

Simulation of CO₂ injection in a depleted gas reservoir: A case study for Upper Miocene sandstone, Northern Croatia

The Mining-Geology-Petroleum Engineering Bulletin
UDC: 622.420
DOI: 10.17794/rgn.2019.1.12

Original scientific paper



Amalia Lekić¹; Lucija Jukić¹; Maja Arnaut¹; Marija Macenić¹

¹The University of Zagreb, Faculty of Mining, Geology and Petroleum Engineering, Pierottijeva 6, Zagreb, Croatia

Abstract

Carbon capture and storage (CCS) technology is a beneficial greenhouse gas mitigating strategy carried out in the last 20 years. Depleted gas reservoirs are promising candidates for the storage of carbon dioxide (CO₂). Therefore, a depleted gas reservoir in the Upper Miocene sandstone located in Northern Croatia was taken as an example. The purpose of this study was to compare CO₂ storage capacity obtained with two analytical equations to total storage capacity obtained through the simulator, in order to validate the equations. The first equation takes the average reservoir pressure and available production data into account, while the other one is more general and includes produced volume, CO₂ density and formation volume factor of the original fluid. The tools used for these calculations were Schlumberger PVTi software, in which the equation of state was obtained, and ECLIPSE (E300 Module) which is a reservoir engineering simulator used for reservoir behaviour prediction. The results confirmed analytical solutions, indicating that, depending on the depth, the mass of the CO₂ that can be injected is twice as big as the mass of CH₄ produced. The results of analytical solutions, 16.7×10^6 m³ and 14.6×10^6 m³, are in accordance with the results obtained by the simulation of CO₂ injection in depleted reservoirs - 16.2×10^6 m³. Based on this, a conclusion is derived that these analytical solutions can be used as a first approximation of injection in a depleted gas reservoir.

Keywords:

carbon capture and storage (CCS); depleted gas reservoir; CO₂ storage simulation, the Upper Miocene sandstone, Northern Croatia.

1. Introduction

There are several possibilities for carbon dioxide (CO₂) sequestration, among which injection into oil and gas reservoirs for enhanced recovery is the most feasible one. This is due to the possibility of recovering additional quantities of oil and gas. However, considering that a vast number of oil and gas fields in Croatia are experiencing a significant decline (Velić et al., 2016), injection into abandoned/depleted oil and gas reservoirs is also an acceptable form of CO₂ reduction. In this case, no additional value is created. Gaurina-Medimurec et al. (2018) stated that hydrocarbon reservoirs are considered one of the most favourable options for CO₂ disposal. Gas reservoirs are the most reliable potential storage locations since produced gas can be considered as an indication that the reservoir would be impermeable for the same volume of injected CO₂ (Vulin, 2010). Additionally, Novak et al. (2013a) report that the reservoirs in the Croatian part of the Pannonian Basin System (CPBS) are at a sufficient depth and of older age, which means that they are consolidated and not prone to tectonic activity. Some of the advantages of depleted reser-

voirs, compared to storage in aquifers and other geological formations, are well-characterized reservoirs with known properties, proven traps capable of retaining fluids for a long time, small exploration costs and a possibility of reusing some of the existing infrastructure (URL1). The advantage of sequestration into depleted reservoirs, compared to enhanced oil/gas recovery (EOR/EGR) processes, is that CO₂ is not produced but trapped underground. There are several trapping mechanisms that hinder CO₂ from escaping the geological formations and these mechanisms depend on the type of formation in which CO₂ is stored. These mechanisms are structural or stratigraphic trapping assured by the cap rock, residual gas trapping connected with the drainage-imbibition process in the post-injection phase – hysteresis, solubility/dissolution trapping in an aquifer, and mineral trapping, which is a reaction of CO₂ with rock minerals to create precipitates (Temitope et al., 2016; Raza et al., 2017). Structural trapping is dominant in the first period after injection stops, with negligible mineral trapping. Later, after 50-150 years, residual trapping becomes more significant. Solubility trapping has an almost constant share but becomes more important at later times (500+ years). Storage security increases with time (Ampomah et al., 2015). Raza et al. (2017) report that

Corresponding author: Lucija Jukić
lucija.jukic@rgn.hr

for short times, residual trapping is most efficient. **Novak (2015)** examines the effect of mineral trapping and finds that 2-5% of CO₂ injected could be permanently stored with this mechanism.

An additional advantage of sequestration in depleted gas reservoirs is geothermal exploitation but is valid only for high-temperature reservoirs. It is based on the fact that supercritical CO₂ has 1.5 times higher heat capacity compared to water (**Cui et al. 2015; Cui et al. 2016**). It is possible to store more CO₂ in a depleted gas reservoir having the same hydrocarbon pore volume than in an oil reservoir. This is due to a higher ultimate recovery of gas reservoirs compared to oil reservoirs, and higher compressibility of the gas (**Lawal and Frailey, 2004; Stein et al., 2010**). While injection into oil reservoirs, which are depleted or near the end of production, is usually accompanied by the EOR process, depleted gas reservoirs should be used as storage only. In the case of injection into depleted gas reservoirs, CO₂ could contaminate the remaining natural gas. Therefore, it is recommended to inject CO₂ only in reservoirs that would not become economic with an increase in gas prices. The study of IEA Greenhouse Gas R&D Programme (**URL1**) estimated that the global potential for CO₂ storage in disused gas reservoirs is 797×10^{12} kg and in disused oil reservoirs 126×10^{12} kg. The cost of sequestration into oil and gas reservoirs could be less than \$2.5/kg for 746×10^{12} kg. When it comes to gas reservoirs, only around 105×10^{12} kg of CO₂ could be stored at a cost of \$0.6/kg, while the storage of an additional 575×10^{12} kg could be achieved at a cost of \$0.8-1.4/kg. The rest of 117×10^{12} kg could be stored at a price from \$1.7 to 8.3/kg (**URL1**). It also showed that only 75-80% of void space left after primary gas recovery could be used for CO₂ storage, mainly due to water inclusion and the field edge effect. However, the same study, along with **Cui et al. (2015)**, indicates that due to the higher compressibility of CO₂ compared to methane, the amount of CO₂ that could be injected is higher than the amount of natural gas produced. This ratio highly depends on the injection depth. At 1000 m, a depleted gas reservoir can withstand 3 times the standard volume of CO₂ compared to a standard volume of CH₄, and at 3000 m, this ratio is only 1.5 (**URL1**). During the injection, the seal integrity or impermeable caprock is crucial since CO₂ is injected in supercritical condition, which means it tends to migrate upwards, relative to water present in the pores, after the gas depletion took place. However, geomechanics and seal stability were not considered and are out of the scope of this paper. It was assumed that the caprock is proven to be reliable and no significant effect on geomechanics would be evident due to a relatively small amount of CO₂ injected. Sequestration in oil reservoirs is better when no previous water injection or enhanced oil recovery is performed (**Pawar et al., 2004**). When it comes to gas reservoirs, low gas saturations are desirable, i.e., it is recommended to have

secondary recovery (**Raza et al., 2018**). In the same study, it was proven that at low residual gas saturation, structural trapping is the main mechanism and at high residual gas saturation (30%), capillary trapping dominates over dissolution and structural trapping. It was also stated that after 1500 years, only 10% of injected CO₂ is dissolved in immobile reservoir water. The effect of residual gas saturation was also studied by **Raza et al. (2018)**. It was concluded that previous research showed a negative influence of residual gas saturation on injectivity and storage capacity since the dissolution of gas mixtures in supercritical CO₂ reduces the density and viscosity of gas mixtures. In addition, it was found that in the case of EGR, stabilization of production occurs in the early years and production decline starts earlier in a high residual gas saturation reservoir. Finally, it was concluded that high residual gas saturation impacts the relative permeability of gas, thus influencing the recovery factor. Low residual fluid reservoirs make better storage locations. **Raza et al. (2017)** proposed a method for estimating trapping capability based on the Laplace model. **Al-Hashami et al. (2005)** observed the effects of CO₂ diffusion and solubility in water and concluded that gas diffusion is important in mixing CO₂ with gas present in the reservoir. A CO₂ breakthrough in the EGR/EOR process is delayed by the dissolution of CO₂ in water. **Loeve et al. (2014)** investigated the propagation of temperature during the injection of CO₂. Carbon dioxide is injected at a minimum of 12 °C. The research showed that after 5 years, a radius of up to 100 m from the borehole has a significantly lower temperature than the rest of the reservoir in the case of high brine saturation. If the brine saturation is low, the cold front does not exist.

Galic et al. (2009) described building a model of CO₂ injection in a depleted gas reservoir through Integrated Production Modelling Petroleum Experts (IPM PETEX) software, with the main focus on the impact of the pipeline surrounding temperature on bottom hole injection temperature and influence of injection manifold pressure change. **Arts et al. (2012)** used Shell's compositional simulator, MoReS, to simulate the injection of CO₂, which was supposed to be collected at the point source of coal power plant, in a depleted offshore gas field in the Netherlands. The simulation was done for a period of 5 years, at the end of which the original pressure was not achieved. The study showed that injection through a previous production well could be prolonged, to the point of reaching the original pressure. The paper also showed a detailed geological setting of the gas reservoir as well as the monitoring plan that was to be set during and after CO₂ injection as a means of controlling CO₂ and reservoir behaviour. **Luo et al. (2013)** investigated the influence of the reservoir heterogeneity and well placement on CO₂ storage with the conclusion that CO₂ is transported faster in the heterogeneous reservoir. Furthermore, if the wells (producer and injector) are located in the lower permeability layer, storage is improved. In this

paper, isothermal conditions are assumed, but there are a number of studies that deal with the change of the temperature and Joule-Thomson Cooling effect (Mathias et al., 2010; Sing et al., 2011; Ziabakhsh-Ganji and Kooi, 2014). According to Chen et al. (2015), calculation of the CO₂ storage capacity can be divided into three groups: volume-based, production-based, and numerical method. The volume-based method is simple and convenient but due to heterogeneity and geological uncertainty, this method is not reliable. The production-based method for CO₂ storage capacity, introduced by Tao and Clarens (2013), is based on historical and projected CH₄ production data. The numerical method is complex, site-specific and the required data must be very detailed. Valbuena et al. (2012) developed an algorithm for estimating cumulative CO₂ storage capacity where 1.023 pore volumes of CO₂ were injected. Injection rate and a number of wells determine only the duration of injection and CO₂ storage capacity depends on saturation, temperature, pressure differential and fluid composition and characteristics.

Several studies deal with the material balance of CO₂ injection in depleted gas reservoirs (Lawal and Frailey, 2004; Stein et al., 2010; Lai et al., 2015). Although calculation in the IPM PETEX MBAL (Material Balance) module is somewhat simplified, Lawal and Frailey (2004) obtained a p/z vs. G_p curve for hydrocarbon gas and for CO₂ and showed that the volume of CO₂ that could be injected is less than double the volume of hydrocarbon produced. The p/z vs. G_p method is used for volumetric dry gas reservoirs, in which the ratio of pressure and z -factor yields a straight line when plotted versus cumulative gas production. This straight line is extrapolated to a value of p/z to zero for initial gas in place estimation and can also be used to estimate the ultimate recovery at a selected p/z value. Iogna et al. (2017) simulated injection of CO₂ in a depleted gas field using the Black Oil module in ECLIPSE, but the paper mainly dealt with EGR. The obtained results were a bit more conservative than results from a fully compositional model. It was found that reservoir properties, the conversion sequence, well positioning and the faults transmissivity effect enhanced gas recovery.

There are a number of studies regarding seal stability (Orlic, 2009; Okamoto et al., 2005), fault stability (Streit and Hillis, 2004), seismic monitoring of CO₂ (Pawar et al., 2004; Underschultz et al., 2011), geomechanics (Orlic, 2009; Shi and Durcan, 2009), risks of CO₂ leakage (Gaurina-Medimurec et al., 2017), sequestration in aquifers (Ghomian et al., 2008; Pham et al., 2013; Rathnaweera et al., 2017; Vulin et al., 2012; Vulin et al., 2018a), enhanced oil recovery (Novak et al., 2013a; Novak et al., 2013b; Bossie-Codreanu and Le Gallo, 2004; Vulin et al., 2018b) and enhanced gas recovery (Biagi et al., 2016; Patel et al., 2016; Luo et al., 2013). It was observed, from the literature review presented in this work so far, that research on the simula-

tion of CO₂ injection into depleted gas reservoirs is rather scarce, with only Arts et al. (2012), presenting a geological sequestration of CO₂ without either form of enhanced recovery. However, the data presented in the paper is insufficient for the work to be reproducible and applicable to the case of Croatian sandstone and the simulation was done in a different simulator than this research. Various studies dealing with different CO₂ storage issues have been published over the last twenty years (Orlic, 2009; Okamoto et al., 2005; Streit and Hillis, 2004; Gaurina-Medimurec et al., 2017; Ghomian et al., 2008; Pham et al., 2013; Rathnaweera et al., 2017; Vulin et al., 2012; Vulin et al., 2018a). Published studies mainly dealt with CO₂ injection into oil reservoirs (Novak et al., 2013a; Novak et al., 2013b; Bossie-Codreanu and Le Gallo, 2004; Vulin et al., 2018b) and in cases when the storage in the gas reservoir was considered, EGR was taken into account (Biagi et al., 2016; Patel et al., 2016; Luo et al., 2013). Therefore, previously developed simulation models almost always contained a production well and calculated the additional recovery (Iogna et al., 2017). A simulation model of this case study for Croatian sandstone contains only one well which was used as a production well until production ended and then the same well is used for CO₂ injection with the aim of permanent CO₂ storage. As mentioned, geological sequestration without the enhanced recovery practically could not be found in the literature, except for one paper (Arts et al., 2012), and the relevance of this work can be found in the applicability of simulation for a typical Croatian gas reservoir. An example of a small depleted gas reservoir was considered in terms of the gas production history of the field, reservoir pressure and CO₂ that could be injected to replace the produced gas. Simulation in the Schlumberger ECLIPSE (E300) Package was made to check the cumulative injection of CO₂ compared to published, theoretical amounts and also in order to monitor the reservoir pressure so it does not exceed the fracturing pressure.

Carbon capture and storage (CCS) is a methodology which includes the capture, transport, and storage of CO₂ (Gaurina-Medimurec et al., 2018). Considering the emission quantities, Croatia is not a big emitter of CO₂ - around 20×10^9 kg in 2015, according to European Commission (URL2). Therefore, the need for storage is accordingly small so quantities of CO₂ stored obtained from the simulation are realistic and would mean an elimination of around 0.18% of CO₂ emitted in Croatia. The research presented in this manuscript deals with the storage process of CO₂ in a depleted gas reservoir, while the capture and transport processes were not considered.

2. Methods

There are several published analytical methods presented by Lai (Lai et al., 2015), Bachu (Bachu et al.,

CHRONOSTRATIGRAPHIC UNITS FOR CENTRAL PARATETHYS				Neogene and Quaternary megacycles	LITHOSTRATIGRAPHIC UNITS (formations)					
					Mura depression	Sava depression	Drava depression (western part)	Slavonia-Srijem & Drava dep. (eastern part)		
CENOZOIC	QUAT.	HOLOCENE		3 rd megacycle	Mura formation	Lonja formation		Vuka formation		
		PLEISTOCENE								
	PLIOCENE	ROMANIAN								
		DACIAN								
	NEOGENE	UPPER	PONTIAN			2 nd megacycle	Lendava formation ----- ? ----- ----- ? -----	Široko polje formation	Bilogora formation	Vera formation
			PANNONIAN		Kloštar Ivanić formation			Vinkovci formation		
					Ivanić-Grad formation					
		MIDDLE	SARMATIAN		1 st megacycle	Murska Sobota formation	Prkos formation	Moslavačka gora formation		Vukovar formation
			BADENIAN				Prečec formation			
MESOSOIC AND PALEOZOIC					Bedrock					

Figure 1: Chronostratigraphic and lithostratigraphic units of the Croatian part of the Pannonian Basin (CPBS) with denoted approximate age of the analysed reservoir (modified from Velić, et al., 2012)

2007) and Schuppers (Schuppers et al., 2003) for estimating CO₂ storage capacity in depleted gas reservoirs and two of them were used for comparison with simulated results. Lai et al. (2015) found that by reverting pressure to the initial reservoir pressure, the total volume of CO₂ stored could be 1.4 times larger than that of the gas production. In this work, Equation 1 was used for calculating the theoretical amount of CO₂ that could be injected in the reservoir MALM. The material balance equation (MBE) is used for estimating the original gas in place (OGIP) from the available production data and average reservoir pressure. It was assumed that the hydrocarbon pore volume of the gas reservoir was unchanged during gas production and CO₂ injection and that reservoir volume of the OGIP should be equal to the reservoir volume of the mixture of remaining gas in the reservoir and injected CO₂. The liquid production was eliminated from the MBE and the formula for CO₂ storage in the depleted dry gas reservoir was given (Lai et al., 2015):

$$G_{injCO_2} = G_p - G_i + \frac{p_r}{z_{mix}} \times \frac{z_i}{p_i} \times G_i \quad (1)$$

Where G_{injCO_2} = cumulative CO₂ injected at s.c. (m³), G_p = cumulative gas production at s.c. (m³), G_i = original gas in place volume at s.c. (m³), p_r = reverted pressure of gas reservoir with a mixture of gas and CO₂ (bar), z_{mix} = gas deviation factor of the mixture of natural gas and CO₂ (dimensionless), z_i = gas deviation factor (z-factor) at initial reservoir condition (dimensionless), p_i = initial reservoir pressure (bar)

Schuppers et al. (2003) gave this general formula for CO₂ mass injection calculation:

$$m_{CO_2} = G_p \times \rho_{CO_2} \times B_{gi} \quad (2)$$

Where m_{CO_2} = mass of CO₂ that can be injected (kg), ρ_{CO_2} = CO₂ density at reservoir conditions (kg/m³), B_{gi} = formation volume factor of natural gas (m³/m³)

Water production is neglected in **Equation 2**, which is applicable in this case since water production was either not reported properly or negligible. **Equations 1** and **2** represent the theoretical capacity for CO₂ sequestration and in order to obtain the effective capacity, some other factors have to be taken into account, such as the mobility ratio of CO₂ and reservoir fluid, the production mechanism, reservoir heterogeneity, water saturation and other effects (Novak, 2015). The novelty of this work is an attempt to incorporate all of the stated effects in the simulation.

Regarding the pore pressure and overburden pressure, the injection bottom hole pressure of 200 bar was taken, since Chen et al. (2015) recommended injection pressure below lithostatic. Due to the normal pore pressure and overburden (geostatic) pressure, the CO₂ injection pressure of 200 bar was taken. The perforation depth is 1569 m. According to Eaton (1972), normal pore pressure for sandstones equals 0.10519 bar/m which gives a pressure of 165.04 bar, while the overburden gradient for sandstones equals 0.22621 bar/m which gives a pressure of 354.92 bar.

2.1. Geological setting of the reservoir

There are around 4500 exploration, production or development oil and gas wells altogether in Croatia (URL3). Of that number, there are around 950 exploration wells which are located in the Croatian part of the Pannonian Basin System (CPBS) (Velić et al., 2002). The CPBS is located in the southwestern parts of the larger unit of the Pannonian Basin (PBS). It is divided into four main depressions: Sava, Drava, Mura, and Slavonija-Srijem. In continental Croatia, hydrocarbon reservoirs are found within these main depressions. The CPBS was formed during the Neogene, with three megacycles of sedimentation (Velić et al., 2002). The sediments are usually of Quaternary and Tertiary origin, and they overly crystalline bedrock or Mesozoic sedimentary rocks (Velić et al., 2012). The reservoirs are usually found within the sediments of the 1st and 2nd megacycle which are mainly represented by sandstones, breccias, basal conglomerates, turbiditic lobes, sand sheets, etc. (Saftić et al., 2003). **Figure 1** shows chronostratigraphic and lithostratigraphic units for each of the depressions with assumed development of the lithostratigraphic facies. The thickness of Neogene and Quaternary sediments varies within depressions. The thickness of sediments in the Drava depression reach up to 7000 m in the thickest parts, in the Sava and Mura depression around 5000 m and up to 4000 m in the Slavonija-Srijem depression (Saftić et al., 2003; Velić et al., 2012). The chosen depleted gas reservoir is located in the Upper Miocene formation, with a general geographical location in Northern Croatia. The Upper Miocene sediments of the 2nd megacycle, are mainly comprised of sandstones of turbiditic or deltaic origin (Saftić et al., 2003). They are important hydrocarbon reservoirs. **Figure 2**

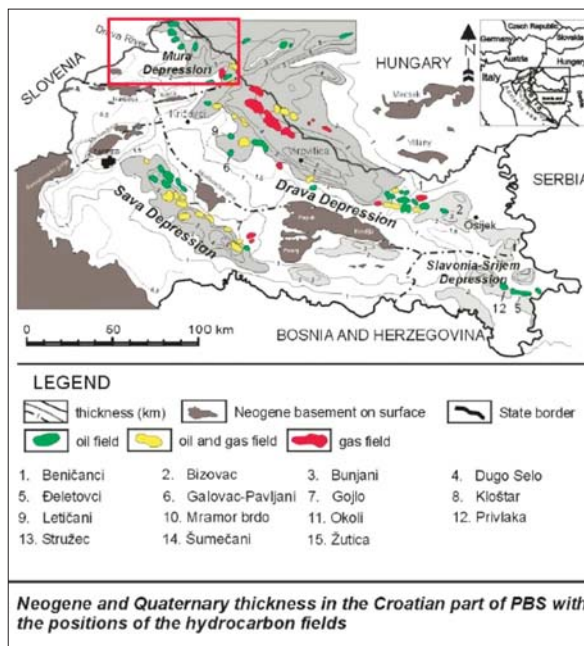


Figure 2: Locations of four main depressions within the CPBS with sediment thickness and location of the researched area (modified from Velić et al., 2012)

shows the locations of the PBS and the CPBS, with sediment thickness and major oil, gas and condensate fields. Northern Croatia is a geographical area, which spans over the Mura depression, partly over the Drava depression and in a small part over the Sava depression and its approximate area is marked by a red rectangle in **Figure 2**.

2.2. Reservoir properties

In this case study, an example of a typical small depleted and abandoned gas reservoir was used. The reservoir is located in the CPBS in Northern Croatia, in the Upper Miocene fine-grained quartz mica sandstones. The caprock is a relatively thin marl deposition (10 m) which represents a good isolator that hinders hydrocarbon migration. The area of the reservoir is 238 400 m² and the volume is 631 680 m³. The average net pay (thickness) of the reservoir is 2.68 m. The reservoir was developed by only one well with a total depth of 3000 m. Proved geological reserves of free natural gas are estimated to 15 211 684 m³ and a recovery factor of around 50% was achieved. Other main reservoir characteristics are given in **Table 1**. Reservoir natural gas composition is given in **Table 2**.

The first step in modelling was to characterize the reservoir fluid in Schlumberger ECLIPSE PVTi. The fluid composition was imported, and Peng-Robinson (1976) equation of state was applied. The obtained file was included in the data file for ECLIPSE E300. The model was initialized with a 10×5×1 grid, with the same permeabilities in the x and y-direction and 10 times smaller

permeability in the z -direction. Relative permeabilities were calculated using Corey's exponents. Although certain production decline can be observed for gas reservoir MALM in **Figure 3**, no clear trend can be approximated by known decline equations. Production varied throughout history with a maximum of 570 000 m³/mo. at the beginning and a steep decline towards the end of production history, ending with around 48 000 m³/mo. The first and important step in constructing the reservoir model is to calibrate the model against historical production and pressure data. The model must reproduce past reservoir performance accurately before it is used to reliably pre-

dict future performance. **Figure 4** presents actual field production and production simulated in ECLIPSE, i.e., history matching is shown. Based on observed past production, history matching was done by gas rate control and with a flowing bottom hole pressure of 64 bar.

3. Results and discussion

Production of gas started in October 1984 and it lasted until May 7th, 1986 and satisfactory history matching was achieved. Simulated bottomhole pressure (BHP) after closing the well was 69.75 bar. Formation pressure dropped down from 160 bar to 82.05 bar. The well was shut from May 8th, 1986 until September 29th, 2017. Simulation of CO₂ injection started on September 30th, 2017 through the same wellbore. The simulation showed that after 1 219 days (3 and a half years) of injection, bottom hole pressure will reach its upper limit and the amount of injected CO₂ will reach its maximum of 16 200 000 m³ which is 2.191 times more than the produced natural gas. Daily and cumulative CO₂ injection, formation pressure and cumulative gas in place (gas and injected CO₂) are given in **Figure 5** and **Figure 6**. The default rate of 27 000 m³/day was constant for 14 months after which it started to decrease to reach the formation pressure at 200 bar. The injection of CO₂ lasted for 40 months, during which a total of 16 200 000 m³ was injected. In **Figure 6**, cumulative injection and formation pressure show a similar trend. Profiles show CO₂ injection rates and corresponding formation pressure during injection, starting with September 30th, 2017 and end date of January 31st, 2021. It should be noted that formation pressure is 199.65 bar and does not exceed the chosen injection bottom hole pressure value of 200 bar.

Injection capacity calculated by **Equation 1** was 16 738 479 m³. According to **Equation 2**, available capacity for CO₂ sequestration in reservoir MALM is 26 912 114 kg, which equals to 14 592 444 m³.

Table 1. Characteristics of the MALM reservoir

Reservoir Properties	Values
perforation depth, h	1569 m
pressure at the perforation depth (formation pressure), p	160 bar
porosity, ϕ	0.226
average initial water saturation, S_{wi}	0.3
average initial gas saturation, S_{gi}	0.7
average permeability, k (lab testing)	$38 \times 10^{-3} \mu\text{m}^2$
average permeability, k (drill stem test - DST)	$16.64 \times 10^{-3} \mu\text{m}^2$
gas formation volume factor, B_{gi}	0.006395 m ³ /m ³

Table 2. Reservoir natural gas composition

Composition	%	Composition	%
N ₂	9.057	i-C ₅ H ₁₂	0.920
CO ₂	0.896	n-C ₅ H ₁₂	0.846
CH ₄	75.269	C ₆ H ₁₄	1.023
C ₂ H ₆	4.084	C ₇ H ₁₆	0.638
C ₃ H ₈	3.313	C ₈ H ₁₈	0.455
i-C ₄ H ₁₀	1.346	C ₉ H ₂₀	0.217
n-C ₄ H ₁₀	1.710	C ₁₀ H ₂₂₊	0.226

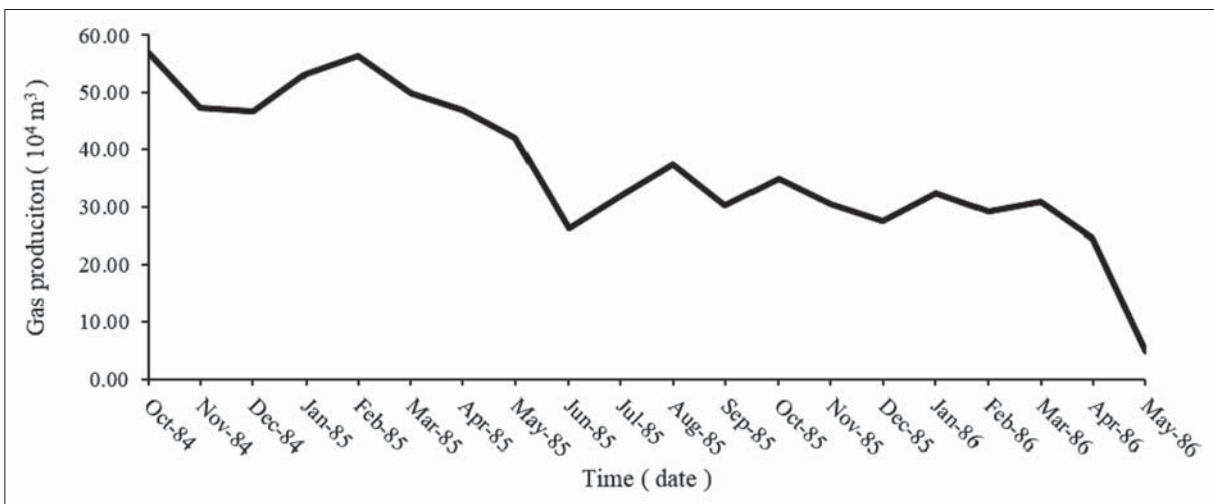


Figure 3: Monthly gas production for gas reservoir MALM.

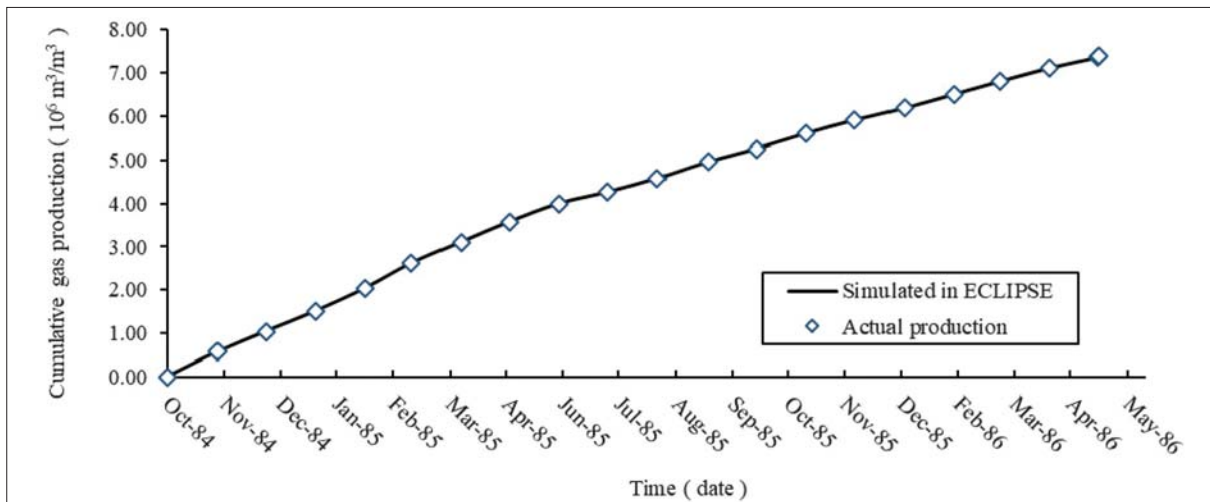


Figure 4: History matching of production.

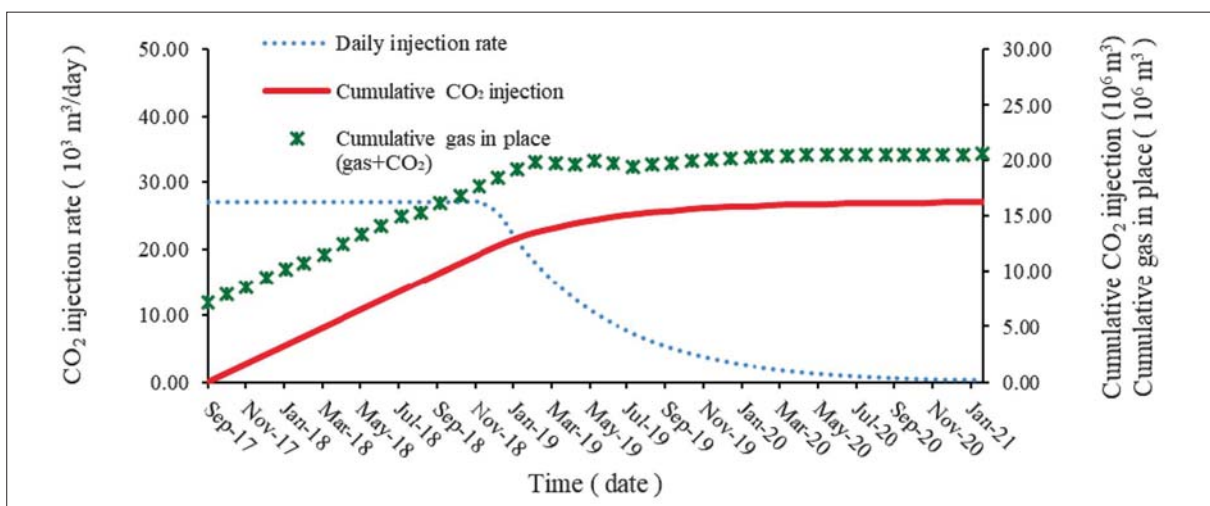


Figure 5: Cumulative CO₂ injection and gas in place.

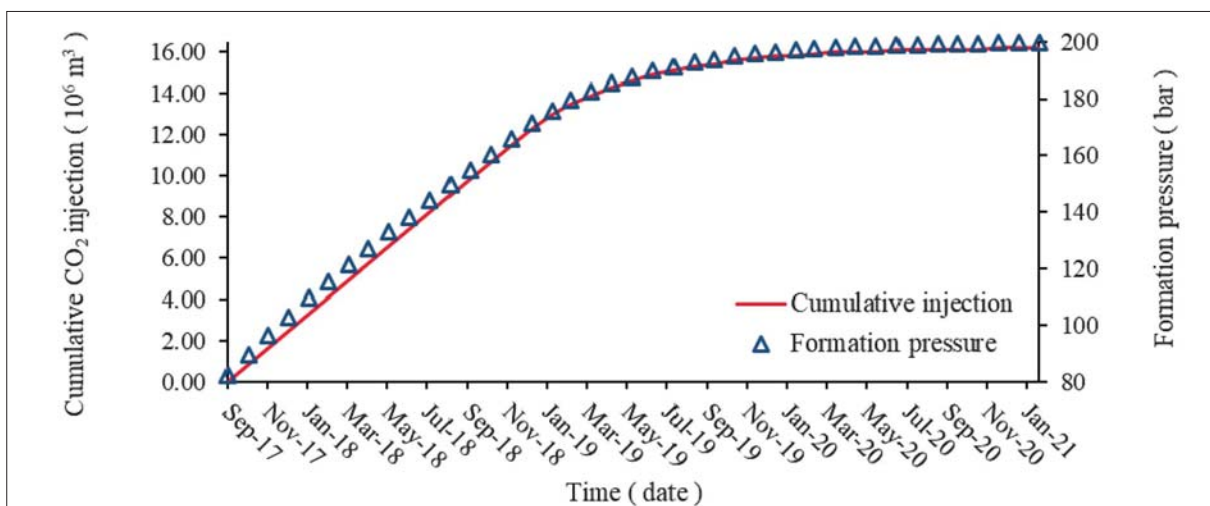


Figure 6: Formation pressure and cumulative CO₂ injection.

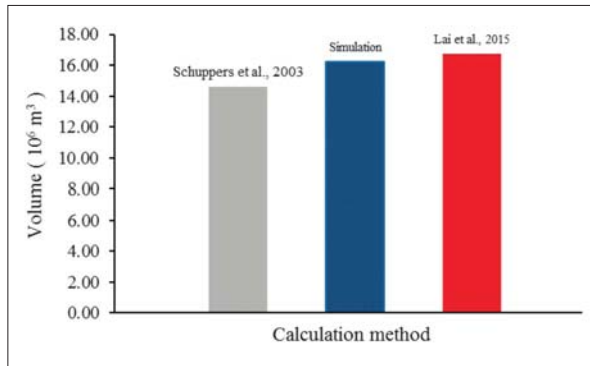


Figure 7: Cumulative injected CO₂ volumes obtained with two analytical methods (Schuppers et al., 2003; Lai et al., 2015) and with simulation done in ECLIPSE.

The relevance of obtained results can be found in confirmation of analytical solutions validity. The simulation shows that analytical equations are a good first approximation for CO₂ injection capacity of the reservoir. However, **Equation 1** depicts higher accuracy compared to **Equation 2** since differences between simulated quantities and results obtained by stated formulas are 3% and 10%, respectively, as shown in **Figure 7**. These accuracies could be confirmed with actual CO₂ injection in the reservoir in question.

4. Conclusions

With the increasing need for greenhouse gas mitigation, any attempt of emission avoidance is a case of good industrial practice. That is the main reason why many studies were directed towards CO₂ injection into hydrocarbon reservoirs with subsequent additional recovery. However, those studies considered oil or gas production, which is also a source of CO₂ emissions, while in this research, CO₂ is sequestered without any of it being emitted. The injection of CO₂ in a small and relatively shallow depleted gas reservoir in Croatia was studied and simulated with ECLIPSE E300. The first step was to get a history match for field production and pressure drop in ECLIPSE E300 and it resulted with high accuracy for production rates, ending with field pressure close to measured. After a conducted history match, a production well is shut and CO₂ injection simulation through it starts. Simulation analysis shows how total injection capacity decreases with an increase in bottom hole pressure during injection. The baseline scenario takes bottom hole pressure of 200 bar, which is 25% higher than the initial reservoir pressure.

The end result of baseline simulation is in accordance with the analytical equations used in this study for the estimation of CO₂ storage capacity. The surface amount of CO₂ that could be injected in the reservoir during the injection period of 40 months is almost two times larger, $16.2 \times 10^6 \text{ m}^3$, than the amount of natural gas, $7.4 \times 10^6 \text{ m}^3$, obtained during a production period of 19 months.

The novelty of this work lies in the fact that a history match was done for a real reservoir, along with CO₂ injection simulation and the final result was compared with two analytical expressions for storage capacity. In the last 15 years, no reproducible study has been carried out in terms of simulation of CO₂ injection into a depleted gas reservoir for Croatian sandstone for the purpose of sequestration only. This study could serve as a benchmark for future CO₂ sequestration in larger depleted gas reservoirs in Croatia and can easily be adjusted for the same types of sandstone in the CPBS. Furthermore, an experimental study should be conducted to verify the equations and simulation results.

5. References

- Al-Hasami, A., Ren, S. and Tohidi, B. (2005): CO₂ Injection for Enhanced Gas Recovery and Geo-Storage: Reservoir Simulation and Economics. SPE Europe/EAGE Annual Conference, Madrid, Spain, 13-16 June 2005. Society of Petroleum Engineers. [https://doi.org/10.2118/94129-MS]
- Ampomah, W., Balch, R.S., Grigg, R.B., Dai, Z. and Pan, F. (2015): Compositional Simulation of CO₂ Storage Capacity in Depleted Oil Reservoirs. Carbon Management Technology Conference, Sugar Land, Texas, USA, 17-19 November 2015. Carbon Management Technology Conference [https://doi.org/10.7122/439476-MS]
- Arts, R.J., Vanweijer, V.P., Hofstee, C., Pluymaekers, M.P.D., Loeve, D., Kopp, A. and Plug, W.J. (2012): The feasibility of CO₂ storage in the depleted P18-4 gas field offshore the Netherlands (the ROAD project). International Journal of Greenhouse Gas Control, 11, S10-S20. [https://doi.org/10.1016/j.ijggc.2012.09.010]
- Biagi, J., Agarwal, R. and Zhang, Z. (2016): Simulation and optimization of enhanced gas recovery utilizing CO₂. Energy, 94, 78-86. [https://doi.org/10.1016/j.energy.2015.10.115]
- Bossie-Codreanu, D., and Le Gallo, Y. (2004): A simulation method for the rapid screening of potential depleted oil reservoirs for CO₂ sequestration. Energy, 29, 9-10, 1347-1359. [https://doi.org/10.1016/j.energy.2004.03.070]
- Chen, Z., Liao, X., Zhao, X., Feng, X., Zang, J. and He, L. (2015): A new analytical method based on pressure transient analysis to estimate carbon storage capacity of depleted shales: A case study. International Journal of Greenhouse Gas Control, 42, 46-58. [https://doi.org/10.1016/j.ijggc.2015.07.030]
- Cui, G., Zhang, L.; Ren, B., Zhuang, Y., Li, X., Ren, S. and Wang, X. (2015): Geothermal Exploitation with Considering CO₂ Mineral Sequestration in High Temperature Depleted Gas Reservoir by CO₂ Injection. Carbon Management Technology Conference, Sugar Land, Texas, USA, 17-19 November 2015. Carbon Management Technology Conference [https://doi.org/10.7122/439516-MS]
- Cui, G., Zhang, L., Ren, B., Enechukwu, C., Liu, Y. and Ren, S. (2016): Geothermal exploitation from depleted high temperature gas reservoirs via recycling supercritical CO₂: Heat mining rate and salt precipitation effects. Applied En-

- ergy, 183, 837-852. [https://doi.org/10.1016/j.apenergy.2016.09.029]
- Eaton, B.A. (1972): The Effect of Overburden Stress on Geopressure Prediction from Well Logs. *Journal of Petroleum Technology*, 24, 08, 929-934. [https://doi.org/10.2118/3719-PA]
- Galic, H., Cawley, S. J., Bishop, S. R., Gas, F. and Todman, S. (2009): CO₂ Injection Into Depleted Gas Reservoirs. SPE Offshore Oil & Gas Conference & Exhibition, Aberdeen, UK, 8-11 September 2009. Society of Petroleum Engineers [https://doi.org/10.2118/123788-MS]
- Gaurina-Medimurec, N. and Novak Mavar, K. (2017): Depleted hydrocarbon reservoirs and CO₂ injection wells –CO₂ leakage assessment. *The Mining-Geology-Petroleum Engineering Bulletin* 2017, 15-27. [10.17794/rgn.2017.2.3]
- Gaurina-Medimurec, N., Novak-Mavar, K. and Majić, M. (2018): Carbon Capture and Storage (CCS): Technology, Projects and Monitoring Review. *The Mining-Geology-Petroleum Engineering Bulletin* 2018, 1-15 [10.17794/rgn.2018.2.1]
- Ghomian, Y., Pope, G. A. and Sepehrnoori, K. (2008): Reservoir simulation of CO₂ sequestration pilot in Frio brine formation, USA Gulf Coast. *Energy*, 33, 1055-1067. [https://doi.org/10.1016/j.energy.2008.02.011]
- Iogna, A., Guillet-Lhermite, J., Wood, C. and Deflandre, J.P. (2017): CO₂ Storage and Enhanced Gas Recovery: Using Extended Black Oil Modelling to Simulate CO₂ Injection on a North Sea Depleted Gas Field. SPE Europec featured at 79th EAGE Conference and Exhibition, Paris, France, 12-15 June 2017. Society of Petroleum Engineers. [https://doi.org/10.2118/185859-MS]
- Lai, Y.-T., Shen, C.-H., Tseng, C.-C., Fan, C.-H. and Hsieh, B.-Z. (2015): Estimation of Carbon Dioxide Storage Capacity for Depleted Gas Reservoirs. *Energy Procedia*, 76, 470-476. [https://doi.org/10.1016/j.egypro.2015.07.887]
- Lawal, A.S. and Frailey, S.M. (2004): Material Balance Reservoir Model for CO₂ Sequestration in Depleted Gas Reservoirs. SPE Annual Technical Conference and Exhibition, Houston, Texas, USA, 26-29 September 2004. Society of Petroleum Engineers. [https://doi.org/10.2118/90669-MS]
- Loeve, D., Hofstee, C. and Maas, J. (2014): Thermal effects in a depleted gas field by cold CO₂ injection in the presence of methane. *Energy Procedia*, 63, 3632-3647. [https://doi.org/10.2118/94129-MS]
- Luo, F., Xu, R.-N. and Jiang, P.-X. (2013): Numerical investigation of the influence of vertical permeability heterogeneity in stratified formation and of injection/production well perforation placement on CO₂ geological storage with enhanced CH₄ recovery. *Applied Energy*, 102, 1314-1323. [https://doi.org/10.1016/j.apenergy.2012.07.008]
- Mathias, S.A., Gluyas, J.G., Oldenburg, C.M. and Tsang, C.-F. (2010): Analytical solution for Joule-Thomson cooling during CO₂ geo-sequestration in depleted oil and gas reservoirs. *International Journal of Greenhouse Gas Control*, 4, 5, 806-810. [https://doi.org/10.1016/j.ijggc.2010.05.008]
- Novak, K., Malvić, T. and Simon, K. (2013a): Increased hydrocarbon recovery and CO₂ management, a Croatian example. *Environmental earth sciences*. 68, 4, 1187-1197
- Novak, K., Malvić, T., Velić, J. and Simon, K. (2013b): Increased hydrocarbon recovery and CO₂ management, PVT relations and volumes, a Croatian example. Part II. *Environmental earth sciences*. 71, 8, 3641-3653.
- Novak, K. (2015): Modeliranje površinskoga transporta i geološki aspekti skladištenja ugljikova dioksida u neogenska pješčenjačka ležišta sjeverne Hrvatske na primjeru polja Ivanić. Phd thesis, University of Zagreb: Faculty of Mining, Geology and Petroleum Engineering, Zagreb, Croatia. (Summary in English)
- Okamoto, I., Li, X. and Ohsumi, T. (2005): Effect of supercritical CO₂ as the organic solvent on cap rock sealing performance for underground storage. *Energy*, 30, 11-12, 2344-2351. [https://doi.org/10.1016/j.energy.2003.10.025]
- Orlic, B. (2009): Some geomechanical aspects of geological CO₂ sequestration. *KSCE Journal of Civil Engineering*, 13, 4, 225-232. [https://doi.org/10.1007/s12205-009-0225-2]
- Patel, M. J., May, E. F. and Johns, M. L. (2016): High-fidelity reservoir simulations of enhanced gas recovery with supercritical CO₂. *Energy*, 111, 548-559. [https://doi.org/10.1016/j.energy.2016.04.120]
- Pawar, R. J., Warpinski, N. R., Benson, R. D., Grigg, R. B., Krumhansl, J. L. and Stubbs, B. A. (2004): Geologic Sequestration of CO₂ in a Depleted Oil Reservoir: An Overview of a Field Demonstration Project. SPE Annual Technical Conference and Exhibition, Houston, Texas, USA, 26-29 September 2004. Society of Petroleum Engineers. [https://doi.org/10.2118/90936-MS]
- Peng, D.Y. and Robinson, D.B., 1976. A new two-constant equation of state. *Industrial & Engineering Chemistry Fundamentals*, 15(1), pp.59-64.
- Pham, V., Riis, F., Gjeldvik, I., Tappel, I. and Aagaard, P. (2013): Assessment of CO₂ injection into the south Utsira-Skade aquifer, the North Sea, Norway. *Energy*, 55, 529-540. [https://doi.org/10.1016/j.energy.2013.03.026]
- Rathnaweera, T., Ranjith, P., Perera, M., Ranathunga, A., Wanniarachchi, W., Yang, S.L.A. and Al Arifi, N. (2017): An experimental investigation of coupled chemico-mineralogical and mechanical changes in varyingly-cemented sandstones upon CO₂ injection in deep saline aquifer environments. *Energy*, 133, 404-414. [https://doi.org/10.1016/j.energy.2017.05.154]
- Raza, A., Gholami, R., Rezaee, R., Bing, C.H., Nagarajan, R. and Hamid, M.A. (2017): Assessment of CO₂ residual trapping in depleted reservoirs used for geosequestration. *Journal of Natural Gas Science and Engineering*, 43, 137-155. [https://doi.org/10.1016/j.jngse.2017.04.001]
- Raza, A., Gholami, R., Rezaee, R., Bing, C.H., Nagarajan, R. and Hamid, M.A. (2018): CO₂ storage in depleted gas reservoirs: A study on the effect of residual gas saturation. *Petroleum*, 4, 1, 95-107. [https://doi.org/10.1016/j.petlm.2017.05.005]
- Tao, Z. and Clarens, A. (2013): Estimating the Carbon Sequestration Capacity of Shale Formations Using Methane Production Rates. *Environmental Science & Technology*, 47, 19, 11318-11325. [https://doi.org/10.1021/es401221j]
- Temitope, A., Sulemana, N., Gomes J.S. and Oppong, R. (2016): Statistical Uncertainty Analysis and Design Opti-

- mization of CO₂ Trapping Mechanisms in Saline Aquifers. International Petroleum Technology Conference, Bangkok, Thailand, 14-16 November 2016. International Petroleum Technology Conference [https://doi.org/10.2523/IPTC-18837-MS]
- Saftić, B., Velić, J., Sztano, O., Juhasz, G., and Ivković, Ž. (2003): Tertiary subsurface facies, source rocks and hydrocarbon reservoirs in the SW part of the Pannonian Basin (northern Croatia and south-western Hungary). *Geologia Croatica*, 56, 1, 101-122.
- Schuppers, J.D., Holloway, S., May, F., Gerling, P., Bøe, R., Magnus, C., Riis, F., Osmundsen, P.T., Larsen, M., Andersen, P.R. and Hatzzyannis, G. (2003): Storage capacity and quality of hydrocarbon structures in the North Sea and the Aegean region. TNO-report NITG 02-020-B, Netherland's Institute of Applied Geoscience, 54 p., Utrecht.
- Shi, J.-Q. and Durucan, S. A. (2009): coupled reservoir-geomechanical simulation study of CO₂ storage in a nearly depleted natural gas reservoir. *Energy Procedia*, 1, 1, 3039-3046. [https://doi.org/10.1016/j.egypro.2009.02.082]
- Singh, A.K., Goerke, U.-J. and Kolditz, O. (2011): Numerical simulation of non-isothermal compositional gas flow: Application to carbon dioxide injection into gas reservoirs. *Energy*, 36, 5, 3446-3458. [https://doi.org/10.1016/j.energy.2011.03.049]
- Stein, M. H., Ghotekar, A. L. and Avasthi, S. M. (2010): CO₂ Sequestration in a Depleted Gas Field: A Material Balance Study. SPE EUROPEC/EAGE Annual Conference and Exhibition, Barcelona, Spain, 14-17 June 2010. Society of Petroleum Engineers. [https://doi.org/10.2118/131384-MS]
- Streit, J. E. and Hillis, R. R. (2004): Estimating fault stability and sustainable fluid pressures for underground storage of CO₂ in porous rock *Energy*, 29, 9-10, 1445-1456. [https://doi.org/10.1016/j.energy.2004.03.078]
- Underschultz, J., Boreham, C., Dance, T., Stalker, L., Freifeld, B., Kirste, D. and Ennis-King, J. (2011): CO₂ storage in a depleted gas field: An overview of the CO₂CRC Otway Project and initial results. *International Journal of Greenhouse Gas Control*, 5, 4, 922-932. [https://doi.org/10.1016/j.ijggc.2011.02.009]
- Valbuena, E., Barrufet, M. and Falcone, G. (2012): Analytical Estimation of CO₂ Storage Capacity in Depleted Oil and Gas Reservoirs Based on Thermodynamic State Functions. SPE Latin America and Caribbean Petroleum Engineering Conference, Mexico City, Mexico, 16-18 April 2012. Society of Petroleum Engineers. [https://doi.org/10.2118/153307-MS]
- Velić, J., Weisser, M., Saftić, B., Vrbanac, B., and Ivković, Ž. (2002): Petroleum-geological characteristics and exploration level of tree Neogene depositional megacycles in the Croatian part of the Pannonian basin. *Nafta*, 53, 6-7, 239-249.
- Velić, J., Malvić, T., Cvetković, M., and Vrbanac, B. (2012): Reservoir Geology, Hydrocarbon Reserves and Production in the Croatian part of the Pannonian Basin System. *Geologia Croatica*, 65, 1, 91-101.
- Velić, J., Kišić, K. and Krasić, D. (2016): The characteristics of the production and processing of oil and natural gas in Croatia from 2000 to 2014. *The Mining-Geology-Petroleum Engineering Bulletin (Rudarsko-geološko-naftni zbornik)*, 31, 2, 69-112. [10.17794/rgn.2016.2.6]
- Vulin, D. (2010): Modeliranje termodinamičkih i petrofizičkih parametara za geološko skladištenje ugljičnog dioksida (Modeling Thermodynamic and Petrophysical Parameters for Geological Storage of Carbon Dioxide). Phd thesis, University of Zagreb: Faculty of Mining, Geology and Petroleum Engineering, Zagreb, Croatia. (Summary in English)
- Vulin, D., Kurevija, T. and Kolenkovic, I. (2012): The effect of mechanical rock properties on CO₂ storage capacity. *Energy*, 45, 1, 512-518. [https://doi.org/10.1016/j.energy.2012.01.059]
- Vulin, D., Saftić, B. and Macenić, M. (2018a): Estimate of dynamic change of fluid saturation during CO₂ injection — Case study of a regional aquifer in Croatia. *Interpretation*, 6, 1, SB51-SB64. [https://doi.org/10.1190/INT-2017-0077.1]
- Vulin, D., Gačina, M., and Biličić, V. (2018b): Slim-tube simulation model for CO₂ injection EOR. *The Mining-Geology-Petroleum Engineering Bulletin (Rudarsko-geološko-naftni zbornik)*, 33, 2, 37-49. [https://doi.org/10.17794/rgn.2018.2.4]
- Ziabakhsh-Ganji, Z. and Kooi, H. (2014): Sensitivity of Joule-Thomson cooling to impure CO₂ injection in depleted gas reservoirs. *Applied Energy*, 113, 434-451. [https://doi.org/10.1016/j.apenergy.2013.07.059]

Internet sources:

- URL1: https://ieaghg.org/docs/General_Docs/Reports/PH3_22%20Storage%20in%20oil%20and%20gas%20fields.pdf, (Accessed on 25th July 2017)
- URL2: <http://edgar.jrc.ec.europa.eu/overview.php?v=CO2ts1990-2015> (Accessed on 24th October 2018)
- URL3: https://www.ina.hr/UserDocsImages/investitori/objave/2018/INA_AR_2017_cro_30_4%20FINAL.pdf (Accessed on 27th October 2018)

SAŽETAK

Simulacija utiskivanja CO₂ u napušteno plinsko ležište: Analiza slučaja pješčenjaka gornjega miocena, sjeverna Hrvatska

Tehnologija hvatanja i skladištenja ugljičnoga dioksida (CCS) koristan je dio strategije smanjenja stakleničkih plinova u posljednjih 20 godina. Iscrpljena plinska ležišta obećavajući su kandidati za skladištenje CO₂. Cilj je rada usporediti kapacitete skladištenja CO₂, dobivene dvjema analitičkim metodama, te usporediti rezultate s kapacitetom skladištenja kao rezultat simulacije i na taj način potvrditi analitičke metode. Prvi analitički izraz uzima u obzir prosječni ležišni tlak i dostupne podatke o proizvodnji. Drugi je izraz općenitiji te uključuje volumen proizvodnje, gustoću CO₂ i volumni faktor formacije originalnoga fluida. Za potrebe rada korišteni su softveri Schlumberger PVTi za proračun jednadžbe stanja i ECLIPSE (modul E300) za ležišno modeliranje. Rezultati simulacije potvrdili su analitička rješenja, što upućuje na mogućnost utiskivanja dva puta veće mase CO₂ od proizvedenoga CH₄, ovisno o dubini ležišne stijene. Iako jedno rješenje pokazuje nešto višu ($16.7 \times 10^6 \text{ m}^3$), a drugo nešto nižu ($14.6 \times 10^6 \text{ m}^3$) procjenu količina CO₂ koje bi se mogle utisnuti u ležište od simulacije ($16.2 \times 10^6 \text{ m}^3$), oba rješenja mogu se koristiti za prve procjene i analize s obzirom na to da su razlike neznatne.

Ključne riječi:

hvatanje i skladištenje CO₂ (CCS), iscrpljeno plinsko ležište, simulacija skladištenja CO₂, pješčenjaci gornjega miocena, sjeverna

Authors contribution

Amalia Lekić (mag. ing. petrol., research assistant, thermodynamics) conceived the idea, designed the research and performed the history match; **Lucija Jukić** (mag. ing. petrol., research assistant, reservoir engineering) provided the literature overview and performed the fluid characterization; **Maja Arnaut** (mag. ing. petrol., research assistant, CO₂ mitigation) calculated the analytical capacities and wrote the majority of the input txt file; **Marija Macenić** (mag. ing. min., research assistant, geothermal energy) described the geology, analysed the results and contributed to the literature overview. Each author wrote a part of the paper.