coals, \( N = (0.39 - 0.013 \times K) \))
b - Adsorption constant due to temperature change (cc/g/°C).

\[ T = \text{Geothermal Gradient} \times \left( \frac{h}{100} \right) + T_0 \]

- \( T \) - Temperature at given depth
- \( T_0 \) - Ground temperature
- \( h \) - Depth (m)

For the case of Jiul Valley coal, the studies revealed that the gas volume which can be desorbed vary between 5 and 35 m³/ton, the value depending on the location of the seam in the coalfield (western side having higher methane content), the depth of seam, the pressure and temperature in the sample collection point.

In these conditions, the carbon dioxide storing capacity in Jiu Valley’s coal seams can be assessed based on the data related to the methane content using a multiplying factor of \((1.5\ldots2) / 1\) in the favor of \( \text{CO}_2 \). Using this approach, the theoretical storage capacity is assessed to 116.5 billion m³ \( \text{CO}_2 \).

The determination of the real storage capacity implies complex laboratory and in situ studies, which allows the exact adsorption-desorption parameters for methane and carbon dioxide, for each relevant coal seam and for each perimeter supposed to be appropriate for \( \text{CO}_2 \) storage and performing injection drill tests for validating the laboratory tests. The main issue is to pay attention to both stages of the process, i.e. the \( \text{CH}_4 \) desorption and the \( \text{CO}_2 \) absorption.

### 6. EXTRACTION OF METHANE (CBM) BY \( \text{CO}_2 \) INJECTION IN JIUL VALLEY’S VIRGIN COAL SEAMS

The methane gas associated with virgin coal seams (CBM) represents valuable reserves of natural gas outside the conventional oil and gas producing reservoirs. It presents a lot of advantages, as follows: it is a clean energy resource, its extraction prior or simultaneously with coal mining avoids the release in the atmosphere of a GHG gas and loss of a valuable resource; beneficiation of CBM can increase the safety and profitability of coal mining.

In many cases, injection of \( \text{CO}_2 \) into a geologic formation can improve the recovery of hydrocarbons, adding value to the base products, which may compensate the costs involved by its capture and sequestration. On the other hand, the capture and sequestration of carbon dioxide contributes to reduce the emissions at the level of coal fired power plants.

The storage capacity, due to its dependence on temperature, pressure and rank of coal, reduced to the dependence on depth reveals an optimal depth as schematically shown in figure 11.
Taking into account all the available data and considering only the virgin seams in closed or under closure mining perimeters, we assessed the storing capacity of CO₂ at a minimal value of 114 Mt CO₂.

This potential has been calculated for a minimal gas content of 5 m³ CH₄/t, and for the conversion to CO₂ a rate of 2 molecules of CO₂ adsorbed for one molecule of desorbed CH₄ (table 1).

In principle, the injection of carbon dioxide in coal seams integrated with CBM recovery implies to drill at least two wells from the ground to the coal seam, one for CO₂ injection and the second for methane recovery (figure 12).

The release of methane from the coal matrix is based on the different affinity of coal, higher for CO₂ comparative with CH₄, the absorption capacity being 30 - 35 m³CO₂/t at pressure over 5 - 8 MPa, one molecule of methane being replaced by 1.5 - 5 molecules of CO₂, depending on available pressure.

This estimated capacity may be greater, if the methane content, or the absorption capacity will be higher in reality than those taken into consideration.

### Table 1: Storage potential of carbon dioxide in Jiul Valley’s closed mining perimeters

<table>
<thead>
<tr>
<th>Item \ coalfield</th>
<th>Lonea</th>
<th>Pilier</th>
<th>Dâlja</th>
<th>Aninoasa</th>
<th>Bărbăteni</th>
<th>Câmpul lui Neag</th>
<th>Valea de Brazi</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal reserve (mil t)</td>
<td>125</td>
<td>80</td>
<td>160</td>
<td>100</td>
<td>130</td>
<td>65</td>
<td>100</td>
<td>750</td>
</tr>
<tr>
<td>Elevation ground level (m)</td>
<td>710</td>
<td>700</td>
<td>610</td>
<td>670</td>
<td>800</td>
<td>810</td>
<td>735</td>
<td></td>
</tr>
<tr>
<td>Minimal depth of coal seams</td>
<td>-220</td>
<td>-350</td>
<td>-450</td>
<td>-200</td>
<td>-100</td>
<td>-50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CBM estimate (mil m³ CH₄)</td>
<td>625</td>
<td>400</td>
<td>800</td>
<td>500</td>
<td>650</td>
<td>325</td>
<td>500</td>
<td>2800</td>
</tr>
<tr>
<td>CO₂ storage potential estim. (Mt)</td>
<td>18,75</td>
<td>12</td>
<td>24</td>
<td>15</td>
<td>19,5</td>
<td>9,75</td>
<td>15</td>
<td>114</td>
</tr>
</tbody>
</table>

### 7. CONCLUSION

While the carbon dioxide from the coal fired power plants is responsible for about 80 % of the total amount of GHG emissions, it is evident that the first actions to be performed in view to reduce them is to be focused on this direction, mainly because the contribution of energy production sector in the total emissions is the most relevant.

From the point of view of CCS technology, it is demonstrated that the underground geologic structures are the most appropriate, due both to accumulated knowledge, high storing capacity and safety.

This possibility is relevant for the unexploited coal seams in Jiul Valley coalfield, taking into account that the main beneficiary of the mined out coal, the Paroseni power plant, is located in the middle of the coal basin, so the maximal distance from the source to the storing location is less than 20 km.

In plus, the implementation of an integrated project CCS – CBM will pay back the involved costs, by increasing the efficiency of the Energy Producing Complex.

While the capture, processing and transport of carbon dioxide are well studied, the storage in coal seams is a subject of specificity of different coal basins, and in this respect, the actual paper deals mainly with the aspects related to storage (sequestration), focusing on the storage capacity and the factors which influence it.

Future research is to be performed to acquire more knowledge in view to highlight some detail aspects, mainly related to the carbon dioxide absorption and methane release, being aware that the classical CBM recovery attempts in the Jiul Valley coalfield were unsuccessful because the low permeability of the coal.
This first estimation of the storing capacity for carbon dioxide based on the assessment of total methane content of coal seams, based on available theoretical approaches and experimental data is promising to continue the research in this issue.

REFERENCES


O SOLUTIE DE STOCARE A DIOXIDULUI DE CARBON SI DE VALORIFICARE A GAZULUI METAN DIN ZACAMANTUL CARBONIFER VALEA JIULUI

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Rezumat: Lucrarea de față își propune să ofere o soluție pentru un ipotetic proiect integrat de captare și stocare a CO2 provenit de la termocentralele beneficiaire a huielui extrase din bazinul carbonifer al Văii Jiului și exploatarea concomitentă a metanului adsorbit în straturile de cărbune din bazin (sub denumirea generică de gaz de mină), și utilizarea acestuia în aplicații energetice care vor avea consecințe favorabile în reducerea costurilor de producere a energiei termice și electrice. Depozitele de cărbune considerate neexploataibile din punct de vedere tehnic sau economic, se pot constitui în medii care pot asigura volume importante pentru stocarea bioxidului de carbon rezultat în urma procesului de captare din fluxul general al gazelor de ardere de la termocentralele pe combustibili fosili sau din alte surse de emisie staționare mari, deoarece cărbunele prin structura sa microporoasă care poate absorbi o serie de gaze precum azotul, bi oxidul de carbon și metanul, cu precizia că testele de laborator au demonstrat că acesta prezintă cea mai mare afinitate pentru bioxidul de carbon. Deoarece captarea , procesarea și transportul CO2 sunt tehnic rezolvate, lucrarea pune accent pe problema stocării respectiv a combinării acesteia cu înlocuirea și extracția forțată a metanului din straturile de cărbune. Ambele aceste procese au ca principal parametru de influență capacitatea de adsorbție/ desorbtie a cărbunelui relativ la CH4 și CO2, pe baza căreia se poate determina atât conținutul de metan desorbabil cât și capacitatea de stocare a CO2. Principalul rezultat al studiului este demonstrarea făzabilității acestei tehnologii combine, a cărei implementare ar contribui la revitalizarea activității miniere și energetice din Valea Jiului. 