

Tracing coalbed gas dynamics and origin of gases in advancement of the working faces at mining areas Preloge and Pesje, Velenje Basin

Spremljanje sestave premogovega plina in izvor plinov z napredovanjem čela delovišč na pridobivalnih (rudarskih) območjih jam Preloge in Pesje, Velenjski bazen

TJAŠA KANDUČ^{1, *}, JANJA ŽULA², SIMON ZAVŠEK²

¹Jožef Stefan Institute, Jamova 39, SI - 1000 Ljubljana, Slovenia

²Velenje Coal mine, Partizanska 78, SI - 3320 Velenje, Slovenia

*Corresponding author. E-mail: tjasa.kanduc@gmail.com

Received: May 9, 2011

Accepted: September 7, 2011

Abstract: During excavation of lignite in the Velenje Coal Mine coalmine, seam problems with gas outbursts occur. Geochemical investigations are designed to help predict, prevent, and manage coal mine gas outbursts and to study their origin and mechanisms. However, geochemical studies of the coalbed gases in the Velenje basin have been initiated since year 2000. Temporal changes in chemical and isotopic composition of “free” seam gases were observed as a function of the advancement of the working face –120/B, G2/C and –50/B within boreholes jpk-28/10, jpk-30/10, jpk-31/10, jpk-22/09 and jpk-23/09. Mass spectrometry and isotope mass spectrometry methods were used to determine gas composition and perform gas characterization. Coalbed gases in the Velenje basin are highly variable in both their concentrations and stable isotope composition. Major gas components are CO₂ and methane. Concentrations and isotopic studies revealed several genetic types of coalbed gases: endogenic CO₂ (including CO₂ originating from dissolution of carbonates), microbial methane and CO₂.

Izveček: Med izkopavanjem lignita se lahko pojavljajo plinski izbruhi, zato je pomembno izvajati nadzorne meritve premogovnih plinov na odkopih. Geokemične raziskave premogovnega plina so pomembne

za razumevanje mehanizma nastanka, preprečevanja in napovedovanja plinskih izbruhov. Raziskave premogovnega plina v Velenjskem bazenu potekajo od leta 2000. Časovne spremembe v kemijski in izotopski sestavi "prostih" premogovnih plinov smo spremljali kot funkcijo približevanja čel delovišč 120/B, G2/C in -50/B v vrtnah jpk-28/10, jpk-30/10, jpk-31/10, jpk-22/09 in jpk-23/09. Sestavo in izotopsko sestavo premogovnih plinov smo določili z metodama masne spektrometrije in izotopske masne spektrometrije. Premogovni plini v Velenjskem bazenu se spreminjajo tako po vsebnosti kot tudi po izotopski sestavi. Glavni plinski komponenti sta CO₂ in metan. Raziskave vsebnosti in stabilnih izotopov premogovnih plinov kažejo različne izvore plinov: endogeni CO₂, (vključno s CO₂, ki nastaja zaradi raztapljanja karbonatov) ter mikrobní metan in CO₂.

Key words: coalbed gas composition, working faces, carbon isotopes, gas origin, Velenje basin

Ključne besede: sestava premogovnih plinov, odkopi, ogljikovi izotopi, izvor plinov, Velenjski bazen

INTRODUCTION

An increasing demand for coal, as a result of changes in the availability and cost of other fossil fuels, has re-focused attention on the problem of outbursting in deeper coal mines. When the rate of advance of the cutting face is slow, better opportunities for the slow escape of the gases under high pressure in the virgin coal exist. However, at the faster rates of advance of the coal face now required, less time is available for the equalization of gas pressures and mining induced stresses. Thus, the hazard of instantaneous outbursting of gas and coal is increased, although under favorable circumstances some control may be

achieved by gas drainage (SMITH & GOULD, 1980). It is generally assumed that the pressure and volume of gases held within the virgin coal play a major part in producing outbursts; however, some doubt still exists as to whether outbursts are actually triggered by gas pressure or by stresses induced in the rock itself during mining operations (FLORES, 1998).

The most trivial definition of coalbed gas is "gas from coal". Coalbed gas usually consist of hydrocarbons (mainly methane), CO₂ in concentrations from 0 to greater than 99 %, and occasionally small percentages of nitrogen (CLAYTON, 1998). A numbers of models were developed

to describe sources of hydrocarbon gases (SHOELL, 1983, KOTARBA, 1990, SCOTT, 1993, KOTARBA, 2001, ARAVENA, 2003). Stable carbon isotope analyses of methane and CO₂ can be applied to identify the origin of coalbed gases, their migration pathways, and accumulation processes. There are three main sources of hydrocarbon gases and CO₂ in sedimentary basins: abiogenic, microbial and thermogenic gas (SCOTT, 1993). In general, thermogenic gases are typically associated with high rank coal, whereas microbial gases are typically associated with low rank coals and could have been produced throughout the basin history, as long as the coalbeds were never pasteurized. Abiogenic sources of gas are typically found in deep subsurface (SHERWOOD LOLLAR et al., 2006).

Details of isotopic composition of different lithotypes of lignite and the origin of coalbed CO₂ gas based on tectonic events during formation of the basin using cluster analysis and CDMI index (carbon dioxide methane index) of different gases are presented in KANDUČ et al. (2005a) and KANDUČ & PEZDIČ (2005b). The study revealed levels of microbial methane and CO₂, and endogenic CO₂. Unexpected organic arsenic compounds found in Velenje lignite indicated their relation with biogeochemical degradation of organic material (ŠLEJKOVEC & KANDUČ, 2005c).

The aim of the study is to explain concentrations and origin of gases as a function of the advancement of the working faces –120/B, G2/C and –50/B in mining areas of Preloge South, Preloge North and Pesje in Velenje Basin.

MATERIALS AND METHODS

Sampling procedure

Sampling of coalbed gas was performed at working faces –120/B (mining area Preloge South), G2/C (Preloge North) and –50/B (Pesje) from November 2009 till November 2010, in the lignite seam of the Velenje basin with purpose to determine concentrations (CO₂, methane, N₂ and O₂) and δ¹³C of methane and CO₂ from pillar coal in advancement with the working face (Figure 1). Boreholes were drilled in pillar coal to a depth of 20 m. After drilling, the capillary tube was inserted in the borehole. Boreholes (jpk-28/10 - Preloge South, jpk-30/10, jpk-31/10 - Preloge North, jpk-22/09 and jpk-23/09 - Pesje) and working faces (–120/B, G2/C, and –50/B) are shown on Figure 1. “Free gas” emitted from the borehole was collected in a 50 mL plastic syringe and then transferred to a 12 mL evacuated ampoule with a septum. After sampling “free gas” from the boreholes, the ampoules were stored at normal atmospheric conditions un-

til analysis. Free gas includes both the volatiles filling the pores and cracks within the coal structure and some gas degassed from the coal during drilling and sampling (KOTARBA, 2001). Some boreholes were compressed in advancement of the working faces, which caused too much air contamination in boreholes and therefore unable the interpretation. In this study only data of coalbed gases, which contained below 50 % of air were used for interpretation.

Analytical procedure

Determinations of the concentrations of methane, CO₂, nitrogen, oxygen and argon were performed using a home-made mass NIER spectrometer. The method of singular decomposition of matrix was used, to obtain the simultaneous analysis of the gases. The precision of the method was $\pm 3\%$.

Isotope composition of methane, CO₂ was determined using an Europa 20-20 continuous flow isotope ratio

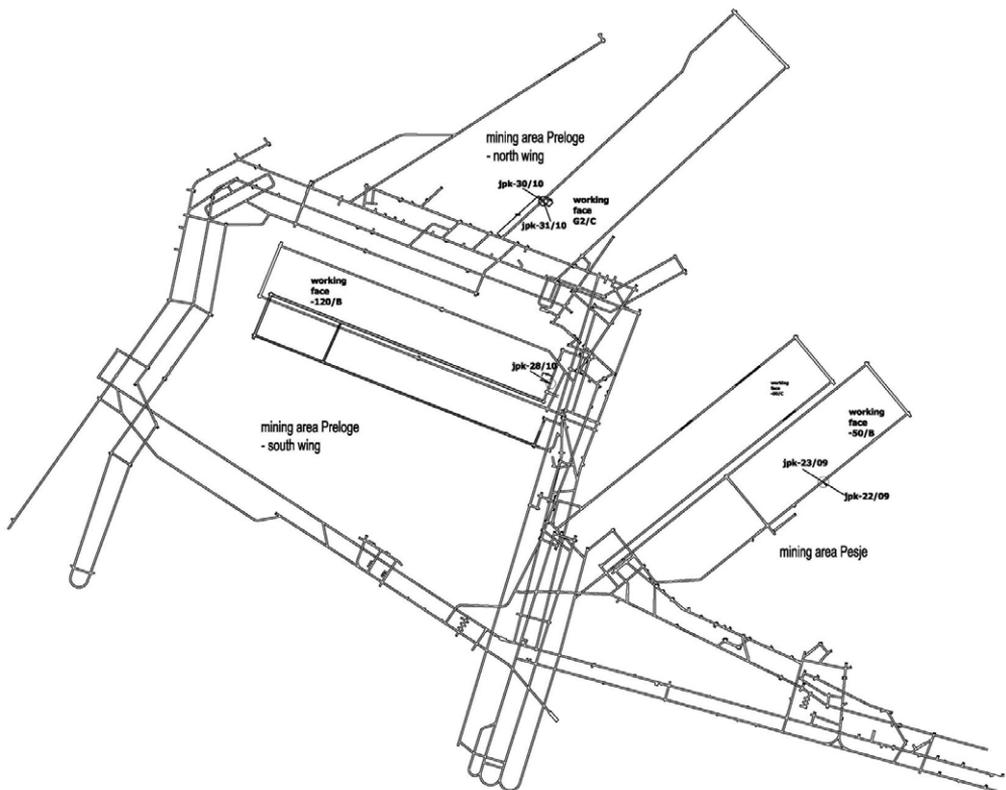


Figure 1. Map of sampling locations of coalbed gases from the lignite strata at working faces (-120/B – Preloge South, G2/C – Preloge North and -50/B - Pesje)

mass spectrometer with ANCA – TG preparation module. First water was removed and then CO₂ was directly analyzed for ¹³C content. For methane measurements first CO₂ was removed and then methane was combusted over hot 10 % platinum CuO (1000 °C). The methane completely converted to CO₂ was then directly analyzed for isotopic composition of carbon (δ¹³C). Working standards calibrated to IAEA (International Atomic Energy Agency) reference materials were used with value of –3.2 ‰ for CO₂ and value of –47.5 ‰ for methane relatively to VPDB (Vienna Pee Dee Belemnite). Analytical precision for carbon isotope composition is estimated to be ±0.2 ‰. The stable carbon isotopes are presented in the δ – notation relative to VPDB standards and expressed in parts per million (COPLÉN, 1996) as follows (O'NEIL, 1979):

$$\delta^{13}C_{\text{vz}} = \frac{R_s - R_{RM}}{R_{RM}} \cdot 1000 \quad [\text{‰}] \quad (1)$$

Where:

R_s – ratio ¹³C/¹²C in sample

R_{RM} – ratio ¹³C/¹²C in reference material

RESULTS AND DISCUSSION

“Free gases” accumulated within the lignite coal seam showed a considerable variability in concentrations and isotopic composition. Due to air con-

tamination within boreholes and the capillary system samples were recalculated on an air - free basis. Major gas components were CO₂ and methane. Only one sample from our study had nitrogen, meaning that it was in excess. Concentrations of CO₂ varied from 20.8 % to 86.9 %, methane from 13.1 % to 58.9 %. Geochemical index CDMI ((CO₂/ (CO₂ + CH₄) × 100 %) vary from 26.1 % to 86.9 % and stable isotope ratios varied in the following ranges: δ¹³C_{CO₂} from –12.5 ‰ to 2.3 ‰ and δ¹³C_{CH₄} from –69.1 ‰ to –26.9 ‰ (Table 1).

High correlation (r between 0.95 and 1) is obtained between methane and CO₂ concentrations (Figure 2) in a lignite seam within boreholes as a function of the advancement of the working faces (–120/B, G2/C and –50/C). Working faces from different mining areas (Preloge North, Preloge South and Pesje) have different composition of coalbed gases. At all investigated mining areas Preloge South (–120/B), Preloge North (G2/C) and Pesje (–50/B) CO₂ prevails under methane (Figure 2). The highest CO₂ concentrations are observed in mining area Preloge South (except 1 sample) where N₂ concentrations were in excess of air (Table 1). The results of areas of high and low methane concentrations (Figure 2) are in physico-chemical properties of CO₂ and methane (ATKINS, 1994). Fissures generated

Table 1. Composition of coalbed gases and isotopic composition of carbon ($\delta^{13}\text{C}$) of coalbed gases (CO_2 and methane) at working faces: -120/B, G2/C and -50/B within boreholes jpk - 28/10, jpk - 30/10, jpk - 31/10, jpk - 22/09 and jpk - 23/09. CDMI index = $(\text{CO}_2/(\text{CO}_2 + \text{CH}_4) \times 100 \%)$

Working face -120/B, borehole jpk-28/10, mining area Preloge South

Date of sampling	Distance of the working face (m)	CH_4 (vol. %)	CO_2 (vol. %)	N_2 (vol. %)	CDMI index (%)	$\delta^{13}\text{C}_{\text{CO}_2}$ (‰)	$\delta^{13}\text{C}_{\text{CH}_4}$ (‰)
March 3, 2010	191	13.1	86.9	0.0	86.9	-5.7	-62.7
March 12, 2010	160	58.9	20.8	20.3	26.1	-7.9	-64.4
March 17, 2010	151	13.8	86.2	0.0	86.2	-7.1	-63.1
April 9, 2010	92	17.5	82.9	0.0	82.6	-4.8	-50.6
May 4, 2010	45	20.5	79.5	0.0	79.5	-9.6	-69.1
May 11, 2010	37	19.8	80.2	0.0	80.2	-8.1	-62.7
May 13, 2010	32	23.0	77.0	0.0	77.0	-8.6	-62.9
May 14, 2010	31	20.0	80.0	0.0	80.0	-8.5	-61.9
May 18, 2010	30	24.3	75.7	0.0	75.7	-12.5	-63.3
June 1, 2010	30	29.1	70.9	0.0	70.9	-7.6	-51.1

Working face G2/C, borehole jpk-30/10, mining area Preloge North

Date of sampling	Distance of the working face (m)	CH_4 (vol. %)	CO_2 (vol. %)	N_2 (vol. %)	CDMI index (%)	$\delta^{13}\text{C}_{\text{CO}_2}$ (‰)	$\delta^{13}\text{C}_{\text{CH}_4}$ (‰)
August 18, 2010	341	42.2	57.8	0.0	57.8	1.8	-31.0
August 31, 2010	316.4	43.5	56.5	0.0	56.5	-1.1	-37.2
September 22, 2010	307.5	46.1	53.9	0	53.9	-6.6	-29.8
November 30, 2010	152.1	42.3	57.7	0.0	57.7	0.9	-50.0

Working face G2/C, borehole jpk-31/10, mining area Preloge North

Date of sampling	Distance of the working face	CH_4 vol. %	CO_2 vol %	N_2 vol. %	CDMI index (%)	$\delta^{13}\text{C}_{\text{CO}_2}$ (‰)	$\delta^{13}\text{C}_{\text{CH}_4}$ (‰)
August 20, 2010	335.3	45.7	54.3	0.0	54.3	-1.7	-45.5
August 27, 2010	316.4	30.7	69.3	0.0	69.3	-9.1	
September 22, 2010	307.5	36.6	63.4	0.0	63.4	-3.9	-60.4
November 30, 2010	152.1	43.3	56.7	0.0	56.7	-0.7	-50.3

Working face -50/B, borehole jpk-22/09, mining area Pesje

Date of sampling	Distance of the working face	CH_4 vol. %	CO_2 vol %	N_2 vol. %	CDMI index (%)	$\delta^{13}\text{C}_{\text{CO}_2}$ (‰)	$\delta^{13}\text{C}_{\text{CH}_4}$ (‰)
November 16, 2009	267	41.3	58.7	0.0	58.7	2.28	-26.9
December 14, 2009	214	19.9	80.1	0.0	80.1	-4.76	-44.4
January 11, 2010	181	33.1	66.9	0.0	66.9	-0.70	-42.6
February 22, 2010	79	24.5	75.5	0.0	75.5	-2.1	-58.0
February 24, 2010	76	28.0	72.0	0.0	72.0	-4.4	-60.6
March 15, 2010	35	42.1	57.9	0.0	57.9	-0.1	-48.3
March 22, 2010	26	27.6	72.4	0.0	72.4	1.0	-56.6

Working face -50/B, borehole jpk-23/09, mining area Pesje

Date of sampling	Distance of the working face	CH_4 vol. %	CO_2 vol %	N_2 vol. %	CDMI index (%)	$\delta^{13}\text{C}_{\text{CO}_2}$ (‰)	$\delta^{13}\text{C}_{\text{CH}_4}$ (‰)
November 16, 2009	267	38.7	61.3	0.0	61.3	0.44	-49.4
February 22, 2010	79	24.5	75.5	0.0	75.5	-2.2	-58.3
February 24, 2010	76	28.0	72.0	0.0	72.0	-4.4	-60.6
March 8, 2010	48.2	19.2	80.8	0.0	80.8	-1.3	-54.6
March 15, 2010	35	26.0	74.0	0.0	74.0	-2.5	-59.6

with advance of the working face enable migration of methane through lignite seam in surrounding strata or to a surface, while CO_2 remains adsorbed in lignite seam.

Figures 3 A, B and C show concentrations of CO_2 and methane at researched mining areas (Preloge North, Preloge South and Pesje) in advancement of the working face (-120/B, G2/C and -50/B). Generally, at all working faces it was observed that methane migrates faster than CO_2 with advance of the working face, therefore the trend of maximum of methane concentration coincides with minimum CO_2 concentrations (Figures 3 A, B and C). Tempo-

ral changes of coalbed concentrations (CO_2 and methane) fluctuate with the rate of advancement of working faces (Figures 3 A, B and C). At the working face -120/B it was observed that at the distance of the working face 92 m (rate of advancement of working face 2.5 m/d) caused highest concentrations in methane and lowest concentration in CO_2 (Figure 3 A). At the distance of the working face 45 m (rate of advancement of the working face cca. 2 m/d) the next maximum of CO_2 was detected, coinciding with minimum of methane concentrations. After May 13 the rate of working face approaching to borehole jpk-28/10 gradually slowed down (rate of advancement

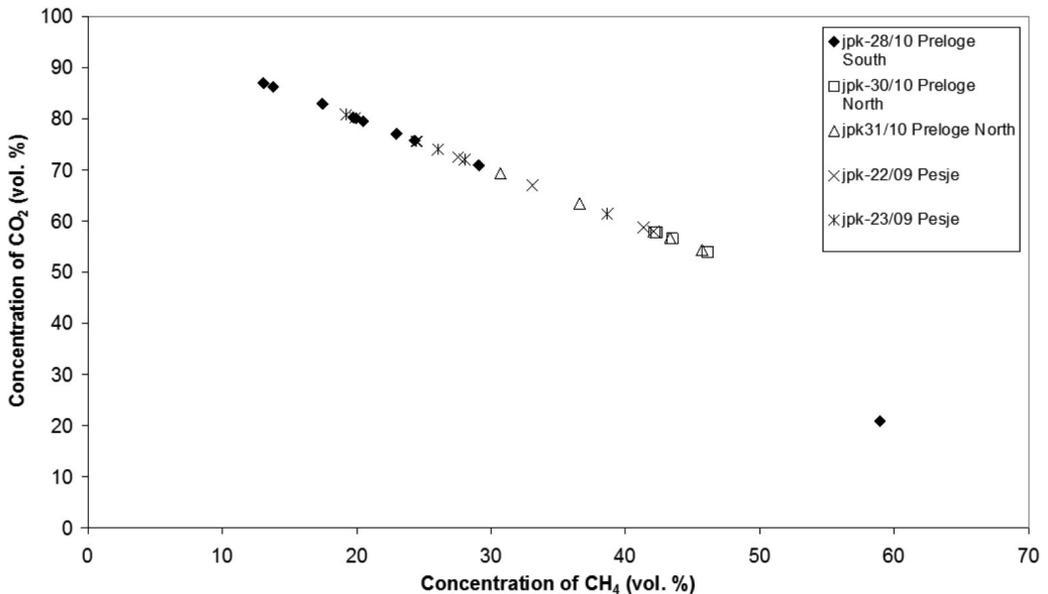


Figure 2. Concentration of CO_2 versus concentration of methane in lignite seam in advancement of the working faces (-120/B Preloge South, G2/C Preloge North, -50/B Pesje)

of working face cca. 1 m/d) causing lower fluctuations in concentration of CO₂ and methane. At the working face G2/C no trends of increasing/decreasing of CO₂ and methane concentrations are observed, probably due to constant approaching of the working face with average rate 1.9 m/d to the boreholes jpk-30/10 and jpk-31/10 (Figure 3 B). The rate of advancement of the working face -50/B was from 0.9 m/d to 2.4 m/d. Maximum methane and minimum methane concentrations were traced within borehole jpk-22/09 at the distance of the working face 35 m (rate of advancement of working face cca. 2.2 m/d) (Figure 3 C). Approaching of the working face also influence on stress situation at working face (Figure 4). During excavation of lignite secondary fissures are generated due to rearrangement of primary stress conditions, enabling releasing of coalbed gas preserved in pores of coalbed reservoir. These stress conditions are presented in Figure 4 modified after WILLIAM (1999). Results of changing of stresses were investigated by three axis cells build in lignite structure. The research revealed that at the distance of 120 m from the working face vertical stresses start to increase. At the distance of 80 m from the working face shearing and collapsing of lignite structure occur; vertical stresses continue to increase while horizontal and transverse stresses decrease. At the distance of the working face 30–50 m from three axis

cell vertical stresses are so high that the lignite structure collapse (ZAVŠEK, 1990). Research of temporal variations of concentrations (CO₂ and methane) within borehole 780H IV at working face -80c similar trends as at working faces -120/B, G2/C and -50/B in concentrations of CO₂ and methane were observed; at the distance of the working face 177 m and 122 m maximum concentrations of methane were traced and coincide with minimum concentrations of CO₂ (KANDUČ, 2004). Besides the rate of advancement of the working face concentrations of methane and CO₂ measured in lignite seam within boreholes (jpk-28/10, jpk-30/10, jpk-31/10, jpk-22/09 and jpk-23/09) also depends on permeability and porosity of lignite seam. When methane and CO₂ reaches strata with high permeability such as fault zones, their concentrations start to increase, therefore also areas with high concentrations of methane and CO₂ might be expected. CO₂ behaves at certain condition (above its critical temperature 31.1 °C and critical pressure 7.39 MPa, expanding to fill its container like a gas but with a density like that of a liquid) as supercritical fluid (ATKINS, 1994), meaning that could be at liquid and gas phases. The conditions of critical temperature and pressure for CO₂ are possibly reached at working faces causing its adsorption (liquid phase)/desorption (gas phase). Areas with high CO₂ content (CDMI index) might be potentially danger-

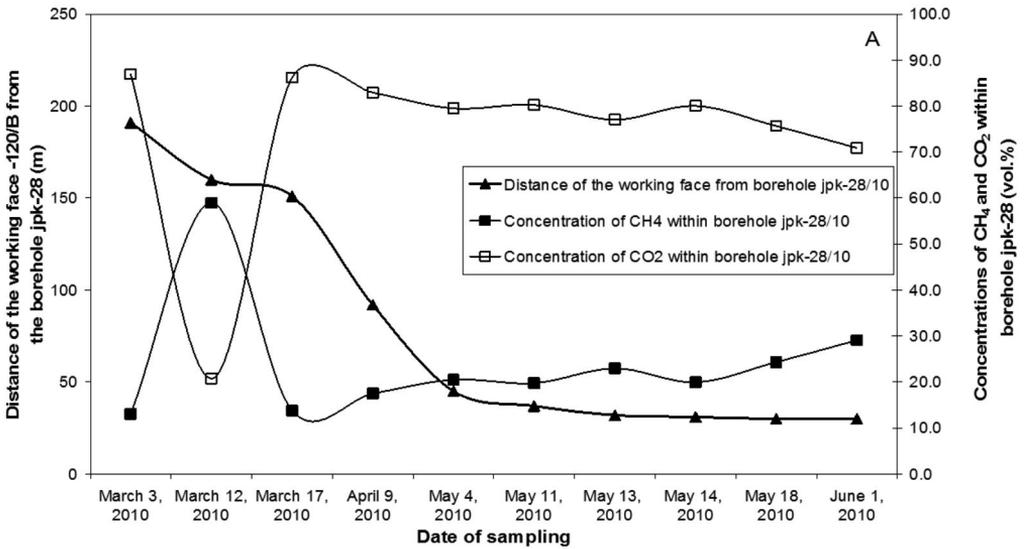


Figure 3A. Concentration of methane and CO₂ versus date of sampling in advancement of the working face -120/B (Preloge South)

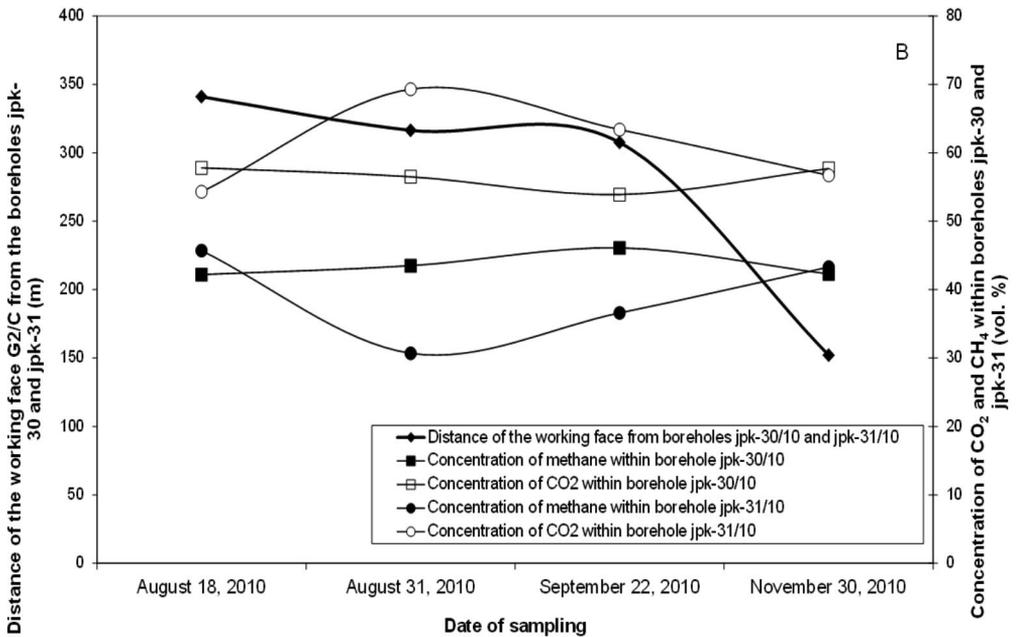


Figure 3B. Concentration of methane and CO₂ versus date of sampling in advancement of the working face G2/C (Preloge North)

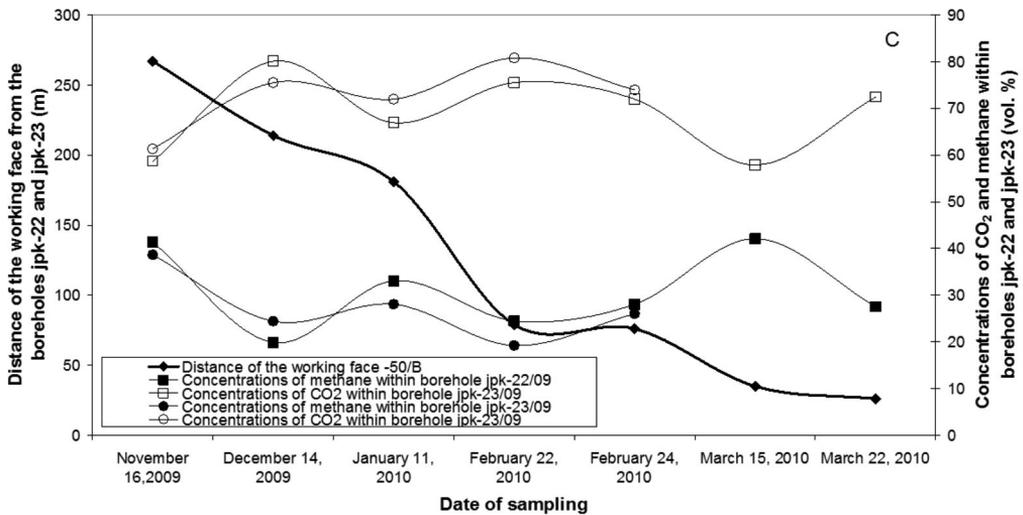


Figure 3C. Concentration of methane and CO₂ versus date of sampling in advancement of the working face –50/B (Pesje)

ous for gas outbursts (CLAYTON, 1998). Anyway, investigation of gas concentrations at each working face should be further related to petrological characteristics of lignite (lithotype type e. g. xylite, detrite), tectonically characteristics (characteristics of fault zones) and geotechnical conditions (pressures, porosity and permeability) to get better insight to coalbed gas migration as well sorption/desorption processes, especially CO₂ through lignite.

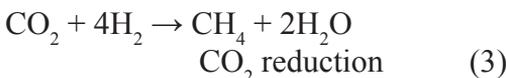
Interpretation of coalbed gases from investigated mining areas of Pesje and Preloge was performed according to previous study of tracing inorganic and organic carbon cycles in different geological media (calcified xylite, carbonate lenses in the lignite seam, lignite and Pliocene, Triassic and Lithotam-

nium aquifers) (KANDUČ et al., 2010, in review). From the results it was concluded that coalbed gases in the Velenje Basin are mainly microbial (bacterial) origin, while CO₂ could be also endogenic. Microbes that generate methane (methanogens) could have either of been deposited with the coal sediments in the geologic past or transported in more recently with active groundwater recharge. To thrive methanogens require an anoxic, aqueous environment with organic carbon substrates and the absence of other free-energy electron acceptors, such as NO₃⁻ and SO₄²⁻. Fermentative bacteria degrade complex organic matter in coalbeds (e.g. structures of carbohydrates, proteins and lipids that originate in vegetation and sediments) to simpler molecules including acetate (CH₃COOH), fatty

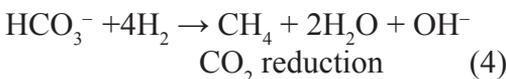
acids, CO_2 and H_2 gas. Acetogenic bacteria thrive on fatty acid products to produce acetate, with CO_2 and H_2 by products (KOTELNIKOVA, 2002). The products of these reactions support a variety of methanogens. Some methanogens use an acetate food source to produce CO_2 and methane, according to following reactions:



While other methanogens use the hydrogen gas to reduce CO_2 :



or



We applied diagrams $\delta^{13}\text{C}_{\text{CH}_4}$ versus $\delta^{13}\text{C}_{\text{CO}_2}$ (Figure 5) to explain the origin of methane and $\delta^{13}\text{C}_{\text{CO}_2}$ versus CDMI index (Figure 6) to explain the origin of CO_2 . $\delta^{13}\text{C}_{\text{CH}_4}$ (Figure 4) in the Velenje basin indicate the successive origin of methane: microbial (CO_2 reduction) with $\delta^{13}\text{C}_{\text{CH}_4}$ values from -40% to -50% , microbial (acetate fermentation) with $\delta^{13}\text{C}_{\text{CH}_4}$ less than -50% and mixed origin between these two (CLAYTON, 1998). Enrichment with ^{13}C in methane could be also due to microbial oxidation of methane, which results in an enrichment of residual methane

with the ^{13}C isotope and depletion of ^{12}C in generated CO_2 (Figure 5).

It is known that coalbed lignite strata were formed in the Pliocene in a calm sedimentary environment (MARKIČ & SACHSENHOFER, 1997), but the proportion of early stage microbial gas retained in the lignite structure (SMITH & PALLASER, 1996) is difficult to estimate. Microbial methane in Velenje basin was generated by microbial reduction and/or by microbial fermentation. Also recent microbial activity (methanogenic and methanotrophic bacteria) might generate microbial

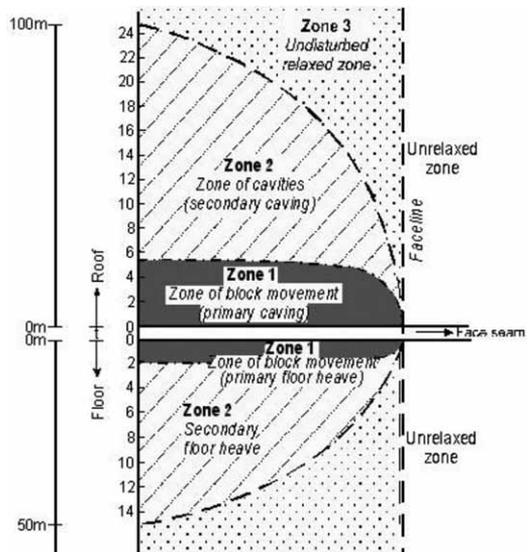


Figure 4. Geomechanical conditions and generation of secondary fissures due to longwall method of excavation of lignite, causing a release of coalbed gases inside of demolished zone (adapted after WILLIAMS, 1999)

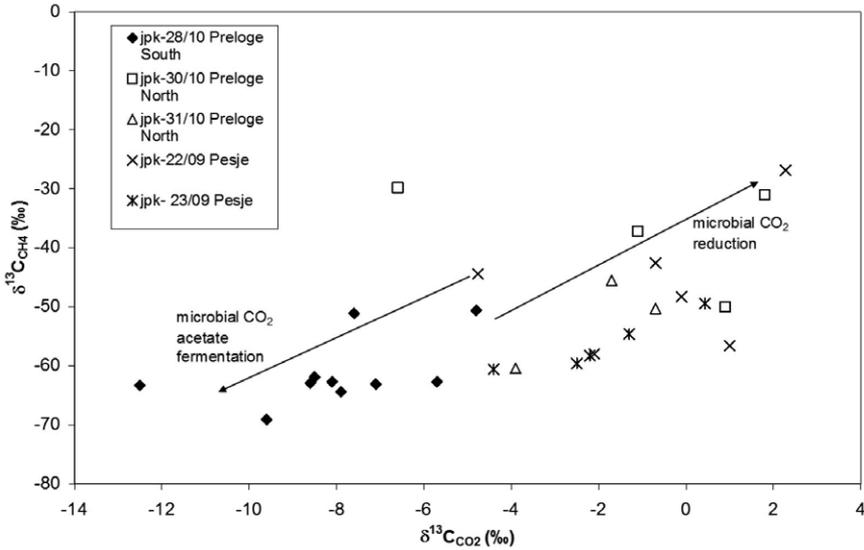


Figure 5. Interpretation of the origin of methane in the Velenje basin using $\delta^{13}\text{C}_{\text{CH}_4}$ versus $\delta^{13}\text{C}_{\text{CO}_2}$ in a lignite seam at boreholes (jpk – 28/10, jpk – 30/10, jpk – 31/10, jpk – 22/09 and jpk – 23/09) in advancement of the working faces (–120/B, G2/C and –50/B)

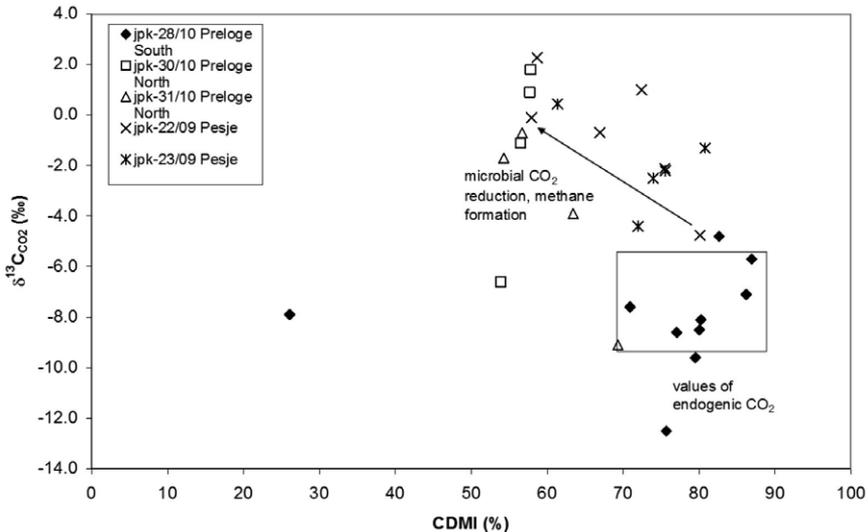


Figure 6. Interpretation of the origin of CO_2 at working faces (–120/B, G2/C in –50/B) using $\delta^{13}\text{C}_{\text{CO}_2}$ versus CDMI index in a lignite seam in boreholes (jpk – 28/10, jpk – 30/10, jpk – 31/10, jpk – 22/09 and jpk – 23/09) ahead of the working faces (–120/B, G2/C and –50/B)

gas (KOTELNIKOVA, 2002). Methane and CO₂ were/are generated by microbial fermentation process while methane was/is generated by CO₂ reduction process. CO₂ generated by fermentation process is characterized by $\delta^{13}\text{C}_{\text{CO}_2}$ similar that organic matter around -25‰ , while microbial reduction process results in an enrichment with the ^{13}C of residual CO₂ (Figures 5 and 6). Microbial CO₂ reduction is characteristic in mining area Preloge North, while at Preloge South $\delta^{13}\text{C}_{\text{CH}_4}$ indicate bacterial origin via fermentation. At mining area Pesje both microbial (CO₂ reduction and methane fermentation) processes generated methane formation (Figure 5).

The origin of CO₂ is interesting due to its relation with outbursts in coalmines. High concentrations of carbon dioxide in seam gases in Australian coals occur in regions of igneous activity and associated faulting and this component has been described as being of presumed pneumatolytic origin (SMITH & GOULD, 1980). In our study CDMI index versus $\delta^{13}\text{C}_{\text{CO}_2}$ (Figure 5) was used to explain the origin of CO₂ (KOTARBA, 2001) and indicate endogenic CO₂ (including CO₂ originating from carbonates) and CO₂ of microbial origin in relation to microbial methane (working face Preloge North, jpk-30/10) discussed above. At working face Pesje -50/B (jpk-22/09

and jpk-23/09) $\delta^{13}\text{C}_{\text{CO}_2}$ indicate microbial and endogenic origin (Figure 6). Typical endogenic values of $\delta^{13}\text{C}_{\text{CO}_2}$ are about -7‰ (KOTARBA, 2001) and high CDMI index found in our study (at working face Preloge South, jpk-28/10) are probably related to the tectonics of the Šoštanj and Smrekovec faults at the time of formation of the Velenje basin.

$\delta^{13}\text{C}_{\text{CO}_2}$ derived from carbonates is dependent on $\delta^{13}\text{C}$ of carbonates and the temperature of their degradation. The resulting products are clay minerals and CO₂. Supposing that dolomites underwent thermal decomposition and are located below lignite seam along the Šoštanj fault zone values of $\delta^{13}\text{C}_{\text{CO}_2}$ from -2‰ to -6‰ might indicate CO₂ of thermal decomposition of dolomites (Figure 6). This source of CO₂ has similar values as endogenic CO₂ from the fault zones and can not be distinguished with $\delta^{13}\text{C}_{\text{CO}_2}$.

Also secondary processes should be considered since they might camouflage the origin of gases. Migration of gases as a secondary process caused by reduction of pressure in lignite seam causes enrichment in light ^{12}C isotope in methane and in CO₂. During migration of coalbed gases, gases of different origin might be mixed together and complicate interpretation of gas origin.

CONCLUSIONS

Gas outbursts remain for coalminers one of the main problems in the Velenje coalmine, therefore geochemical investigations are one of the important parameters used in case of prediction or prevention gas outbursts.

Concentrations of methane and CO₂ change in advance of the working face. Areas with high CO₂ concentrations accompany with low methane concentrations and could be related with the rate of advancement of the working face. The rate of advancement of the working face is one of the crucial parameters influencing on gas composition at working faces.

Concentrations and stable isotope studies of coalbed gases at working faces allow the possible interpretation of the origin of coalbed gas in the Velenje basin. Considering also the results of previous studies, it can be concluded that coalbed CO₂ from investigated working faces is endogenic and bacterial origin. Methane is microbial origin (formed through microbial fermentation and/or CO₂ reduction). Secondary processes like migration, adsorption/desorption and mixing of gases of different origin during excavation complicate the interpretation of gas origin and were neglected in interpretation of the origin of coalbed gases. Examination of the origin of nitrogen (at loca-

tions with excess of nitrogen) in coalbed gases from Velenje Basin needs further research.

Acknowledgements

This study was conducted in the framework of project Z1-2052 funded by the Slovenian Research Agency (ARRS) and the Velenje Coalmine d.d. The authors are also grateful to Mr. Tedej Zagoričnik, Mr. Robert Lah and Mr. Stojan Žigon for technical support, assistance in the field sampling and laboratory analyses. Sincere thanks to Dr. Jennifer McIntosh for improving the English of the manuscript.

REFERENCES

- ARAVENA, R., HARRISON, S. M., BARKER, J. F., ABERCROMBIE, H. & RUDOLPH, D. (2003): Origin of methane in the Elk Valley coalfield, south-eastern British Columbia, Canada. *Chem. Geol.*; Vol. 195, pp. 219–227.
- ATKINS, P. W. (1994): *Physical Chemistry*, fifth ed. Oxford Univ. Press, Oxford, pp. 1031.
- CLAYTON, J. L. (1998): Geochemistry of coalbed gas – A review. *Inter. J. Coal Geol.*; Vol. 35, pp. 159–173.
- COPLIN, T. B. (1996): New guidelines for reporting stable hydrogen, carbon and oxygen isotopes ratio data. *Geochim. Cosmochim. Acta.*; Vol.

- 60, pp. 390–3360.
- FLORES, R. M. (1998): Coalbed methane: From hazard to resource. *Inter. J. Coal Geol.*; Vol. 35, pp. 3–26.
- KANDUČ, T. (2004): *Isotopic characteristics of coalbed gases in Velenje Basin*. Master Thesis. Ljubljana: University of Ljubljana 2004; pp. 78 (in Slovene).
- KANDUČ, T., MARKIČ, M. & PEZDIČ, J. (2005a). Stable isotope geochemistry of different lithotypes of the Velenje lignite (Slovenia), *Geologija*; Vol. 48, pp. 83–92.
- KANDUČ, T. & PEZDIČ, J. (2005b). Origin and distribution of coalbed gases from the Velenje Basin, Slovenia. *Geochem. J.*; Vol. 39, pp. 397–409.
- KANDUČ, T. & ŠLEJKOVEC, Z. (2005c). Unexpected arsenic compounds in low-rank coals. *Environ. Sci. Technol.*; Vol. 39, pp. 3450–3454.
- KANDUČ, T., MARKIČ, M., ZAVŠEK, S. & MCINTOSH, J. (2010). Methanogenesis in the Pliocene Velenje Coal Basin, Slovenia, inferred from stable carbon isotopes. *Inter. J. Coal Geol.* (in review).
- KOTARBA, M. (1990): Isotopic geochemistry and habitat of the natural gases from the Upper Carboniferous Zacler coal – bearing formation in the Nowa Ruda coal district (Lower Silesia, Poland). *Org. Geochem.*; 16, pp. 549–560
- KOTARBA, M. J. (2001): Composition and origin of coalbed gases in the Upper Silesian and Lublin basins, Poland. *Org. Geochem.*; 32, pp. 163–180
- KOTELNIKOVA, S. (2002): Microbial production and oxidation of methane in deep subsurface. *Earth – Science Reviews.*; Vol. 58, pp. 367–395.
- MARKIČ, M. & SACHSENHOFER, R. F. (1997): Petrographic composition and depositional environments of the Pliocene Velenje lignite seam (Slovenia). *Inter. J. Coal Geol.* 33, pp. 229–254
- O’NEIL, J. R. (1979): Stable Isotope Geochemistry of Rocks and Minerals. - V: Lectures in Isotope Geology, Jager, E., Hunzinger, J. C., (Eds). - Springer Verlag, 235–263, Berlin.
- SCOTT, A. R. (1993): Composition and origin of coalbed gases from selected basins in the United States. *Proceeding of the 1993 International Methane Symposium, Birmingham, Alabama*. Vol. 1, pp. 207–222.
- SHERWOOD LOLLAR, B., LACRAMPE-COULOUME, G., SLATER, G. F., WARD, J., MOSER, D. P., GIHRING, T. M., LIN, L.-H. & ONSTOTT, T. C. (2006): Unravelling abiogenic and biogenic sources of methane in the Earth’s deep subsurface. *Chem. Geol.*; Vol. 226, pp. 328–339.
- SHOELL, M. (1983): Genetic characterization of natural gases. *Amer. Ass. Petrol. Geol. Bull.*; Vol. 67, pp. 2225–2238.
- SMITH, J. W. & PALLASER, R. (1996): Microbial origin of Australian coalbed methane. *Amer. Ass. Petrol. Geol. Bull.*; Vol. 80, pp. 891–897.
- SMITH, J. W. & GOULD, K. W. (1980): An isotopic study of the role of carbon dioxide in outbursts in coal

mines. *Geochem. J.*; Vol. 14, pp. 27–32.

ZAVŠEK, S. (1990): Projekt raziskovalne proge na k. +75 v jami Škale, projektna študija, rudarski project, REK Velenje, DO Rudnik Lignita Velenje. Velenje: Premogovnik

Velenje, Hidrogeološki oddelek, pp. 30 (in Slovene).

WILLIAM, D. J. Fugitive emissions from coal mining (online). 1999, November 23.12.2003 [citirano 11. 11. 1999]. Dostopno na svetovnem spletu:<<http://www.atse.org.au>>.