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HYDROCHEMICAL MODEL OF CO_2 INJECTION INTO THE LOWER BADENIAN AQUIFER WITHIN THE UPPER SILESIAN COAL BASIN (CZECH REPUBLIC)

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ABSTRACT. The paper presents an example of the CO_2 storage dynamic behavior model for a potential host rock from the USCB – the Dębowiec Fm. sandstone. The modeling was performed assuming the formation pressure at the level of 70 bar. The zone of changes in the gas-water-rock system, for the assumed parameters and for a short injection time (100 days) does not exceed 60 m from the center of injection well. The main reaction that rules CO_2 trapping is albite dissolution, and dawsonite precipitation. Mineral-trapping capacity, for a period of 20000 years, calculated according to the results of modeling for the example rock, is close to 1.9 kgCO_2/m^3,and the solubility trapping capacity equals to almost 1 kg CO_2/m^3 of formation.

ХИДРОХИМИЧЕН МОДЕЛ НА CO_2 НАГНЕТЯВАНЕ В ДОЛНОБАДЕНСКАТА ВОДОНОСНА СТРУКТУРА НА ГОРНОСИЛЕЗИЙКИЯ ВЪГЛИЩЕН БАСЕЙН (РЕПУБЛИКА ЧЕХИЯ)

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РЕЗЮМЕ. В статията се представя модел на динамичното поведение на CO_2 при подземното му съхраняване в потенциално вместващи скали от Горносилезийкия въглищен басейн – Dębowiec пясъчникова формация. Моделирането предвижда съдаване на налягания от 70 bar. Зоната на въздействие върху системата газ-вода-скала, за относително кратко време за нагнетяване (100 дни) не превишава 60 m от центъра на нагнетателния сондаж. Основната реакция, която се осъществява в резултат на нагнетяването на CO_2 е разтваряне на албита и утаяването на даусонит. Минералното разтваряне, което се формира за период от 20000 години изчислено в резултат намоделиране върху експерименталния пласт, съставлява 1.9 kgCO_2/m^3, а разтворителното съхраняване възлиза на около 1.0 kg CO_2/m^3.

Introduction

According to the Directive of the European Parliament and of the Council on the geological storage of carbon dioxide – CO_2 storage is considered as a technology that will contribute to mitigating climate change. Stabilization of greenhouse gas concentrations in the atmosphere at a level preventing anthropogenic interference with the climate system is the main objective of the UN Framework Convention on Climate Change, which was approved by the Council. Article 4 of the Directive - Selection of storage sites-qualifies the Member States right to determine the areas from which storage sites may be selected in accordance to the requirements of this Directive. The suitability of a geological formation for use as a storage site shall be determined through an evaluation and assessment of the potential storage formation.

Perspective localities for CO_2 sequestration in Poland comprise mainly the oil and gas fields, coal seams, and saline aquifers within Mesozoic anticlinal structures of Central Poland. Results of numerous tests (White et al., 2005) prove however, the possibility of long-term binding of injected CO_2 also in the structures other than distinct anticlines. In this context, also the saline aquifers of Tertiary and of Carboniferous productive formation of the Upper Silesian Coal Basin (USCB), on the borderland of Poland and Czech Republic (Fig. 1), are interesting as potential greenhouse gases repositories (Labus, 2008). This work gives an example of the storage dynamic behavior characterisation for a potential host rock from the USCB. The following issues are presented: reactive processes (the reactions of the injected CO_2 with the rock matrix); short and long-term simulations (to establish CO_2 impact and behaviour over decades and millennia including the rate of dissolution of CO_2 in water); changes in formation fluid (pore water) chemistry and subsequent reactions (e.g. pH change, mineral formation).

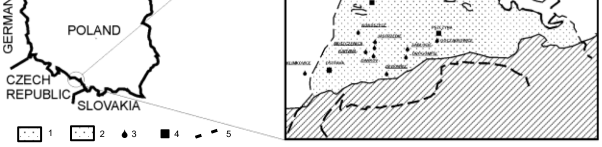

Fig. 1. **The Upper Silesian Coal Basin – USCB (Labus, Grmela, 2003): 1 – Tertiary overburden; 2 – Carpathians; 3 – medicinal waters exploitation; 4 – towns; 5 – borders of the USCB**

Hydrogeology

The main, primary hydrostructures of the area are the multiaquifer formations of: Quaternary, Tertiary and Carboniferous. Considering the carbon dioxide sequestration the latter two ones might be taken into account. The example of potential host rock presented in this paper belongs to the Tertiary coarse-grained sediments of Lower Badenian that fill deep depressions in the roof of Carboniferous formation and, considering the conditions of coal exploitation, form the most important hydrostructure within the Czech part of the Upper Silesian Coal Basin (Fig. 2).

Two hydrochemical environments were defined in this structure (Labus, Grmela, 2004). The environment I covers the western part of the Bludovice depression, NE slope of the Ostrava-Karvina Ridge and the Rychvald depression. Waters of the HCO_3-(SO_4-Cl) - Na(Ca-Mg) type occur in the western part of the environment I, while waters of Cl-Na type are observed in its remaining part. Exclusively stagnant waters of the Cl-Na type represent the environment II – typical mainly for the Detmarovice depression (Labus, Grmela, 2004). The deepest parts of the Detmarovice depression reach 700 m below sea level, and up to 1100 m in case of the Bludovice depression. Maximal thicknesses of the analysed sediments reaches 268 m (Hufova, 1971).

Hydrochemical modeling – method

Simulations of water-rock-gas interactions were performed with use of the Geochemist's Workbench (GWB) 7.0.1. – geochemical software (Bethke, 2008). The GWB package was used for equilibrium, and kinetic modeling of gas-brine-water system. The reactions quality and progress were monitored and their effects on mineral sequestration capacity (CO_2 trapping in form of carbonates) were calculated. The kinetic transport modeling was carried out in order to evaluate changes in the hydrogeochemical environment of the formation, due to the injection and CO_2 storage. This enabled the assessment of volumes and amounts of mineral phase precipitating or being dissolved during the simulated reactions, and amounts of CO_2 sequestered. The model required the thermodynamic data for the reacting minerals, their abundance in the assemblage within the host rock (tab. 1), relative fraction of pore water and the information on its physic-chemical parameters (Table 2).

Composition of mineral assemblage was determined by means of planimetric analysis of thin sections, using Axioscope Zeiss Microscope (Fig. 3). Additional XRD analysis was performed on HZG-4 X-ray diffractometer, with the use of CuK_{α} lamp in the following conditions: voltage 30kV, intensity 20 mA, angle range 2 theta 4-64°, step 0.02°. For determining the porosimetric properties of the examined rocks the Mercury Intrusion Porosimetry (Autopore 9220 Micrometrics Injection Porosimeter) was used. Reaction models required the input of the mineral specific surface areas – SSA. They were calculated assuming spherical grains of different diameters for sandstones and fine-grained rocks.

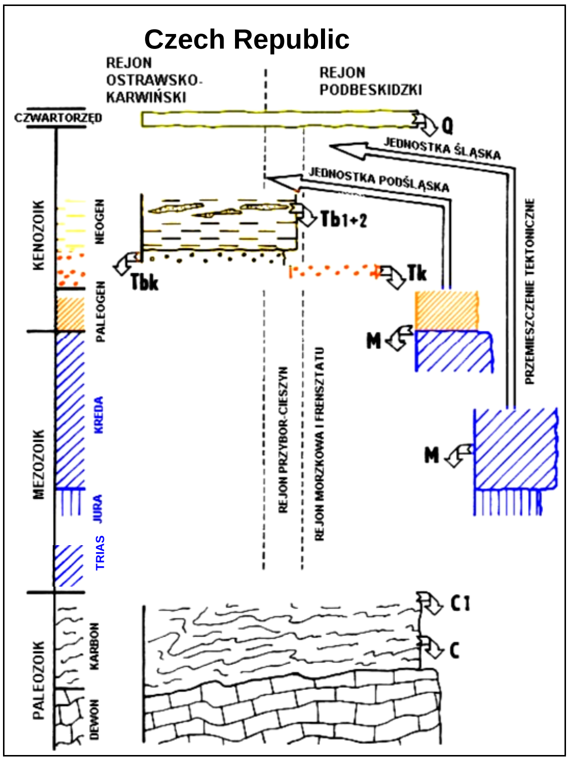

Fig. 2. Hydrostratigraphical profile of the Czech part of the USCB (after Labus, Grmela, 2003): Q – Quaternary complex; T_b, T_{b1+2}- waters of Lower Badenian sandy horizons within clayey cover of the Carboniferous complex (Skawina Formation); T_{bk}- waters of sandy-gravel sediments of Lower Badenian (Dębowiec Formation); T_k – waters of sandy and sandstone aquifers of autochtoneous Carpatian; M - fissure waters of the Subsilesian Nappes; C_1- fissure and pore waters of Carboniferous; C – waters of fissure-fault system of upper Carboniferous and its basement. Arrows indicate the possibility of groundwater downward migration into the deeper aquifers

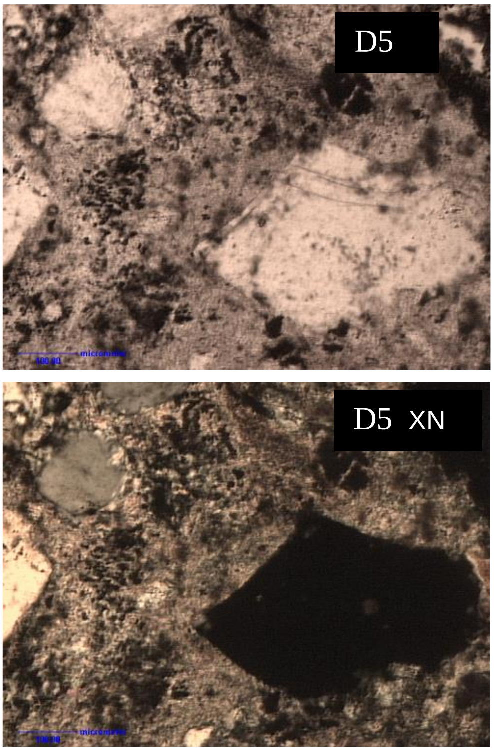

Fig. 3. Microscopic photos of rock sample thin section (symbol: XN – crossed Nicols); D5 – poorly sorted sandstone, highly porous; feldspar crystals deeply kaolinized; sericite-loamy-ferruginous matrix

Table 1

Composition of mineral assemblage, specific surface areas, kinetic rate parameters at 25°C (Palandri, Kharaka, 2004) and recalculated values for 30°C, considered in the model. Lower Badenian Dębowiec Fm.NP631 well.

Mineral	[vol%]	SSA [cm^2/g]	Kinetic rate parameters		
			k_{25} [mol/m^{2}s^{-1}]	E_A [J ·mol^{-1}]	k_{30} [mol/m^{2}s^{-1}]
Quartz	75	2,27	$1,02 \cdot 10^{-14}$	87,6	$1,83 \cdot 10^{-14}$
Albite	2	6,95	$9,12 \cdot 10^{-13}$	69,8	$1,45 \cdot 10^{-12}$
K-feldspar	8	7,11	$3,89 \cdot 10^{-13}$	38,0	$5,01 \cdot 10^{-13}$
Muscowite	5	105,98	$2,82 \cdot 10^{-14}$	22,0	$3,26 \cdot 10^{-14}$
Illite	3	108,75	$8,91 \cdot 10^{-16}$	14,0	$9,78 \cdot 10^{-16}$
Kaolinite	7	1156,49	$1,00 \cdot 10^{-13}$	22,2	$1,16 \cdot 10^{-13}$
SSA- Specific surface areas of mineral grains					

The modeling was performed assuming the formation pressure at the level of hydrostatic pressure of 70 bar. As the utilized software – GWB – requires the gas pressure input in form of fugacity - a measure of a chemical potential in the form of adjusted pressure. The appropriate value (tab. 1) was calculated using on-line calculator of The Duan Group: http://www.geochem-model.org/models/co2/ (Duan et al., 2006).

Temperature values were estimated basing on the direct measurements and archival data (Karwasiecka, 1996, 2001). Analyses of the formation water were carried out using standard methods; they include also the results of *in situ* measurements, assuring the quality of interpretation. The chemical composition of the formation water in the aquifer – host rock for the purpose of the simulation was obtained by equilibration of the formation water with the minerals assemblage typical for the modeled environment.

Table 2

Initial composition of aquifer pore waters used in the computer simulation

Parameter	Unit	Aquifer
Porosity	-	0,05
f_{CO2}	bar	47
T	°C	30
Na^+	mg/kg	12270
K^+	mg/kg	5,9
Ca^{2+}	mg/kg	964
Mg^{2+}	mg/kg	105,2
Sr	mg/kg	-
HCO_3^-	mg/kg	38,1
Cl^-	mg/kg	20910
SO_4^{2-}	mg/kg	5,88
SiO_2(aq)	mg/kg	8,86
Al^{3+}	mg/kg	0,004
Fe^{2+}	mg/kg	0,7
pH	-	7,37
TDS	mg/kg	34311

The following kinetic dissolution/precipitation rate equation, simplified after Lasaga (1984) was used in the calculations:

$$r_k = A_S k_T \left(1 - \frac{Q}{K}\right) \tag{1}$$

where: r_k – reaction rate ([mol·s^{-1}] ; dissolution – $r_k > 0$, precipitation – $r_k < 0$),
A_S – mineral's surface area [cm^2],
k_T – rate constant [mol·cm^{-2}·s^{-1}] at the temperature T
Q – activity product
K– equilibrium reaction for the dissolution reaction

According to the above equation a given mineral precipitates when it is supersaturated or dissolves when it is undersaturated at a rate proportional to its rate constant and the surface area.

Reactive transport model; trapping capacity

The X1t program (part of the GWB) was used to model reactive transport in radial dimension (Fig. 4). The transport calculation take into account the movement of groundwater and the transport of chemical species dissolved in it by advection, the movement of groundwater through the subsurface, hydrodynamic dispersion, the mechanical mixing within the groundwater flow, and molecular diffusion. The domain was designed in a manner enabling the simulation of the processes within the space situated around the CO_2 injection well. The model accounts for the nature of hydrochemical phenomena rather than for the real scale of their spatial range.

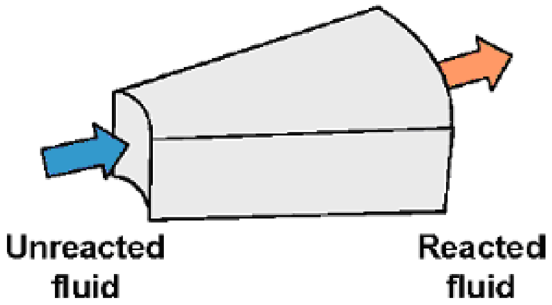

Fig. 4. Scheme of model domain

The following parameters were defined: injection well radius: 10 cm, outer radius of the domain: 100 m, height of a single cell: 5 cm, domain angle: 0.1 rad, number of cells: 10, diffusion coeff.: 10^{-6} cm^2/s, injection pressure: 71 bar.

Modeling was performed in two stages. The first one was aimed at simulating the immediate changes in the aquifer and insulating rocks impacted by the beginning of CO_2 injection (100 days), the second – enabled assessment of long-term effects of sequestration – 20000 years (20 ka).

During the CO_2 injection into the sandstone of the Dębowiec Formation – hydrolysis of kaolinite leads to the production of chalcedony (Fig. 5):

$$\underset{Kaolinite}{Al_2Si_2O_5(OH)_4} + 6H^+ \leftrightarrow \leftrightarrow 5H_2O + 2Al^{3+} + \underset{Chalcedony}{2SiO_2} \qquad (2)$$

The CO_2 fugacity reaches the value of 47 bar, and concentrations of CO_2 (aq) rise from: 0.00003 to 1.321M, and HCO_3^- from 0.0004 to 0.0026M. Pore fluid reaction drops from 7.37 to 3.44 pH. Increase of porosity amount to relative 4%.

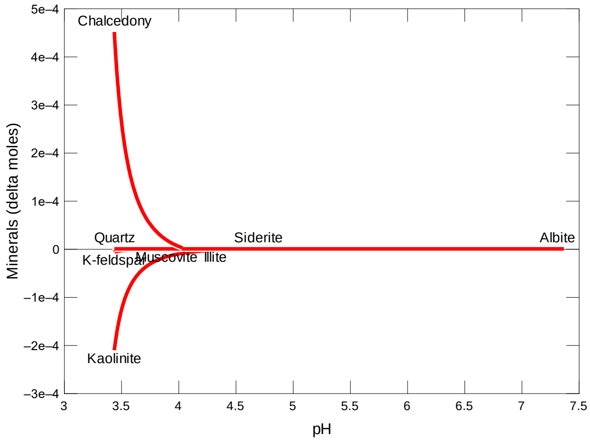

Fig. 5. Changes of minerals quantities as function of pH on the stage of the injection – D5 sample

Analysis of the hydrochemical processes, during the sequestration stage, within the different cells of the domain: 5, 15 and 25 m, is possible on the basis of the Figs. 6 and 7. In this stage, for the period of 20 ka, within the cells situated at 5 and 15 meters from the injection point, the main reaction that rules CO_2 trapping is albite ($NaAlSi_3O_8$) dissolution, and dawsonite precipitation:

$$\underset{Albite}{NaAlSi_3O_8} + 2CO_2(g) + 2H_2O \leftrightarrow \leftrightarrow 2\underset{Dawsonite}{NaAlCO_3(OH)_2} + \underset{Chalcedony}{6SiO_2} \qquad (3)$$

In the zones more distant to the injection well (Fig. 6-7), the CO_2 mineral trapping is not registered. The main reaction that modifies the proportions between the rock matrix components is the dissolution of k-feldspar and kaolinite and chalcedony and muscovite precipitation.

$$\underset{K-feldspar}{KAlSi_3O_8} + \underset{Kaolinite}{Al_2Si_2O_5(OH)_4} \leftrightarrow \leftrightarrow \underset{Muscovite}{KAl_3Si_3O_{10}(OH)_2} + \underset{Quartz}{SiO_2} + H_2O \qquad (4)$$

The CO_2 fugacity reaches 17 bar after a stable decay. $CO_{2(aq)}$ concentration drops to 0.48M, while HCO_3^- rises to 0.013M. The pH goes up to the value of 4.6, and the total porosity lowers slightly to 0.048.

The zone of changes in the gas-water-rock system, for the assumed parameters and for a short injection time does not exceed 60m from the center of injection well. During the sequestration stage the CO_2 fugacity – drops significantly to the value of about 10 bar within the distance of 5m from the injection well (Fig. 6). At the same time a drop of $CO_{2(aq)}$ and HCO_3^- concentrations is noted. The pH, increases to the value of natural background, reached at the distance of 25 m from the injection point (Fig. 6). Relative change in porosity does not exceed 4% (0.002).

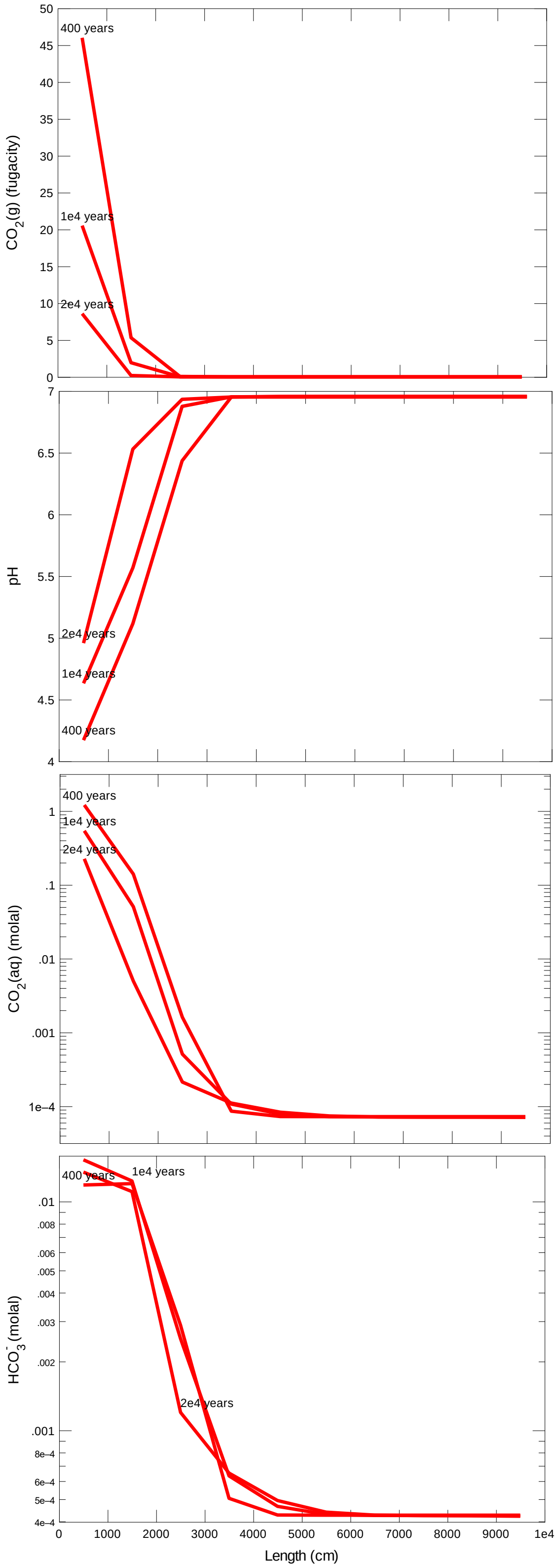

Fig. 6. Changes in: fCO_2, pH, concentrations of $CO_{2(aq)}$ and HCO_3^-, pH, after 0,4, 1,0, and 2ka as function of distance from the injection point

Mineral-trapping capacity was calculated basing on the quantity of newly precipitated dawsonite – Fig. 8. Its value, determined for the first cell – representing the injection point into the Dębowiec Fm. sandstone aquifer – is close to 1.9 $kgCO_2/m^3$.

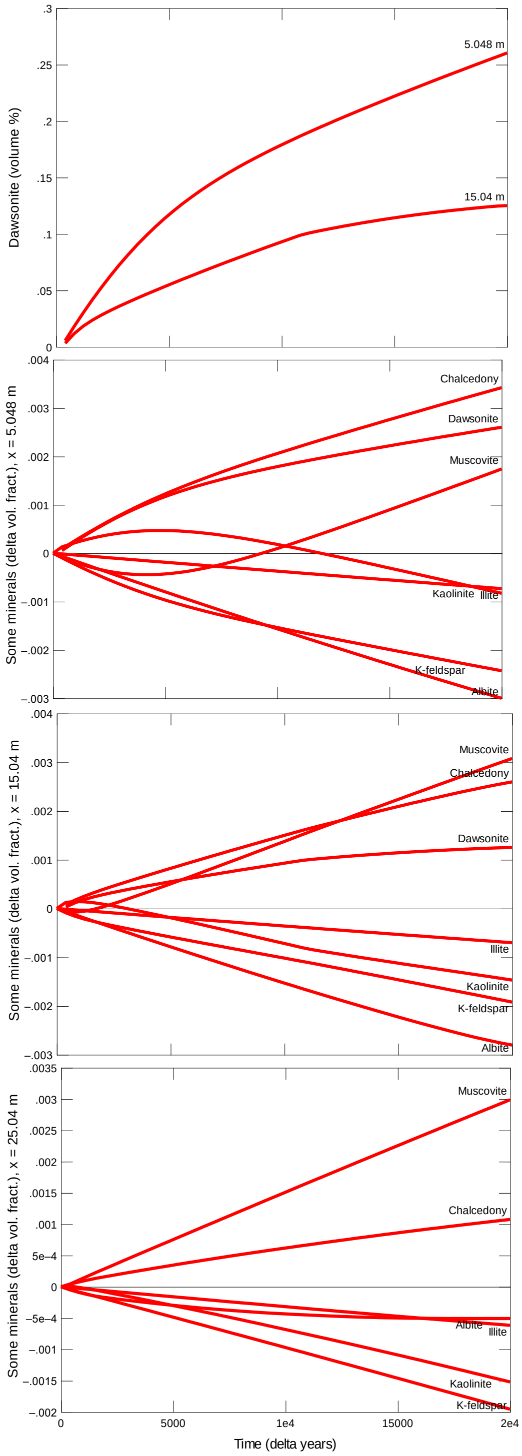

Fig. 7. Changes of minerals volume in the different domain cells: 5, 15 and 25 m from the injection point

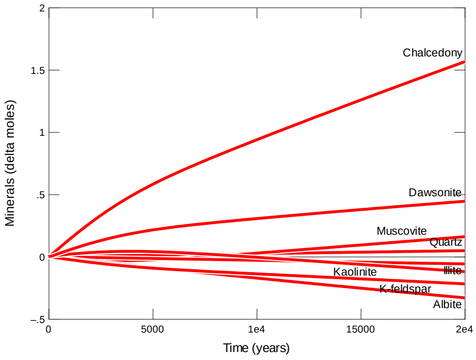

Fig. 8. Changes of minerals quantities in 20ka after the injection termination – D5 sample – the injection point

This value is approximately 2-3 times lower then the ones obtained in simulations regarding other geologic formations considered as perspective CO_2 repositories (eg. Xu et al., 2003; Labus, 2008). Solubility trapping capacity (calculated basing on simulated pore water chemistry) for the modeled formation equals to almost 1 kg CO_2/m^3 (Table 3).

Table 3. *Values of porosity, mineral and dissolution trapping capacity of analyzed formation*

Porosity	n_p -primary - 0 ka	0.050
	n_f - final - 20 ka	0.048
Precipitating Minerals mol/UVR	Dawsonite	0.445
	Dolomite	-
	Siderite	-
Dissolution mol/UVR	Siderite	-
	Kalcite	-
CO_2 Mineral trapping	mol/UVR	0.445
	kg/m^3	1.861
CO_2 Solubility trapping	as HCO_3^- g/l	28.7
	kg CO_2/m^3	0.994
SUM [kg CO_2/m^3]		2.855

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