Study of Istrian Unmineable Coal Utilization

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Abstract:

There are several approaches which can be used to estimate amounts of methane that could be extracted from the coal beds. Several selected sites in Labin basin were observed in order to decide if further researches are significant. Data on the composition of coal, the depths and thicknesses of coal layers were collected to assess methane content in coal by using the Langmuir isotherm.

Detailed literature investigation was conducted with the objective to determine the best method of calculations with the scarce useful data that is available from the old coal mining reports. Curves of sorption were made and evaluation of the quality of each assessment as well.

The fact that some of the largest CO_2 point sources in Croatia are in Istria (power plants near Plomin) was the argument for consideration of CO_2 injection.

By comparing the sorption of pure CH_4 and sorption of CO_2, in order to maintain the pressure in a coal bed it was concluded that CO_2 injection could be suitable option for coal bed methane recovery.

Keywords:

CCS, coal bed methane, enhanced methane recovery, Labin basin

1. Introduction

In order to mitigate the effect of the greenhouse gas emissions from fossil fuels, CO_2 underground storage is one of perspective options. After the ratification of Kyoto protocol signed in 1999, since 2007 Croatia is allowed to increase the base year emission. That made enhanced oil recovery (EOR) projects current not only because of additional oil recovery, but because of possibility of using CO_2 as injected displacement fluid. However, coal deposits are not exploited recently and there are scarce data regarding assessing possibility of CO_2 storage into coal bed.

Table 1. The main point sources of CO_2 in Croatia listed for EU FP6 GeoCapacity projekt (RGNF, 2009)

Company	City	CO_2, kt	Production, GWh	Technology	Fuel
HEP d.d.	Plomin	1878	290	Power plant	coal
HEP d.d.	Rijeka	451	303	Power plant	oil
HEP d.d.	Sisak	546	396	Power plant	oil
HEP d.d.	Zagreb	854	312	Power plant and heat plant	oil
HEP d.d.	Zagreb	423	90	Power plant and heat plant	oil
HEP d.d.	Osijek	160	89	Power plant and heat plant	gas
HEP d.d.	Zagreb	8	83	Power plant and heat plant	gas
INA d.d	Molve	684	0	Central Gas Processing Unit	
	Σ	**5004**	**1563**		

Importance of such oil industry projects for carbon dioxide capture and storage (CCS) is in big investment in pilot carbon dioxide injection project and extensive data acquiring at selected site and the fact that data from pilot well can give a precise model for CO_2 storage. It is to expect that quantity and quality of data related to storage in depleted oil and gas fields and also aquifers will be increased, and preliminary studies were done.

Adequate lists of the main point sources of CO_2 in Croatia were given as the part of EU FP6 GeoCapacity project (table 1). In table 1 are only specified large point sources for which capture and transport will be more feasible.

Larger list of point sources was made as part of KEO (2004), which includes cadastre of greenhouse gases emissions (table 2).

Table 2. Preliminary list of the 15 largest CO_2 sources from (KEO, 2004).

	Possible ETS obligated	County	CO_2 emisssion, t	%
1	Cementara CEMEX	Splitsko Dalmatinska	1353553	16.28%
2	HEP - TE Plomin 2	Istarska	1266144	15.23%
3	INA Rafinerija Rijeka - Urinj	Primorsko Goranska	894291	10.76%
4	HEP - TE-TO Zagreb	Grad Zagreb	853816	10.27%
5	Petrokemija Kutina	Sisačko Moslavačka	753187	9.06%
6	HEP - TE Plomin 1	Istarska	611515	7.35%
7	Cementara Našicecement	Osiječko Baranjska	576118	6.93%
8	HEP - TE Sisak	Sisačko Moslavačka	546005	6.57%
9	HEP - TE Rijeka	Primorsko Goranska	451193	5.43%
10	HEP - EL-TO Zagreb	Grad Zagreb	423024	5.09%
11	HEP - TE-TO Osijek	Osiječko Baranjska	154962	1.86%
12	Belišće	Osiječko Baranjska	148931	1.79%
13	INA Rafinerija Rijeka - Mlaka	Primorsko Goranska	107797	1.30%
14	DIOKI Zagreb	Grad Zagreb	92679	1.11%
15	Šećerana IPK Osijek	Osiječko Baranjska	81758	0.98%
			8314973	100.00%

By far the largest possible capacity is in regional saline aquifers, although data for aquifers are the scarcest. Aquifers were assessed based on the regional geological subsurface maps and by extrapolating reservoir properties (pressure, sandstone variation with depth) from oil and gas fields [1]. Effective geological storage capacity was then calculated using the eq. 1:

$$m_{CO_2} = V \times \phi \times \rho_{CO_2} \times E \qquad (1)$$

where m_{CO_2} is mass of CO_2 that can be stored at reservoir conditions (kg), V is the estimated pore volume (m^3), ϕ is porosity (part of the interconnected pore system that could be reached by injected CO_2), ρ_{CO_2} is density of CO_2 at reservoir pressure and temperature (kg/m^3) and E is storage efficiency.

Because of the fact that the most explored hydrocarbon fields are in northern Croatia, aquifer CO_2 storage estimates for Adriatic area were neglected. Map of regional aquifers, with properties extrapolated from is given in figure 1.

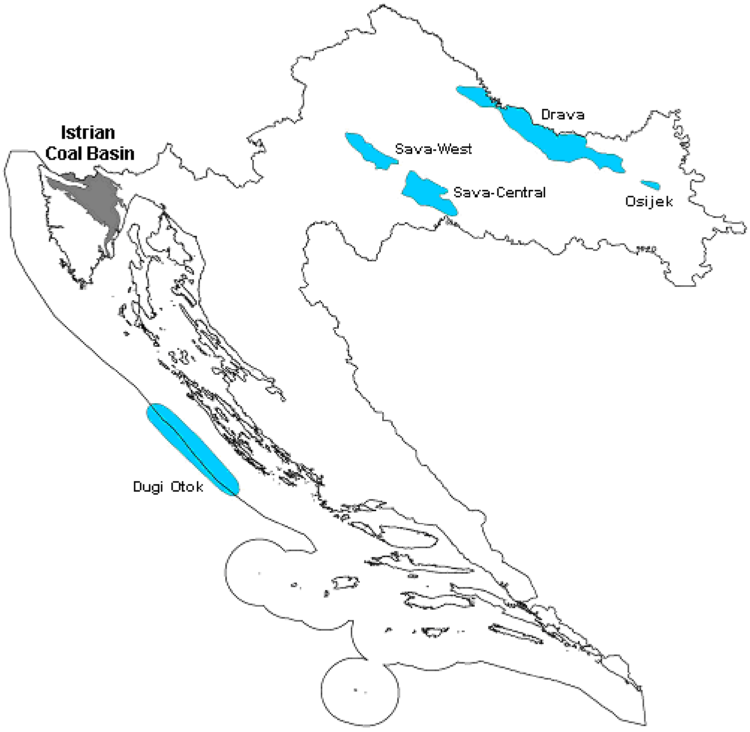

Fig. 1. Map of selected aquifer storage sites in Republic of Croatia (EU GeoCapacity, 2009).

Table 3 shows estimates of CO_2 storage capacity into deep saline aquifers in northern part of Croatia.

Coal production has been appreciably reduced to the minimum during the 1970's [2]. By shutting the last coal mines in Labin, Ripenda and Tupljak (1999), due to unprofitability, production has been completely discontinued. Mentioned Istrian coal mines are characterized by high sulphur content, high content of radioactive substances and unfavorable mining and geological environment. Remaining coal deposits (figure 2) cannot be exploited profitably by standard mining methods. However, the possibility of alternative methods application, such as underground coal gasification and enhanced coalbed methane extraction (by injection of CO_2), should be investigated. The biggest CO_2 point source (Plomin) is located at Labin coal basin and there was not yet considered to inject CO_2 into mature and abandoned coal deposits.

Table 3. Storage capacities in northern Croatia (Vulin, 2010).

Aquifer	Top, m	Base, m	Pressure, bar	H_{ef}, m	porosity	CO_2 storage capacity, Mt
Drava	900	1900	140	600	0.25	2285
Osijek	1000	3500	225	1750	0.20	458
Sava Central	1000	2700	185	550	0.18	791
Sava West	800	2300	155	500	0.17	363
					Σ	3898

Analogously to CO_2 Enhanced Oil Recovery, which is more feasible than CO_2 storage into depleted oil fields, enhanced coal bed methane estimates with CO_2 as injecting fluid make more economical sense than CO_2 storage into coal beds. The second obstacle of CO_2 storage into coal beds of Labin Coal Basin (located in Istria) is low depth (low pore pressure), and nearness of the sea (parts of the basin are characterized by underground connections with the sea). Above mentioned regional properties could lead to higher risk and necessity for detailed studies if pore pressure will increase significantly as a consequence of CO_2 injection. At the other side, it is reported that economical production of methane at depths greater than 900m requires significant advances [3].

In this work results of preliminary study of CO_2 enhanced coal bed methane (ECBM) production from Istrian coal mines are reported. Impetus for the analysis was the fact that the largest CO_2 point source in Croatia is at the same location, and that no coal bed study before was conducted.

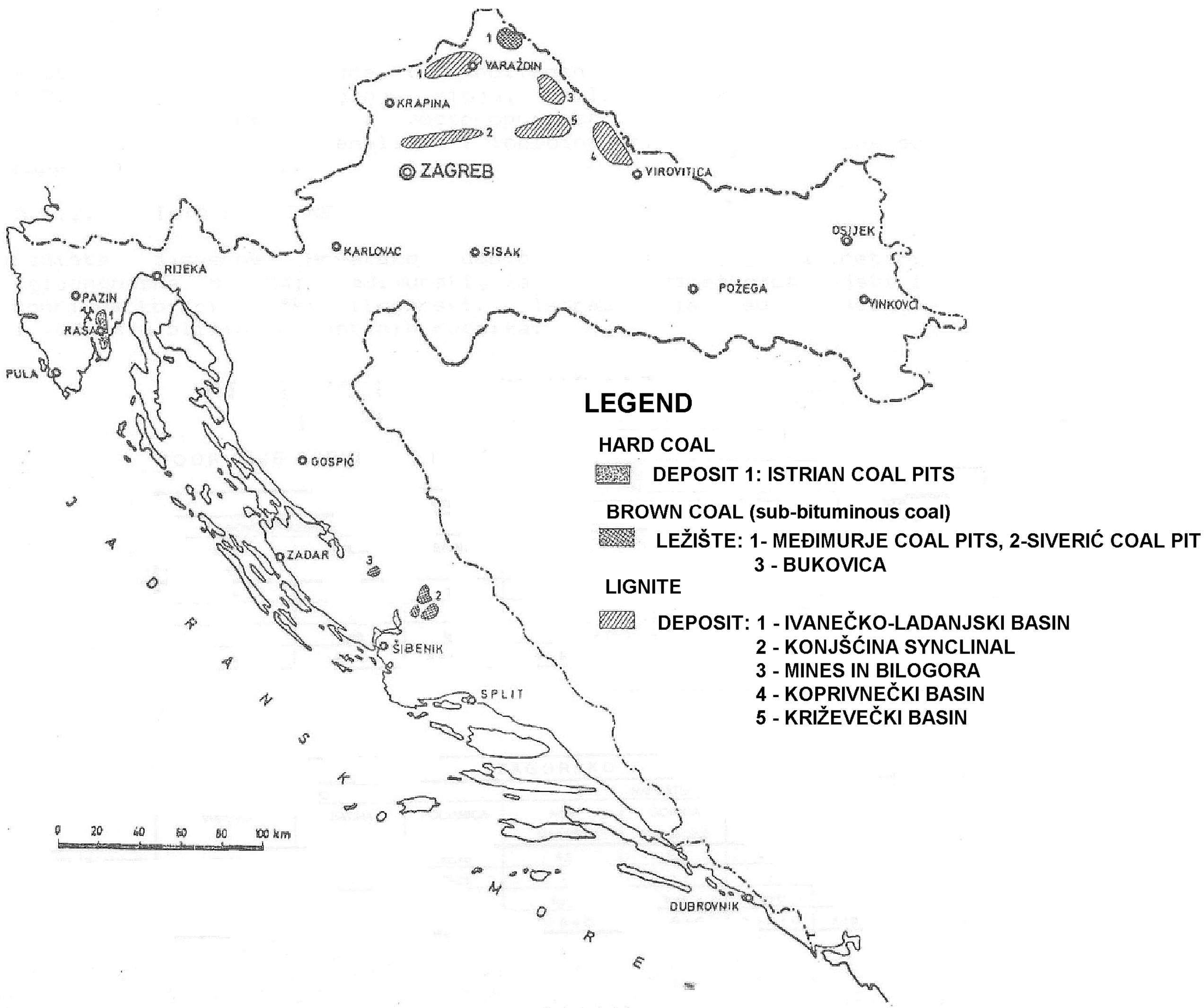

Fig. 2. Coal deposits in Croatia [4].

2. Theoretical background

Coalbed methane originates from the formation of coal as a separate phase. It is dissolved in brine or adsorbed in microscopic organic matter structure, as separated phase that could not retain in coal. The content of gas that can be held in coal will increase with depth and coal rank.

Natural fractures (cleats) in coal bed reservoir are saturated with brine – methane is trapped in fractures and conventional oil and gas discovery methods are not adequate for coalbed methane detection and evaluation. To produce gas from coal mines, large amounts of brine that saturated coalbed reservoir have to be produced. Produced water is a waste that should be adequately treated and disposed.

As methane is safety issue related to coal mining, extracting methane from coalbed reservoir could help in avoidance of that problem, which is possible by drilling before mining works and by fracturing the coal layers. Sometimes, if pressure is too low for eruptive brine production, brine is pumped to the surface.

There is a variety of methods for preliminary estimates methane content and potential.

Gas in place volume is defined as the total amount of gas stored within a reservoir rock volume. In order to calculate the gas in place volume, it is essential to provide drainage area, thickness of the reservoir, average reservoir rock density and an estimate of reservoir gas content (at reservoir conditions):

$$G = Ah\overline{\rho}_c\overline{G}_c \qquad (2)$$

The calculation is to be extended by more data. From laboratory measurements, it is possible to obtain storage capacity, gas content, diffusivity and pore i.e. formation compressibility, relative permeability, porosity and gas composition. From well logs are determined gross and effective thickness, permeability and pressure.

Other fluid and rock properties can be solved numerically (simulation) or by applying correlations.

Gas content can is (a) free gas in pore spaces and (b) gas adsorbed on the surface of the pores and microfissures (figure 3).

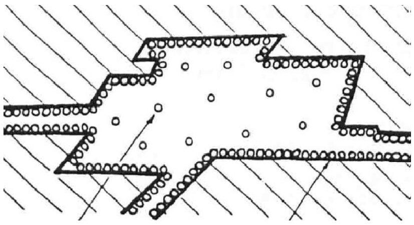

Fig. 3. Methane molecules inside a coal pore [3].

The amount of free gas is a function of porosity, ϕ and gas pressure, p_r.

The greater amount of the gas is in adsorbed form, as a layer on a cleat surface and is functionally dependent on the gas pressure, temperature, T_r, moisture and carbon content of coal.

For the amount of adsorbed gas, vastly used model of coal cleat system is simple fracture network model [5]. Similar models can be suitable for predictions of methane production and for brine flow through the coal model (figure 4).

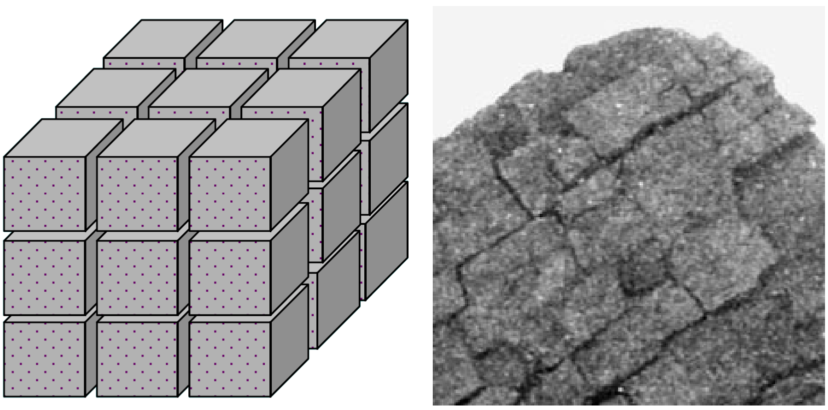

Fig. 4. Coal cleat system.

Flow through the coalbed reservoir mainly occurs in macro-pore space, i.e. cleats and fractures, the most of the methane is contained within the micro-pores, i.e. coal matrix. Instead Darcy law, which can be implemented for a aquifer, oil and gas reservoir flow, molecular diffusion is typically mathematically described for gas flow through coalbed reservoir because gas desorption from the matrix surface causes molecular diffusion within the coal matrix. The diffusion through the coal matrix can be described by Fick's Law:

$$q_{gm} = \sigma D \rho_c V_c \left(\overline{G}_c - G_s \right) \quad (3)$$

Consequently, instead real gas equation of state, more practical approach is to use adsorption/desorption isotherms to describe volumetric changes of gas with changes of pressure (pressure decrease with water production).

Sorption curves are the most crucial coalbed methane volume estimates. Analysis of sorption curves will be more difficult in a case of greater reservoir heterogeneity or in a case of complex fluid composition.

Thus, the representative sorption curves for pure substances or simple mixtures (fluid systems) are the starting point for more complex fluid system estimates. The gas content is determined in the lab, on the coal core sample, and *in situ* conditions. After the initial gas saturation is measured, coal is re-adsorbed with methane in order to measure a set of sorption isotherms. Desorbed part of the gas is gas lost before the experiment and can be extrapolated from desorption based on the time measured between coring and containment of the core in the field (figure 5).

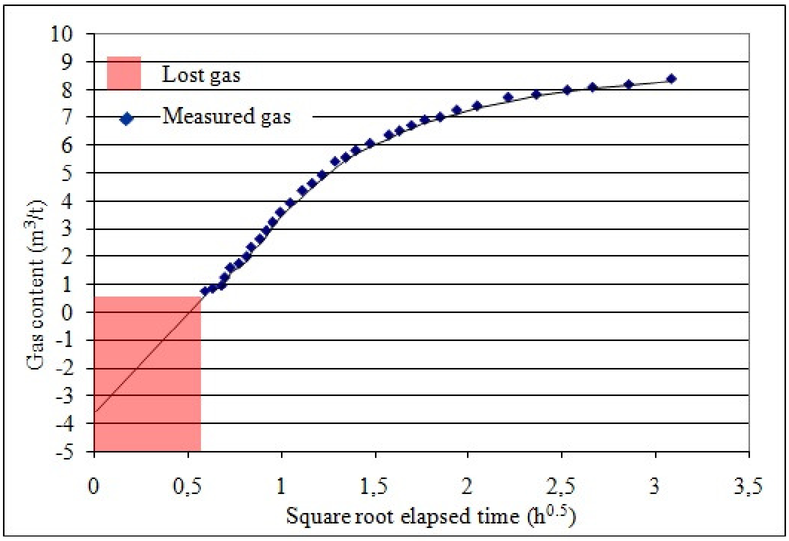

Fig. 5. Time vs. gas desrption curve (and extrapolated gas loss).

Residual gas is the gas that is not desorbed at standard temperature and pressure (15.6°C and 1 bar).

The sum of residual, lost and measured gas volume is total volume contained in coal.

Independently determined moisture, ash and sulphur content allows an estimate of gas saturation by comparison of sorption isotherm and estimates taken from the desorption test i.e. ash, sulphur and moisture content are used to estimate gas content from several desorption experiments and from the on coal layer sample. In addition, it is possible to calculate gas content for a particular zone in coal reservoir, and consequently to calculate gas in place.

Moisture content is also functionally related to the content of non-coal and non-hydrocarbon components.

Because sulphur vaporizes during the ash content analysis, sulphur mass correction is required.

In order to estimate total reservoir gas content correlation of coal rock density (i.e. gas content at the some depth) vs. gas saturation could be made.

The problem could arise for data at greater depths because such measurements are available from oil and gas exploration wells and are not calibrated to detect coal properties. To use data from geophysical measurements, content of ash can be defined:

$$a_d = \frac{\rho - \rho_c}{\rho_a - \rho_c} \quad (4)$$

Gas content is then: $G_c = G_{pc}\left(1 - a_d\right)$ (5)

To describe isothermal sorption of methane analytically, two main variables should be obtained – Langmuirs volume (V_L, m^3) and pressure (p_L, bar) to apply Langmuirs equations [6] and calculate gas content in saturated coal, at desired pressure. If concentration of gas is on the right side of Langmuirs isotherm (figure 6), the sample is in undersaturated state (region) and pressure should be decreased to the Langmuirs isotherm in order to vaporize the first gas (methane) molecule. When the gas concentration is laying on the Langmuirs isotherm, methane will vaporize from the fractures.

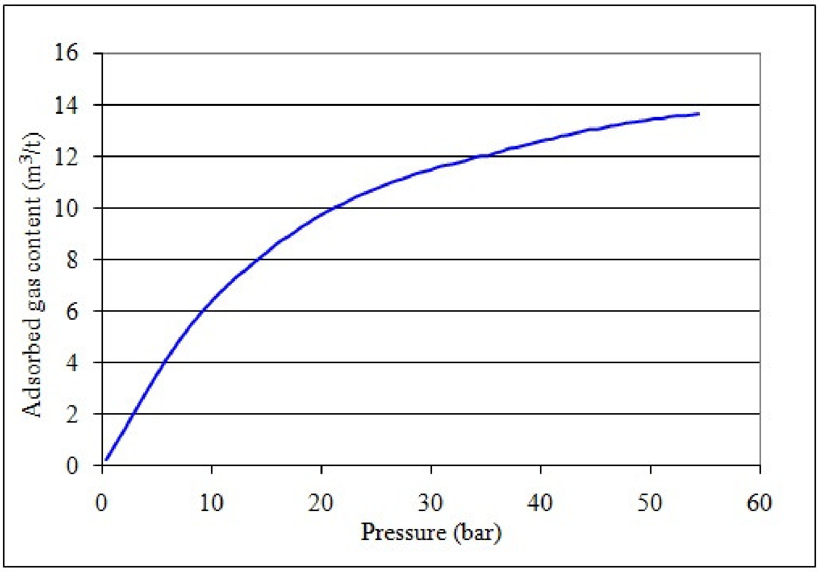

Fig. 6. Measured Langmuir isotherm.

Langmuirs equation is based on the assumption that the volume of a gas adsorbed or desorbed at constant temperature is proportional with free gas content and sorption pressure:

$$G_s = G_{sL}\left(\frac{p_e}{p_e + p_L}\right) \quad (6)$$

Eqn. 6 is used to calculate gas content after certain reservoir pressure drop (that could occur during the exploration or exploitation).

When available data are scarce, Kim's method [7] can be used:

$$G_{pc} = 0.75\left(1 - a - w_c\right) \times \left(k_o\left(0.095d\right)^{n_o} - 0.14\left(\frac{1.8d}{100} + 11\right)\right)$$

$$k_o = 0.8\frac{x_{fc}}{x_{vm}} + 5.6$$

$$n_o = 0.315 - 0.01\frac{x_{fc}}{x_{vm}} \quad (7)$$

Kim's equation is derived from empirical data, by regression of measured results at the different coring depths. Equation does not include petrographic coal composition, but shows that greater gas content is to be expected at greater depths, and at higher coal rank.

In the reservoir, the most of the gas has density similar to liquids (supercritical fluid). Only small part of a gas is in free and gaseous state. After some time of gas desorption and production pressure decreases, which could be avoided by some enhanced coalbed methane methods, i.e. by injecting some other gas to maintain the reservoir pressure, and to decrease only the partial pressure of a gas that was initially in the reservoir. By selection of the suitable injection fluid, methane is displaced from the reservoir. Considering physical and chemical properties and also availability, the most common considered injection fluids are carbon dioxide and nitrogen. By any injection of fluid for enhanced recovery, a part of the fluid remains in the reservoir which means that by injecting CO_2, it is possible to mitigate the effect of greenhouse gases produced during production and exploitation of fossil fuels.

The first and probably the most famous CO_2 ECBM project was carried out in San Juan (USA, New Mexico) – after 6 years of conventional methane production, injection of CO_2 was started in 1995 and in the next 15 years there was stored 277 000 tones of CO_2. During that period methane recovery increased from 77% to 95% in total.

Criteria for selection of perspective ECBM sites are [8]:

- low heterogeneity level
- simple geological structure, minimal occurence of faults and folds
- depth range from 600 to 1500m
- geometry and frequency of coal beds
- coal composition (rank, macerals, as, moisture etc)
- gas saturation and methane content in coal bed [9]
- moisture content
- brine saturation, aquifer performance
- favorable permeability

Volumetric ratio of CO_2 and CH_4 sorption in coal bed increases from mature coalbed reservoirs (1:1) to young coals (1:10).

Coals were classified for CBM and ECBM purposes by three compositional criteria:

- grade, proportion of organic matter vs. inorganic constituents
- type, represents different classes or categories of organic constituents
- rank, i.e. alteration of coal composition and structure during coalification (diagenesis, peatification, dehydration, catagenesis, bituminisation, debituminization, metagenesis and graphitization).

Coal rank is used to include a number of physical and chemical properties of coal. Feasible methane production is not possible if there is no convenient fracture system, and also relative permeability and porosity.

3. Preliminary estimates of ECBM possibility in Labin coal basin

For Labin coal, there was no detailed laboratory sorption analysis conducted. Geological structure maps are also not available, and only preliminary capacity estimate was made for Labin coal basin.

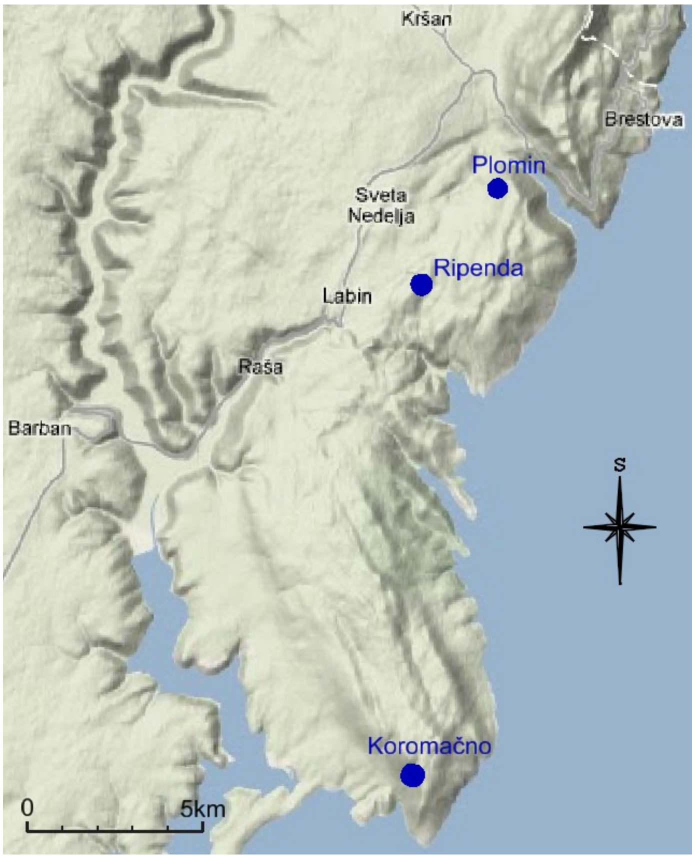

Fig. 7. Sites of interest for ECBM study in Istria.

Considering the fact that higher coal rank correlates with higher methane content, by observing available documentation and coal exploration data, Labin basin [2, 10-16] had the highest perspective to give relevant methane content as a result of the study.

Basically, there are three areas of interest with depths ranging from 400 to 600m – Koromačno, Plomin and Ripenda (figure 7). The other coal deposits were too shallow.

There were 3 methods combined – (1) Langmuirs isotherm and eqn. 6, (2) general sorption correlation for methane (figure 8), that was made by regression of published data and (3) by implementation of Kim's equation and eqn 7.

Final results are given in tables 4, 5 and 6.

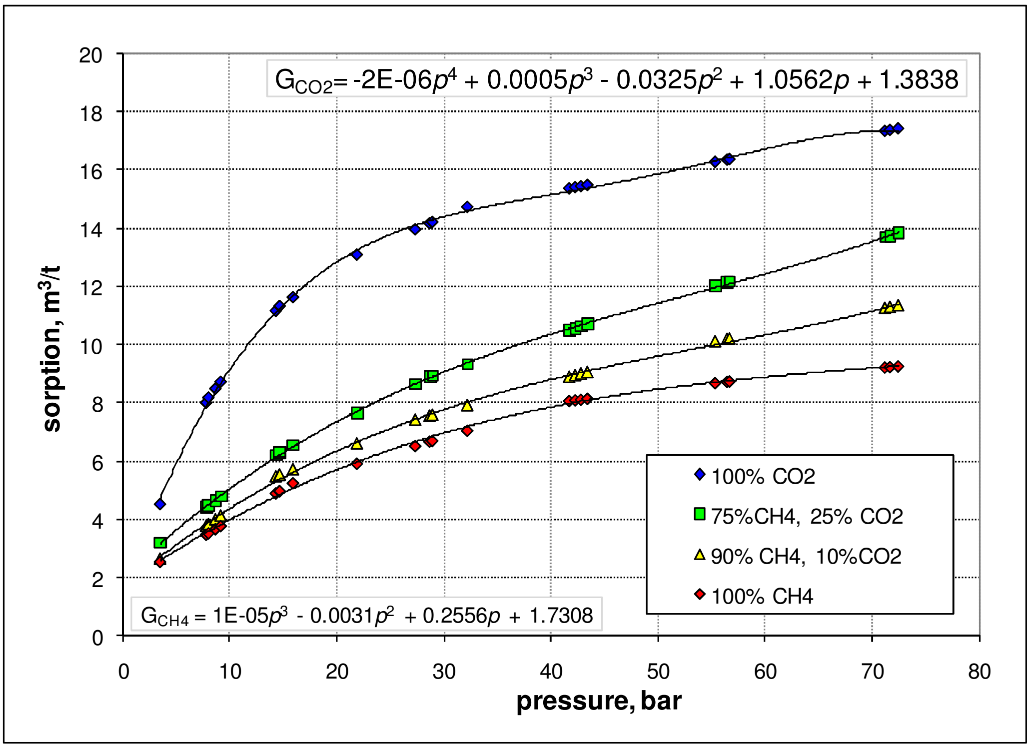

Fig. 8. Sorption curve for pure compounds and binary mixtures (modified from literature [17]).

Table 4. Amounts of methane in the dry coal calculated from the Langmuir isotherm.

site	Well	p_e,bar	p_L,bar	G_{sL}, m³/t	G_s, m³/t
Plomin	Jurašin	55.7	14	14	11.2
	Jurašin 2	51	14	14	11.0
Ripenda	Ripenda 4	47.8	14	14	10.8
	Ripenda 3	51.2	14	14	11.0
Koromačno	B1	45.2	14	14	10.7
	B6	38.4	14	14	10.3
	B9	42.9	14	14	10.6
	B12	29.6	14	14	9.5

Table 5. Sorption of methane and CO_2 in dry coal, determined from generalized sorption curve.

well	P,bar	G_{CH4}, m³/t	G_{CO2}, m³/t	CO2:CH4 sorption ratio
Jurašin	55.7	8.1	26.5	3.3
Jurašin 2	51.0	8.0	23.5	2.9
Ripenda 4	47.8	8.0	21.8	2.7
Ripenda 3	51.2	8.0	23.6	2.9
B1	45.2	7.9	20.5	2.6
B6	38.4	7.5	18.0	2.4
B9	42.9	7.8	19.6	2.5
B12	29.6	6.8	15.6	2.3

Table 6. The Amount of methane in dry coal (no ash and moisture).

well	**d**,m	w_c	**a**	x_{fc}	x_{vm}	**Gas capacity, G_{pc}** (m^3/t)
Jurašin	557.5	0.034	0.12	0.42	0.43	11.7
Jurašin 2	510.6	0.034	0.12	0.42	0.43	11.4
Ripenda 4	478	0.034	0.12	0.42	0.43	11.2
Ripenda 3	512.26	0.034	0.12	0.42	0.43	11.4
B1	451.8	0.01	0.14	0.41	0.48	10.9
B6	383.5	0.01	0.14	0.41	0.48	10.4
B9	429	0.01	0.14	0.41	0.48	10.8
B12	296.15	0.01	0.14	0.41	0.48	9.6

4. Conclusions

The study of data from 3 sites was presented in order to estimate ECBM potential. Following conclusions were made:

- Sorption curve gives significantly different results than other two methods examined.
- Langmuirs isotherm can be used when experimental data from the observed site are not available
- Assumption that reservoir pressure is similar to hydrostatic pressure is good assumption. It can be verified by comparison of Langmuir isotherm (pressure dependent) and Kim's equation (does not include pressure)
- By comparing CO_2 sorption with methane sorption the following ratio was achieved: $\frac{G_{CO_2}}{G_{CH_4}} = 2.3 - 3.3$. Injection of CO2 could result in methane production. However, CO_2 would not be sequestered in geological storage means. It is obvious that 2.3 to 3.3. times more CO_2 would be injected than methane produced.
- Results are given for dry coal and methane dissolved in brine was neglected. To calculate methane content in brine and thus total methane content in coalbed reservoirs, brine analysis (composition) is required. The analyses of brine were not available.
- Described methods do not include sulphur content, which could change the shape of CO_2 sorption curve.
- Further analysis is necessary, for example laboratory measurements of sorption data (curves) from actual data, measurements of actual Langmuirs isotherms and better definition of reservoir geometry.

Nomenclature

A drainage area, m^2
a_d dry ash (mass fraction)
a ash content (mass fraction)
d coring depth, m
D matrix diffusivity constant, 1/s
G_{CH4} Methane sorption,
G_{CO2} CO_2 sorption

G_c gas content, m^3/kg

G_{pc} dry, without ash, gas capacity, cm^3/g

G gas in place volume, m^3

$\overline{G_c}$ average reservoir gas content, m^3/kg

G_s gas content at equilibrium pressure, m^3/kg

G_{sL} gas content at pressure→∞, m^3/kg

h reservoir thickness, m

p pressure, bar

p_e equilibrium pressure, bar

p_L Langmuirs pressure, i.e. pressure at 0.5 G_{sL}, bar

q_{gm} gas production/diffusion rate, m^3/s

w_c moisture, (mass fraction)

x_{fc} fixed carbon, (mass fraction)

x_{vm} volatile components (mass fraction)

x_{fc} fixed carbon, (mass fraction)

x_{vm} volatile components (mass fraction)

x_{fc} fixed carbon content (mass fraction)

x_{vm} Volatile matter (mass fraction)

V_c matrix volume, m^3

Greek symbols

ρ rock density (from density log), g/cm^3

ρ_c density of pure coal, g/cm^3

ρ_a density of dry ash, g/cm^3

σ matrix shape factor, dimensionless

$\overline{\rho}_c$ average rock density, at reservoir conditions, kg/m^3

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