

5. Modelling of geochemical interactions and natural analogues

DUŠAN BODIŠ and LUDOVÍT KUCHARIČ

State Geological Institute of Dionýz Štúr, Mlynská dolina 1, 817 04 Bratislava, Slovak Republic

Geochemical aspects of CO₂ storage

The geochemical issue of CO₂ storing takes into account the quantitative and qualitative parameters, which can be reviewed on the basis of the existing hydrogeochemical and hydrogeological documentation, experimental verification and the geochemical modelling of the options of carbon dioxide injecting. This approach is the most important tool for simulation of geochemical processes in CO₂-water-rock interactions using mathematical modelling of interactions, as well as natural water in particular hydrogeological structure since its formation. The issue is dealt with for the first time in the conditions of the Western Carpathians, and is subordinated to the existing input options, which have been oriented only to potential aquifers. Isolated or closed hydrogeological structures have been designed to obtain geothermal water or natural healing waters sources.

If CO₂ is injected into the collector which contains brine, it generates transport of substances between the gaseous and the liquid phases. The carbon dioxide dissolves in the brine, while its solubility increases with an increase in pressure and temperature, but decreases with increasing the overall mineralisation of the brine. CO₂ dissolving in the brine increases the density of the mixture. Consequently, the water will evaporate from the liquid phase, thus changing the composition of the gaseous phase. The effect, however, is minimal and is neglected in most studies of CO₂ sequestration into the brine environment.

According to Bielinski (2006) in relation to the CO₂ storage the relevant transport processes in the collectors with the brines may be divided as follows:

1. Advection - the CO₂ movement occurs due to pressure gradient. If the CO₂ is injected into the collector with the brine, it penetrates radially from the point with a higher pressure (at the site of injection) into the areas with reduced pressure within the meaning of Darcy's law.

2. Buoyancy - due to density differences between the gaseous and liquid phases. The carbon dioxide with less density than the brine will ascend into upper parts of the structure and the brine will drop to its lower parts.

3. Diffusion - is caused by concentration gradient. A molecule of CO₂ will migrate from areas of higher

pressure to areas of lower pressure until the attainment of steady-state.

The advection is dominant in the injecting period. The buoyancy is a significant transport mechanism, but requires a good vertical communication. The diffusion has a significant effect on the carbon dioxide storage.

A key objective for the injection of the carbon dioxide into the collector with the brine is a guarantee that the injected CO₂ will remain in an underground space during a long time scale. Mechanisms for the CO₂ capture in geological environments are discussed in detail by many authors (e.g. Bielinski, 2006, Ghanbari et al., 2006, Nghiem et al., 2004, Noh et al., 2004, Kumar et al., 2005, etc.). In principle, these mechanisms can be summarized as follows:

1. Hydrodynamic (structural) capture: the injected CO₂ with lower density than the brine will ascend upwards in the form of a cloud until it reaches the impermeable overburden (the barrier will not allow further vertical propagation). Then the carbon dioxide will migrate laterally along the impervious roof.

2. Residual capture (capture in pores, within the intergranular space): at the forefront of migratory cloud the CO₂ displaces the brine and the drainage process is going on. The brine follows the carbon dioxide and fills pore spaces, which had been previously filled with the CO₂ cloud, leading to the capture of CO₂ in the form of a residual phase according to the concept of pore capture (Dullien, 1979).

3. Capture by dissolution: this mechanism is based on the CO₂ capture by its dissolving in the brine. However, it is worth noting that the brine has a lower density prior to being mixed with CO₂, which in turn causes, that the mixture with a higher density will sink and vice versa the brine without CO₂ is going to rise. If the CO₂ will continue to dissolve in the brine, the process will be repeated. This process increases the amount of dissolved carbon dioxide, provided the contact area of the brine and CO₂ is increasing.

4. Mineral capture: CO₂ can react with the mineral phases of the rock environment, which leads to their dissolution and the precipitation in the form of new (secondary) minerals and subsequently to the immobilization of CO₂.

Hydrogeochemical eligibility criteria of hydrogeological structures for CO₂ storing

Geological conditions for the formation of hydrocarbon accumulations in traps are associated also with the issues of migration of fluids in the course of geological-tectonic evolution. Significant tectonic activity of the territory gives rise to a wide range of traps of syndimentary and postsedimentary origin. The traps of non-anticline type dominate; their generation is not controlled by the anticlinal shape of the layers forming the collector, but by different lithological or geomorphologic factors (Freund, 2006).

Hydrogeochemical criteria for the assessment of the suitability of the hydrogeological structures must be based on clear hydrogeothermal characterisation of the closure of these structures. It is due to the fact that carbon dioxide storing is practically possible only in the geological traps (closed structures), in order to avoid the possibility of leakage to a minimum. On the other hand, it is true that the criteria that characterize the groundwater are not completely sufficient, because the gas and its transport in the rock environment show different migration properties. Therefore, more hydrogeochemical criteria were used, among them the composition of the gases. As screening criteria the following characteristics were selected:

1. The use of Palmer classification modified by Gazda (Gazda, 1971), provided the waters should be of a strong S₁(Cl) type with a characteristic representation of S₂(Cl) component and low or zero content of A₁ and A₂. It should be noted that the greater presence of A₁ component indicates degradation of the original (initial) marine waters, most commonly in the geological past. Infiltration degradation, however, can take place under certain conditions, even in the present.

2. The value of total mineralisation of the water in combination with the S₁(Cl) component. It reflects the value of the palaeosalinity of the waters. In compare to the initial oceanic water it is changed mainly due to interactions in the system water-rock-gas. The average oceanic water keeps in the long run a mean salinity of 35 g.l⁻¹. Generally speaking, if the value of the total mineralization of the water is around the above value, we may assume that the hydrogeological structure is closed.

3. Hydrogeochemical coefficients:

- a. HCO₃/Cl indicates the hydrogeochemical closeness or the openness of the hydrogeological structures. Values around 0.1 in terms of CO₂ injecting are already interesting. Typical values are less than 0.1.

- b. Cl/Br - genetic ratio, in sedimentary basins with an abundance of brine and hydrocarbons characteristic values are around 500.

- c. Mg/Ca – enrichment on Mg represents dolomitisation increase with consequent increase in effective porosity. As an auxiliary criterion, it can be assumed that the ratio expressed in the equivalent is more than 0.8.

4. The content of biogenic elements of iodine and bromine, typical elements that accompany the presence of brine and hydrocarbons in waters thanks to similar conditions of their genesis.

5. The content of gases

Characteristic is the content of non-acid gases. In general, with an increasing degree of closure of natural waters structures (collectors) the composition of the non-acid gases turns from the nitrogen gas with a high content of oxygen to the nitrogen without oxygen with an increased share of methane and, in the deeper parts of the sedimentary basins under conditions of limited water exchange dominates methane type of non-acid gases. They represent biochemical gases, lesser the gas of the chemical origin.

6. The contents of the stable oxygen isotopes. If the isotopic composition of natural waters is lower than the meteoric line with a trend toward the SMOW it suggests a closed structure.

To the above hydrogeochemical criteria it should be noted that confirmation by the other methods and knowledge is needed in order to get the real picture about the possibility of CO₂ injecting in the given region. Hydrogeochemical tightness may not be identical with the hydrogeological one and must be evaluated individually for each structure, or aquifer.

In addition to the hydrogeochemical criteria, we may note the other ones (tab. 5.1), which are very significant in terms of the carbon dioxide storage. These criteria can be termed as the geological indicators and are extremely important both in terms of the reservoir, as well as its roof.

From the hydrogeochemical analysis of groundwaters of the Western Carpathians it follows, that the most suitable collectors, which meet the specified criteria for carbon dioxide storing would have been hydrogeochemical collectors with highly mineralised geothermal waters, then relict marine waters, metamorphosed in the rock-water system only. To store CO₂ absolutely inappropriate are geothermal waters with a petrogenetic mineralisation. However, it is important to note that the brines have increased I and Br contents, which makes them suitable for curative purposes. In choosing the appropriate structures for the storage of carbon dioxide the socio-economic interests are of primary importance, which is valid to-date, and, in particular in the future.

At present, when dealing with the CO₂ storage across the world, a wide range of programmes is used (e.g. PHREEQC, COORES, TOUGHREACT, SCALE2000, etc.); their application in a given geological environment depends mainly on the specific conditions (clay environment, hydrocarbons reservoirs, shales, basalts, etc.) and in a way of their binding to the environment (physical, or geochemical), the specific objectives of the modelling (CO₂ reactivity, multiphase transport in reservoir, design and the geochemical quantification of carbon capture), or the availability and modelling code price.

The first, very important component was the analysis of the issue and the search work. Because the regional research aimed into the geologic CO₂ storage has not been realized yet, it was necessary to analyze in detail the methodology and, in particular, approach in terms of geochemistry and hydrogeochemistry and to adopt them from the world literature. In the world such research began almost fifteen years ago, when it rocketed up with the challenge of the protection against global climate

Tab. 5.1 Geological indicators of CO₂ injection into for the reservoir in the rock environment

	Positive indicators	Warning indicators
Total storage capacity	estimated capacity far greater than the total quantity of CO ₂ produced from the source	estimated capacity approximately the same as the total amount of CO ₂ produced from the source
Reservoir properties		
Depth	>1,000 m <2,500 m	<800 m >2,500 m
Thickness	>50 m	<20 m
Porosity	>20%	<10%
Permeability	>300 mD	<10-100 mD
Salinity	>100 g.l ⁻¹	<30 g.l ⁻¹
Overburden properties		
Horizontal connectivity	without faults	horizontal inhomogeneity, tectonic failures
Thickness	>100 m	<20 m
Input capillary pressure	input capillary pressure is much higher than the buoyant force of the estimated amount of the CO ₂ column	input capillary pressure is similar to the estimated buoyant force of a rising column of CO ₂

Note: according to CO₂STORE_BPM_final

change, where CO₂ plays an important role, in conjunction with its negative industrial production.

The up-to-now geochemical and especially hydro-geochemical research in Slovakia was aimed in particular at clarifying the genesis of mineral and geothermal waters (particularly deep hydrogeological and hydrogeothermal structures are a matter of concern for the injection of CO₂). Similarly, the thermodynamic modelling of water-rock interaction – focused on the gas, but not in the sense of entering a high amount of CO₂ in the gaseous and supercritical state into the equilibrium reactions. In other words, the target of interest was groundwater search, defining its origin and quality properties and securing its protection. In the context of modelling the subject of interest has been focused not only in the equilibrium thermodynamic modelling, but also in the reaction kinetics as well as in the reaction transport model.

The most important part was to select and work with the most appropriate geochemical programme, which would offer simulation of various scenarios for CO₂ injecting. The thorough search work identified PHREEQC programme (Parkhurst-Appelo, 1999) as appropriate from the professional and financial point of view. The programme is one of the most used geochemical programmes in the world, which is available for free on the USGS website. In fact, all the previously implemented projects of CO₂ sequestration in their initial phases benefited from this programme. Definitely another important selection criterion was the nature of the input data, which is currently still inadequate as well from the perspective of PHREEQC (such as a modal analyses, the parameters of porosity, etc.). The Programme allows for the characterization of water, in-series modelling of reactions, kinetic reaction, modelling the transport and inverse modelling. There was used the programme PHREEQC Version 2, updated by February 5, 2008. Originally the programme was focused in the modelling of geochemical processes in groundwater at low temperatures and pressures. The

problem was a database of thermodynamic constants and mineral phases, which is currently solved by optional database. The Programme contains a databases phreeqc, phreeqd, minteq, iso, minteq4f, wateq4f, pitzer and llnl, which are possible to apply according to the required issue solution. In particular, the pitzer database is very convenient for the application of the equilibrium constants for CO₂ injection, because it has equilibrium constants depending upon high temperature and high ionic strength of the solution and the database llnl, which works with the largest number of mineral phases. Therefore, it can be used also for other modelling of ex situ sequestration – simulation of reactions in the experiments, in particular, with olivine, serpentinite and wollastonite.

The theoretical foundation of the PHREEQC code are known from a number of publications, of which essential are, in particular, Parkhurst-Appelo (1999), Appelo-Postma (1993) and Merkel et al. (2005) and the basic manual, which can be downloaded from the USGS Web site.

5.1 Structure Marcelová

Hydrogeothermal structure Marcelová is located in the south-western part of the Danube Basin (Figs. 4.1.2.11, page 49). The aquifers in the GTM-1 borehole occur in the depth range 795-1,195 m – they are limestone beds, which alternate with red clayey and calcareous shales. At a depth of about 1,195 – 1,450 m red fine-grained laminated and mica-rich sandstones alternate with red, less green-grey shales. Up to the final depth of 1,763.5 m grey to black shaly and thin-bedded limestones and clayey shales predominate. At places thin horizons of clayey shales and fine-grained laminated sandstones are present (Biely, Kullmanová, 1992). With regard to the above lithology, the brine inflow into the borehole sediment is most likely from a fault zone, which conducts the brine from the jointed Early Triassic sediments (Franko et al., 2011).

The brine from the borehole GTM-1 has a value of total mineralization of 126 g.l^{-1} and is of a distinctive sodium-chloride type. This brine was applied in scenario of carbon dioxide injecting. An overview of the status of the mineral phases before and after the injection of CO_2 documents tab. 5.1.1. The modelling detected the biggest changes at given pH and current mineral phases saturation and, naturally, at increase in the amount of total

dissolved carbon dioxide in the brine. The phases were selected, which exhibit in the natural state the over-saturation, or equilibrium with brine. The scenario was carried out with CO_2 at an injecting pressure of 3.04 MPa, which at the same time was also partial pressure of CO_2 with CO_2 fugacity of 0.30 at 10 MPa pressure of atmospheric carbon dioxide, which was the subject of modelling.

Tab. 5.1.1 The status of mineral phases before and after the CO_2 injecting

Phase	SI ($-\text{CO}_2$)	Dissolved CO_2	SI ($+\text{CO}_2$)	Dissolved CO_2
temperature	54		54	
pH	6.6		3.49	
p CO_2	0.002 MPa	0.0022 mol.kg⁻¹	3.04 MPa	0.39 mol.kg⁻¹
andradite	7.77		-18.51	
aragonite	0.3		-2.7	
calcite	0.44		-2.55	
dolomite	1.83		-4.16	
$\text{Fe}(\text{OH})_3$	1.63		-2.21	
FeOOH	6.41		2.57	
magnesite	-0.08		-3.07	
quartz	0.01		0.02	
strontianite	0.41		-2.59	
talc	0.98		-17.63	

As regards the content of dissolved carbon dioxide, this has increased after the injection on about 177 times, from $0.0022 \text{ mol.kg}^{-1}$ in natural brine to 0.39 mol.kg^{-1} . In view of the mass this represents 17.2 g.l^{-1} of total dissolved CO_2 in the brine after injection. The quantity of CO_2 causes an abrupt change in the pH value on nearly half - from 6.6 to 3.5 and brine solution shall become strongly acidic. Important will be also the subsequent solution reactivity, which will act on the surrounding rock environment. It is clear from the Table 5.1.1 that virtually all phases of the system are not likely to precipitate in their natural state, but on the contrary, they will dissolve, with the only exception of ferric hydroxide. The phase status of quartz will remain unchanged even after the injection of carbon dioxide; it will stay in equilibrium state with the solution. The model is made for a stationary state, the kinetics of the reactions is not included, and it means, the velocity and the time in which they will take place. One fact is obvious, however, that carbon dioxide will dissolve almost immediately in the brine and will generate changes that require evaluation, using the reaction kinetic transport model.

The used programme PHREEQC is adjusted to one dimensional modelling of transport processes, which includes: 1. diffusion, 2. advection, 3. advection and dispersivity, 4. advection and dispersivity in the stagnant zone. The important thing is that all of these processes may be combined with thermodynamic equilibrium states and kinetics of chemical reactions.

At the site Marcelová the transport model was simulated with advection and dispersivity. Partial pressure at the injection was considered for 7.38 MPa and diffusion coefficient was $4.5 \cdot 10^{-11} \text{ m}^2.\text{s}^{-1}$.

The results of the modelling of transport document changes in pH during CO_2 transport. The Figure 5.1.2 presents the result of the simulation after 10 years of injection. Brines are considered in the case of carbon equilibrium with calcite and dolomite. Therefore, a change in pH is biased to a certain distance from the borehole, where equilibrium will be achieved after 10 years with the considered mineral phases.

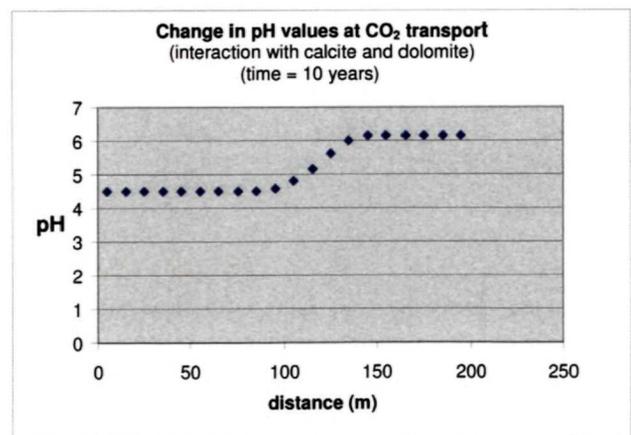


Fig. 5.1.2 Modelled changes in pH transport model

From the chart we can see that the pH value is gradually increased in the range from 100 m to 150 m and then remains steady at around 6.1. This means that at the beginning due to the dissolution of CO_2 the pH is sharply reduced, but at the same time mineral phases of calcite and dolomite present in the solution interact and are being dissolved. The brine in the distance of approximately

100 m away from the CO₂ injection sites no longer loses the neutralisation capacity and the pH value gradually grows, calcite and dolomite stop being dissolved and the system gets into a state of equilibrium. This case occurs at a distance of approximately 150 m from the site of CO₂ injection.

In Figure 5.1.3 the course in total dissolved carbon dioxide content in the brine is shown, depending on the distance of injection for 10 years. Input conditions are the same as in the previous case. It turns out that in the distance of around 75 m from the injection spot the amount of dissolved CO₂ is practically the same, approximately at the level of 0.83 mol.kg⁻¹. Then around the distance of 100 m it drops rapidly to a value of 0.2 mol.kg⁻¹. At a distance of 150 m is the amount of CO₂ close to zero value. This course corresponds very well with the state of calcite and dolomite saturation condition, since, as already aforementioned, at this distance both mineral phases are in equilibrium with the brine.

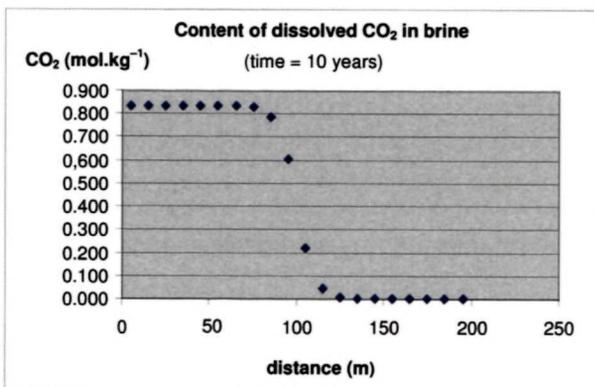


Fig. 5.1.3 Model solution of CO₂ content during transport

The difference between the amount of CO₂ that is captured using the so-called capture by dissolution and mineral capture is presented in Fig. 5.1.4.

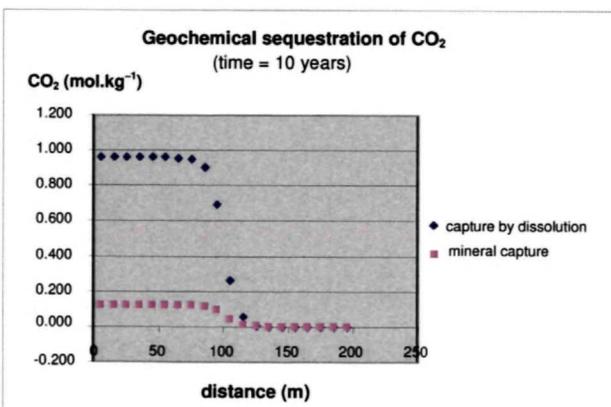


Fig. 5.1.4 Course of CO₂ capture by dissolution in the brine and by mineral capture.

The capture by dissolution is actually identical to the already described total dissolved carbon dioxide content. The mineral capture represents the amount of CO₂ consumed to dissolve calcite and dolomite from the rock environment. Its value is generally much lower in com-

parison with its dissolution in the brine. It should be noted, that the kinetics of reactions was not taken into account, only transport and diffusion.

The situation after 20 years of injection is simulated in Figures 5.1.5 and 5.1.6. Compared with the previous situation, the low pH values will persist within the environment at a greater distance from the site of injection and, of course, the total content of dissolved CO₂.

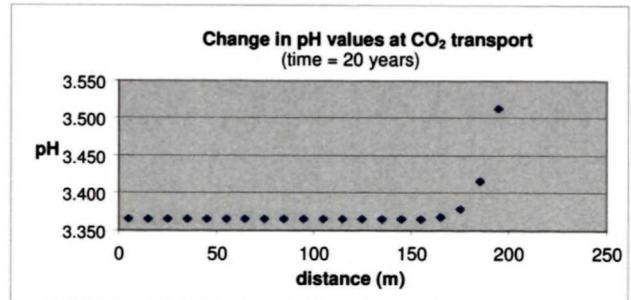


Fig. 5.1.5 Course of the Ph changes after 20 years

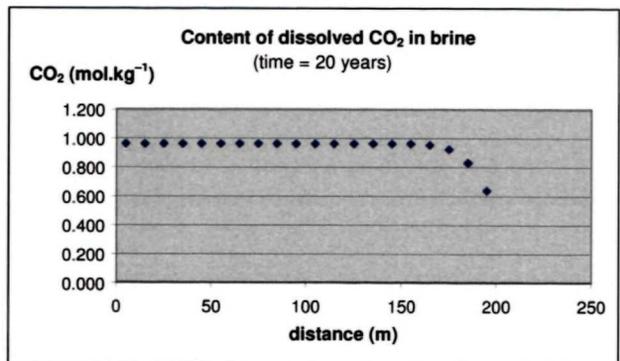


Fig. 5.1.6 Course of CO₂ content after 20 years



Fig. 5.1.7 CO₂ transport with respect to the dissolution kinetics of calcite.

In the next scenario in the transport model the kinetic module for calcite was inserted. The result of the simulation is documented in Figure 5.1.7. It is obvious that at a distance of 250 m from the point of injection the calcite will be undersaturated when compared with the brine and will dissolve. After then, the calcite will be in equilibrium with brine reaching a steady-state.

5.2 The Láb Structure

Under the term Láb structure we understand the Láb-Malacky Elevation with adjoining sunken blocks. In this structure within the Mesozoic basement there have been uncovered brines with the values of total mineralization from 109.8 to 129.8 g.l⁻¹. They are of distinct Na-Cl type with minimum value of A₂ components, which indicates the closeness of the structure in which they are located. The levels of sulphates in the brines are relatively low, but do not exceed the value of 600 mg.l⁻¹ in spite of the presence of anhydrite in collector rocks.

Based on the palaeoreconstruction of the brine in this area, we can say that the Triassic carbonates were overlain by Late Karpatian clays and sands. From this fact it follows that, until the Karpatian period, the whole area was exposed. During the Late Karpatian the whole area of the Slovak part of the Vienna Basin was flooded by the sea, protruding to the Láb-Malacky area, creating lagoons. Within the lagoons due to evaporation brines were formed, which had infiltrated into the Triassic carbonates and were later sealed by Late Karpatian clays. The evaporation didn't reach up to the level of halite precipitation, because the lagoons had been replenished by meteoric waters originating from precipitation and surface flows. These assumptions also supports the value of $^{18}\text{O} = -2.4\text{‰}$ in the brine in the depth range of 1,877-2,873 m in the borehole Láb-120 (Pačes, 1983).

The simulation of CO₂ injecting was under the same conditions as in the structure of Marcelová.

The simulation process of injecting took place under the temperature 122.5 °C and the initial pH of the brine 6.4 (Table 5.2.1).

Tab. 5.2.1 Injection and transport conditions

Site	pressure CO ₂ (MPa)	temper. (°C)	diff. coeff. (m ² .s ⁻¹)	distance (m)	time (years)
Marcelová	7.38	54	4.5.10 ⁻¹¹	200	10, 20
Láb-92	7.38	122.5	4.5.10 ⁻¹¹	200	10, 20

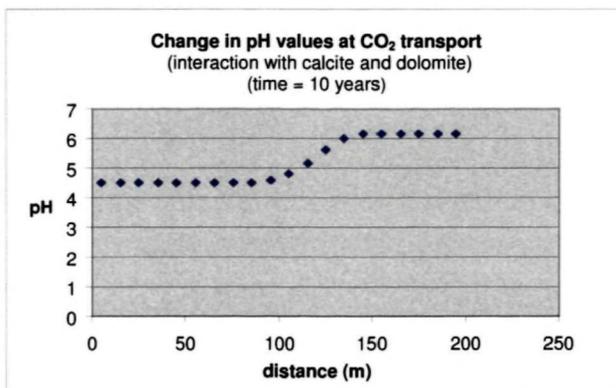


Fig. 5.2.1 Course of pH values at CO₂ transport

From the Fig. 5.2.1 it is evident that at the site of CO₂ injection the pH value drops sharply to 4.49. The change occurs at a distance of up to around 115 m, but its course is not as sharp and, in particular, the pH value is just closing the original one.

A different course is to follow at the CO₂ transport without interactions with rock environment (Fig. 5.2.2). Of course, H⁺ ions are not being consumed and the pH value is steady at a level of to 4.3 up to a distance of around 155 m. There occurs only the CO₂ dispersion by diffusion and to a distance of 200 m from the site of injection, for a period of 20 years, the pH would rise to a value of 4.5 only.

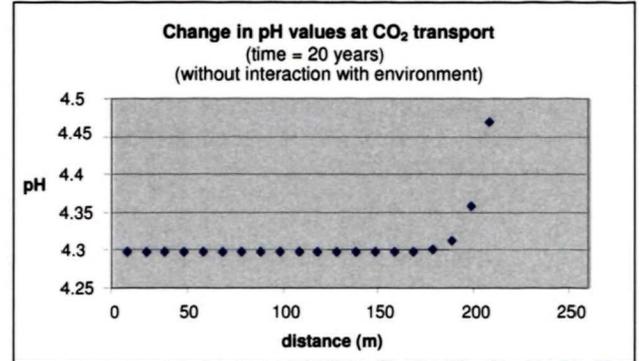


Fig. 5.2.2 Course of pH values at CO₂ transport

The ratio between the capture by dissolution and mineral capture of CO₂ for a period of 10 years of injection shows the Fig. 5.2.3.

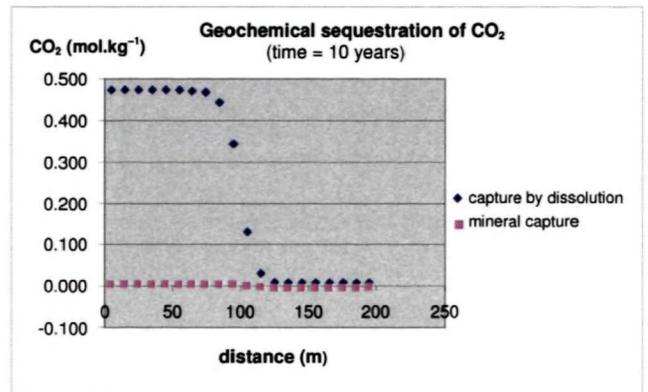


Fig. 5.2.3 Course of mineral capture of CO₂ and dissolution in the brine

The difference between the two types of capture is evident (Figure 5.2.4), the nature of the mineral capture has a much smaller effect and much slower progress.

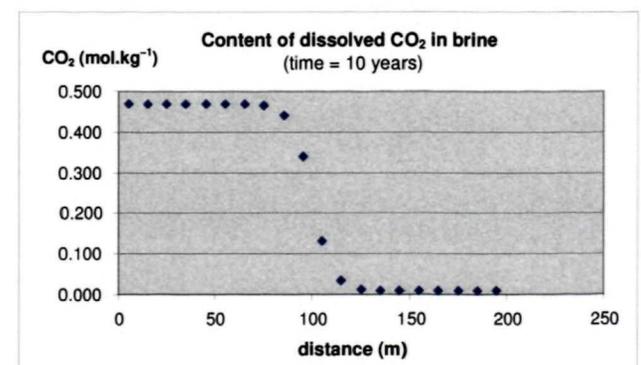


Fig. 5.2.4 Course of dissolved CO₂ content

It is clear that the capture by dissolution corresponds to the already described course of the pH value during the transport in the simulation of steady-state. It is important to note that the calculated CO₂ levels will be distorted by the fact that the modelling was done using the equation for an ideal gas. However, the CO₂ in supercritical condition and the given geological structure does not behave as an ideal gas, this means that its fugacity is not equal to the saturation pressure chart. This fact corresponds also to the amount of dissolved CO₂ in the brine in the Fig. 5.2.4.

5.3 Nature analogues

The study of natural analogues is an important part of the research in options for carbon dioxide storage into the ground. Under the natural analogue we understand a natural accumulation of CO₂ in the geological environment in the form of so-called dry CO₂, or within the groundwater collectors. It is possible to use natural analogues to study the properties of carbon dioxide and the conditions (in particular, pressure and temperature), under which its accumulations are formed underneath the Earth's surface. Furthermore, it is possible to track its interaction with the geological environment, as well as impermeable strata that make up the boundary conditions for an accumulation. Similarly, it is possible to study the interaction of water-gas and water-gas-rock, as well. The basis is the fact that similar conditions are hardly to imitate in the experimental laboratory.

In the scope of the project the thematic unit was studied in the context of the carbon dioxide behaviour under the conditions of higher temperatures and pressures. The geothermal water properties from a borehole Lipany-1, as the natural analogue of geothermal water collector with a high content of carbon dioxide were evaluated on the basis of chemical analyses taken during hydrodynamic tests on the collar of the borehole. All the data have been retrieved from the work of Král' et al. (2010).

At the exploitation of 10 l.s⁻¹ of geothermal water from the borehole the pressure on the collar will be in the range 2.75-2.70 MPa. In the phase ratio of the geothermal water and separated gas under the atmospheric conditions equal to 25 Nm³.m⁻³ the amount of pure carbon dioxide for 1 hour will be 900 Nm³; for 24 hours, this is a production of 21,600 Nm³ of gas.

The modelling (PHREEQC) simulated the quality balance of likely mineral phases in the borehole collar in the water with separated gas and without separated gas. As the likely mineral phases (phases, which will form of the water) are the ones whose index of saturation under the given conditions is greater than 0, or 0.2.

In the case of gaseous phase separation, in the condition of partial CO₂ pressure 0.0443 MPa and temperature 91°C, the geothermal water is strongly oversaturated with mineral phases as indicated in the Table 5.3.1 and virtually all the CO₂ is dissolved in the water (SI = -0.36). These can be summed up in two geochemical categories. The first one is the oversaturation with respect to all potential mineral phases of carbonate equilibrium and the second one is the oversaturation in respect to all mineral

phases with trivalent iron. In the first case the result of the simulation is the formation of carbonate incrusts and in the second case the creation of mineral phases on the basis of trivalent iron, which gives the water a typical brownish yellow haze. At the same time, we can observe an increase in the pH of the water, which is caused by the lack of carbon dioxide in the system, because it was separated away.

Tab. 5.3.1 Likely mineral phases of the geothermal water under the conditions at the borehole collar.

Min. phase	SI (with gas separated)	SI (without separation)
CO ₂	-0.36	1.30
p CO ₂ (MPa)	0.0443	2.022
aragonite	2.13	0.58
calcite	2.27	0.72
dolomite	5.14	1.98
dolomite-ordered	5.15	1.99
dolomite- disordered	3.99	0.83
Fe(OH) ₃	4.20	3.45
goethite FeOOH	8.59	7.84
haematite	18.50	16.99
strontianite	2.02	0.44
pH	7.87	5.74

Note: SI - index of saturation

In the second simulation, when the gas was not separated, under partial CO₂ pressure 2,022 MPa and the same temperature of 91°C the result of the simulation is virtually identical. This basically means that even at a sufficient content of carbon dioxide the mineral phases did not reach equilibrium state, and the resulting effect from the point of view of the mineral phases was similar to the one in the first test. High CO₂ content is reflected in the decline in the pH value to 5.74.

Within the production of anthropogenic emissions of carbon dioxide into the atmosphere, we made an estimate of the natural emissions of this gas in Slovakia, which may be considered as natural background from this source.

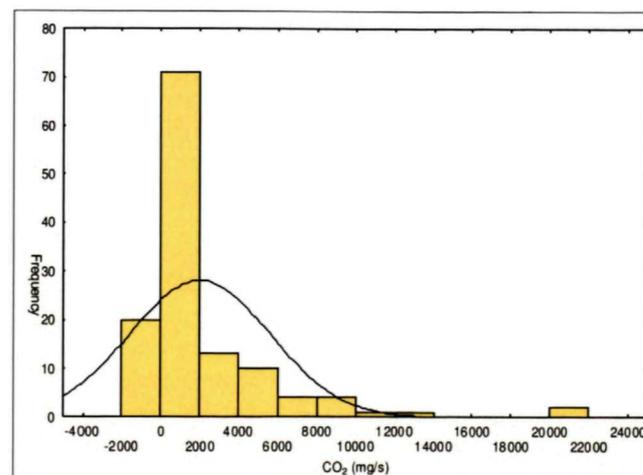


Fig. 5.3.1 Histogram of the distribution of CO₂ production by mineral waters.

Besides organically produced CO₂, CO₂ from soils, CO₂ originating from other natural waters, volcanic activity (in terms of SR is currently extinct) the sources of mineral waters are likely to be its biggest producer.

The estimate of the natural emissions from mineral waters was based on the approach that all the released carbon dioxide, whether for therapeutic purposes when using mineral waters, or stuffed into consumer packaging will ultimately get into the atmosphere.

An estimate has been made on the basis of the registration of mineral waters ISS (Inspectorate of Spas and Springs) MH SR.

Other sources of information about mineral waters cannot be used in practice. The reason is the lack of the yields of the sources, as one of the parameters, from which the estimate was made. It was based on the formula:

$$\text{MOU} = c_{\text{OU}} * Q$$

MOU the amount of carbon dioxide in mg.s⁻¹,

c_{OU} the concentration of carbon dioxide (mg.l⁻¹) in mineral water,

Q yield (l.s⁻¹) of mineral water source.

Recently on the territory of the Slovak Republic there have been registered more than 1700 sources that meet or comply with the criteria for the indication of the mineral water. The number indicates all registered sources, but not all the existing ones. The situation reflects the status of the registration, which is a long-term issue. The status of many sources is uncertain, some of them have been destroyed, and many have disappeared due to anthropogenic interventions. At many sites effluences of dry CO₂ are known, for instance Vyšné Ružbachy, Pribylina, etc. Determination of free carbon dioxide is also problematic. Another uncertainty can also be a lot of sources, maybe even existing, which have not been registered in the database. Similarly, it is difficult to estimate how much CO₂ is released from the wells with negative piezometric level. To conclude we have to note that a significant factor, such as temperature, was not taken into account for the solubility of CO₂.

The first step was determination of the amount of carbon dioxide in the calculation of the sources monitored by ISS MH SR (126 sources); the total number of

sources in the registry is 1,782. Consequently, the amount of carbon dioxide (MOU):

$$\begin{aligned} \text{MOU} &= 140,237 * 250.13 = 35,077,480.81 \text{ mg.s}^{-1} \\ &= 35.078 \text{ kg.s}^{-1} \text{ CO}_2 \end{aligned}$$

Distribution of the quantities of carbon dioxide, expressed in the form of histograms is documented in Fig. 5.3.1. It is obvious that there are zero values in the file, either because of zero content of CO₂, or absencing yield value (this represents about 12% of the sources). The layout of these quantities is apparently associated with the lognormal distribution with the largest frequency 0 to 2,000 mg.s⁻¹ and with maximum of 20,000-22,000 mg.s⁻¹.

For the above considerations, it would be necessary to recalculate the results through a coefficient, which would include the following: incontinuous exploitation, closed boreholes, or boreholes with free water table level, etc. Designed estimation coefficient KCO₂ could be somewhere at the level between 0.5 to 0.6. For the calculation the estimation coefficient 0.55 was used. The result of the MOU after correction is the quantity: MOU = 35.078 * 0.55 = 19.3 kg.s⁻¹ CO₂.

If we take into account that in the overall registration of 1782 sources these need to be corrected on the extinct, liquidated and non-registered boreholes, the estimate factor could be in the range K_r = 0.6 to 0.7 (0.65), which implies that the number boreholes 1,782 * 0.65 = 1,158.

Another coefficient accounted for the fact whether the mineral source has been identified because of the CO₂ content. In such a case the same coefficient K_M = 0.6 to 0.7 (0.65) was used, and the result is 1,158 * 0.65 = 752 sources on the territory of SR with CO₂.

Of the number of 752 sources those calculated in the first step (126) have to be deducted: 752 - 126 = 626.

If we take as a representative the samples in the first step (sources yield, CO₂ content), then the final calculation is 626/126 = 4.96. The total estimated amount of carbon dioxide will be then 6 * 19.3 = 115.8 kg.s⁻¹.

This estimated amount, recalculated to one year represents approximately 3.6 million t of carbon dioxide, which is emitted into the atmosphere from the sources of mineral waters in Slovakia.