1. INTRODUCTION

In order to prevent CO$_2$ concentrations in the atmosphere rising to unacceptable levels, carbon dioxide can be separated from the flue gas of, for example, a power plant and subsequently sequestrated. Different technologies for carbon dioxide sequestration can be proposed. They are:

– storage in depleted gas reservoirs,
– storage in oceans and aquifers,
– sequestration CO$_2$ by means of so-called “mineral CO$_2$ sequestration”.

In this route CO$_2$ is chemically stored in solid carbonates by the carbonation of minerals. Mineral CO$_2$ sequestration are thermodynamically stable and therefore the sequestration of CO$_2$ is permanent and safe. Disadvantages of this method is high price. Then now in the World is preferred the geological CO$_2$ sequestration in depleted reservoirs. Specially there are preferred gas reservoirs. The accumulation and entrapment of lean gas such as methane in the natural gas reservoirs demonstrates the capability of these reservoirs for gas containment for long periods of time. By virtue of their proven records of gas production depleted natural gas reservoirs have proved to have both available volume and the integrity of gas containment.

2. THERMODYNAMIC CHARACTERISTICS OF METHANE, CARBON DIOXIDE AND THEIR MIXTURES

In planning and designing of geologic sequestration projects in depleted gas reservoirs it is important to know how natural gas behaves under reservoir conditions when carbon dioxide is injected into the reservoir. In particular, the $z$-factor, viscosity, density and phase changes
of the gas, are essential in predicting the physical characteristics of the in situ natural gas, the injected gas at reservoir conditions, and the gas mixture.

For natural gases Z-factor can be obtained by means of the different methods. They are:

– analytical methods proposed by Hall–Yarborough, Dranchuk–Purvis–Robinson and Dranchuk–Abou–Kassem [1] and
– the empirical Z-factor chart of Standing and Katz, which is based on measured Z-factors of natural gases that contained very little non-hydrocarbons.

In the process of CO₂ sequestration composition of hydrocarbon gas mixture in reservoir at depleted pressure conditions changes to a very high CO₂. For gases containing nonhydrocarbon components such as hydrogen sulfide, carbon dioxide, and nitrogen pseudocritical parameters of gas must be corrected [5]. There is still lack of appropriate correlations to predict Z-factors for gas mixtures especially at high CO₂ concentrations. Z-factor for pure CO₂ can be evaluated from the chart which is presented in Figure 1. This chart differs from charts for natural gases. The Z-factor of natural gas then decreases as carbon dioxide is added to it. The compressibility factor is directly proportional to \( B_g \) as such if the compressibility factor of a gas sample increases, for a given pressure and temperature, the formation volume factor also increases.

![Fig. 1. Z-factor Chart for pure CO₂](image)

In Figure 2 is presented the phase diagram for CO₂. This diagram indicates that supercritical conditions will prevail in typical gas reservoirs.
In Figures 3 and 4 there are shown profiles of density and viscosity at various pressures as for different composition of CO$_2$ – CH$_4$ system. By comparing end-member properties along either vertical axis, pure CO$_2$ is much denser and more viscous than pure CH$_4$ in gas reservoirs. These differences become larger at higher CO$_2$ concentrations in gas mixture and pressures beyond the critical point. CO$_2$ injectivity will be high due to its low absolute viscosity relative to water, for example, while having large density that will tend to underride existing gas. Furthermore, the relatively larger viscosity of CO$_2$ will make for a favorable mobility ratio displacement of CH$_4$ with diminished tendency to interfinger and mix with the displaced CH$_4$. Thus the density and viscosity differences between pure CO$_2$ and CH$_4$ favor carbon sequestration with enhanced gas recovery by decreasing mixing. However displacement of natural gas by supercritical CO$_2$ has not been done in the field and is not well understood.

Fig. 2. Phase diagram of CO$_2$

Fig. 3. Density of CO$_2$-CH$_4$ gas mixture at various pressures [4]
3. GAS MATERIAL BALANCE EQUATION IN RESERVOIR ENGINEERING

In reservoir engineering material balance equation is a fundamental tool for the evaluation of past and future global reservoir performance. It is based on the Law of Mass Conservation applied to a reservoir at large by considering it as a large tank at a uniform pressure and temperature. Applied to past performance, a material balance analysis provides insight in the prevailing production mechanism and allows the estimation of the hydrocarbons initially in place. In its predictive model the material balance can be used to generate future reservoir performance and to estimate the potential recovery of the hydrocarbons in place.

Material balance for volumetric depletion gas reservoirs in terms of formation volume factor is

\[ G_p B_g = G (B_g - B_{gi}) \] (1)

or using Havlena–Odeh method

\[ F = G \cdot E_g \] (2)

where:

- \( F = G_p B_g, E_g = (B_g - B_{gi}) \)
- \( G_p \) – total gas production [sm³],
- \( G \) – initial gas in place [sm³],
- \( B_g \) and \( B_{gi} \) – gas formation volume factors at initial reservoir pressure and current average pressure.

Fig. 4. Viscosity of CO₂-CH₄ mixture at various pressures [4]
Left hand side of equations (1), (2) expresses total gas withdrawal from the reservoir, whereas right hand side is gas expansion resulting from pressure reduction. The gas formation volume factors for initial and current pressure can be obtained from following relationships:

\[ B_{gi} = \frac{p_{sc} z_i T}{p_i T_{sc}}, \quad B_g = \frac{p_{sc} z T}{p T_{sc}} \]  

(3)

where:

\[ p_{sc}, T_{sc} \] – pressure and temperature at standard conditions, \( p, p \) – initial and current reservoir pressure [Pa], \( T \) – temperature[K], \( z, z \) – gas compressibility factors at initial and current reservoir pressure respectively.

Gas material balance equation can be written in following form:

\[ \frac{p}{z} = \frac{p_i}{z_i} \left( \frac{G_p}{G} \right) \]  

(4)

4. MATERIAL BALANCE EQUATION IN CO₂ SEQUESTRATION PROCESS

During CO₂ injection process the reservoir gas mixture initially is the composition of the hydrocarbon gas at depleted pressure conditions and changes to a very high CO₂ concentration near maximum sequestration pressure (initial reservoir pressure) that may be treated as pure CO₂ in terms of z-factor evaluation. If production is sustained during CO₂ injection, a z-factor is required for the produced gas mixture. Similar to the reservoir gas, produced gas will begin as hydrocarbon gas only and eventually will include some amount of CO₂.

If the injected gas had a z-factor identical to the in-situ gas, material balance equation for volumetric conditions could be used directly with an adaptation to the production term \( G_p \) as follows

\[ G(B_g - B_{gi}) = G_p B_{gi} - G_{inj} B_{s_{inj}} \]  

(5)

However, the z-factor for CO₂ is very different compared to natural gases for most pressure and temperature, than material balance for the case of CO₂ injection into hydrocarbon reservoir reads (A.S. Lawal, S.M. Frailey, 2004)

\[ G(B_g - B_{gi})_{res hc/CO₂} = G_p B_{g_{res hc/CO₂}} - G_{inj} B_{g CO₂} \]  

(6)

The subscripts “res hc/CO₂” and “prd hc/CO₂” refer to the composition of the reservoir gas and the produced gas, respectively. Since gas composition in reservoir changes due to CO₂ injection then initial gas in place \( G \) (mixture of hydrocarbon gas and CO₂) in equation (6) changes as well and is unknown. This parameter can be easily expressed by hydrocarbon gas in place \( G_{hc} \) and a change in gas formation volume factors of hydrocarbon gas and CO₂ at initial reservoir pressure. Since pore volume occupied by gas is constant then
In p/z form mass balance equation (6) with equation (7) becomes form:

\[
\frac{p}{A} = \frac{p_i}{A} \left(1 - \frac{G_p}{A} \frac{z_{\text{prod} / \text{CO}_2}}{z_{\text{res} / \text{CO}_2}} - \frac{G_{\text{inf}}}{A} \frac{z_{\text{CO}_2}}{z_{\text{res} / \text{CO}_2}} + \frac{G_{\text{hc}}}{A} \frac{z_{\text{res} / \text{HC}}}{z_{\text{res} / \text{CO}_2}} \right)
\]

Equation (8) is the modified form of material balance equation for calculations of CO\(_2\) sequestration in depleted gas reservoirs.

5. RESULTS OF THE MODIFIED MATERIAL BALANCE EQUATION USING

Presented in the paper modified material balance equation for CO\(_2\) sequestration process was used in depleted chosen gas reservoir. From documentation of this reservoir it results that during of 20 years period of reservoir life 4.6 bln sm\(^3\) of gas (98.8% CH\(_4\)) was produced and reservoir pressure declined from initial value 15.24 MPa to 2.84 MPa.

In Figure 5 it shown the diagnostic gas material balance plot for chosen reservoir with using of “p/z” and Havlena Odeha methods.

In order to determine reservoir drive mechanism and initial gas reserves the values of production data in form of p/z and F/E\(_g\) vs cumulative gas production were plotted in Figure 5.
As can be seen points on both charts might be approximated with a straight line which is characteristic for volumetric depletion type reservoirs. Extrapolation of the fitted straight line to the abscissa (p/z = 0) gave an initial gas in place at the level of 5.58 bln sm³, which means that current recovery factor is 82.5%.

6. EXAMPLE OF THE CO2 SEQUESTRATION CALCULATIONS FOR A CHOSEN GAS RESERVOIR

The amounts of CO₂ that potentially can be stored in chosen gas reservoir were predicted for various hydrocarbon gas recovery factors ranging from current value of 0.825 to 0.95 and maximum sequestration pressure equal to the initial reservoir pressure. The prognosis of CO₂ sequestration process was made for the following 15 years with the assumption that during first 3 years exploitation of hydrocarbons will proceed. Achieved results are presented in Table 1. A typical cumulative gas production – carbon dioxide injection profile was shown in Figure 6.

<table>
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<tr>
<th>Scenario</th>
<th>Recovery factor [-]</th>
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<td></td>
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<td>[bln sm³]</td>
<td>[Mt]</td>
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Table 1
Carbon dioxide storage capacity of chosen gas reservoir

Fig. 6. Typical cumulative gas production – carbon dioxide injection profile (scenario 1)
Maximum CO₂ storage capacity of the reservoir of a given gas pore volume might be estimated assuming that natural hydrocarbon gas was entirely replaced by CO₂. It can be easily evaluated from equation (7), where \( B_{\text{gi res hc/CO₂}} \) should then be \( B_{\text{gi res CO₂}} \). As CO₂ z-factor is much lower from pure hydrocarbon gases and so formation volume factor then larger surface volume (sm³) of CO₂ gas can be contained compared to the surface volume of hydrocarbon gas. Maximum carbon storage capacity of the chosen reservoir in that case was estimated at the level of 13.52 bln sm³ (26.76 Mt).

Figura 7 presents reservoir pressure-time profile for scenario 1. It is composed of the two periods. First period demonstrates history of hydrocarbon gas production with measured and calculated pressures. As can be seen a good agreement was achieved. Second period is a prognosis of pressure and CO₂ concentration change during injection process. Approaching the conditions close to critical point of CO₂ there is a rapid pressure increase due to quick increase of CO₂ content in reservoir and so gas density. The compressibility of liquid – like supercritical CO₂ is low thus further increase of reservoir pressure takes place at pressures close to the initial reservoir conditions.

![Fig. 7. Chosen reservoir pressure profile – hydrocarbons exploitation and prognosis of CO₂ injection (scenario 1)](image)

7. CONCLUSIONS

A classical gas material balance equation was adapted for carbon sequestration to predict CO₂ storage capacity of a depleted gas reservoir. Performed calculations for chosen gas reservoir shows that gas reservoirs are capable to store large amounts of CO₂ depending on
hydrocarbons recovery factor. Physical properties of CO$_2$ and CH$_4$ at reservoirs conditions may strongly influence the process of CO$_2$ sequestration.

REFERENCES


[8] Seo J.G., Mamora D.D.: Experimental and Simulation Studies of Sequestration of Supercritical Carbon Dioxide in Depleted Gas Reservoirs, SPE 81200
