

Conceptual geochemical models of groundwater chemistry against aquifer mineralogy (Stephanian-Autunian sedimentary rocks, the Intra-Sudetic basin, SW Poland)

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Abstract. In Carboniferous-Permian aquifer in the vicinity of Sokołowsko and Unisław Śląski (Intra-Sudetic Basin, the Sudetes, SW Poland) the effects of gradual chemical evolution have been found. Groundwater chemistry varies from the fresh bicarbonate-calcium-magnesium water at the recharge area to sulphate-calcium-sodium mineral water downwards the basin. The main aqueous chemistry features are controlled by the dedolomitization process and calcium common-ion effects. Dissolution of gypsum and dolomite favours the calcite precipitation and cation exchange. Geochemical model presented in the paper was chosen after the selection of different variants. The effects of conceptual model assumptions on geochemical modelling results are discussed.

Key words: groundwater chemistry, geochemical modelling, sulphates, the Sudetes, Poland

Introduction

Drinking-water exploration works allowed to recognize the aquifer abound in the groundwater resources in Carboniferous and Permian sedimentary rocks south of Wałbrzych (the Intra-Sudetic Basin, the Sudetes). Waters are abstracted only in the northern part of the aquifer. Groundwaters in the southern part do not comply drinking water standards due to increased level of sulphate, hardness, iron, manganese, and trace elements (e.g. boron, arsenic, cadmium, lead).

Inverse mass balance and mixing geochemical modelling have been used to identify the groundwater quality origin and diversity (Dobrzański, 2005). The paper presents preliminary modelling results and is focussed on the discussion of the effect of conceptual model assumptions on obtained models.

Methods

Groundwaters were sampled in wells of the intake in Unisław Śląski (wells Nos. 1, 2, 7, and 8) and in the unused borehole 5p in Sokołowsko after performed research pumping test (Fig. 1). Field measurements included SEC, pH, Eh, and T. Water samples were filtered in the field by cellulose-nitrate membrane 0.45 µm filters and stored in LDPE bottles. Anions were determined by spectrophotometric, HPLC or volumetric methods, and cations and trace elements by ICP-AES or FAAS methods. Computer code PHREEQCI v.2.11 (Parkhurst & Appelo, 1999) was used for geochemical modelling.

Geology and hydrogeology outlines

Studied area is located in the Intra-Sudetic Basin (central part of the Sudetes Mts). The basin is filled by the Lower Carboniferous-Lower Permian terrestrial molasse locally overlaid by the thin cover of terrestrial Lower Triassic sandstones and Upper Cretaceous marine deposits (Dziedzic & Teisseire, 1990). The area of Unisław Śląski-Sokołowsko is built of Upper Carboniferous-Lower Permian sedimentary and volcanic rocks (Fig. 1). Studied groundwaters occur in lithostratigraphic members of Upper Stephanian and Lower Autunian ages (Tab. 1). Sedimentary rocks are deposited in alluvial and lacustrine environments (Bossowski & Ihnatowicz, 1994) and have varied mineral composition (Tab. 1). From the viewpoint of the groundwater chemistry the most important is the presence of reactive phases: gypsum, carbonate minerals (calcite, dolomite and siderite), sulphides (surely mainly pyrite) and dispersed organic matter.

Groundwaters occur mainly in fissured sandstones and mudstones. Total discharge of the intake in Unisław Śląski varied between 123.4 and 154.4 thousands m³/month. Wells Nos. 1, 2, 7, and 8 give about 85 % of the total intake discharge. Intake is located in the upper part of the Ścinawka river catchment. Borehole No. 5p in Sokołowsko was drilled in 1980, and is unused due to poor water quality. Ścinawka river is the main base level of groundwater drainage in the upper part of catchment, and Sokołowiec – tributary of Ścinawka – is the one in the Sokołowsko valley (Fig. 1). Groundwater abstraction affected the natural hydrologic regime and probably

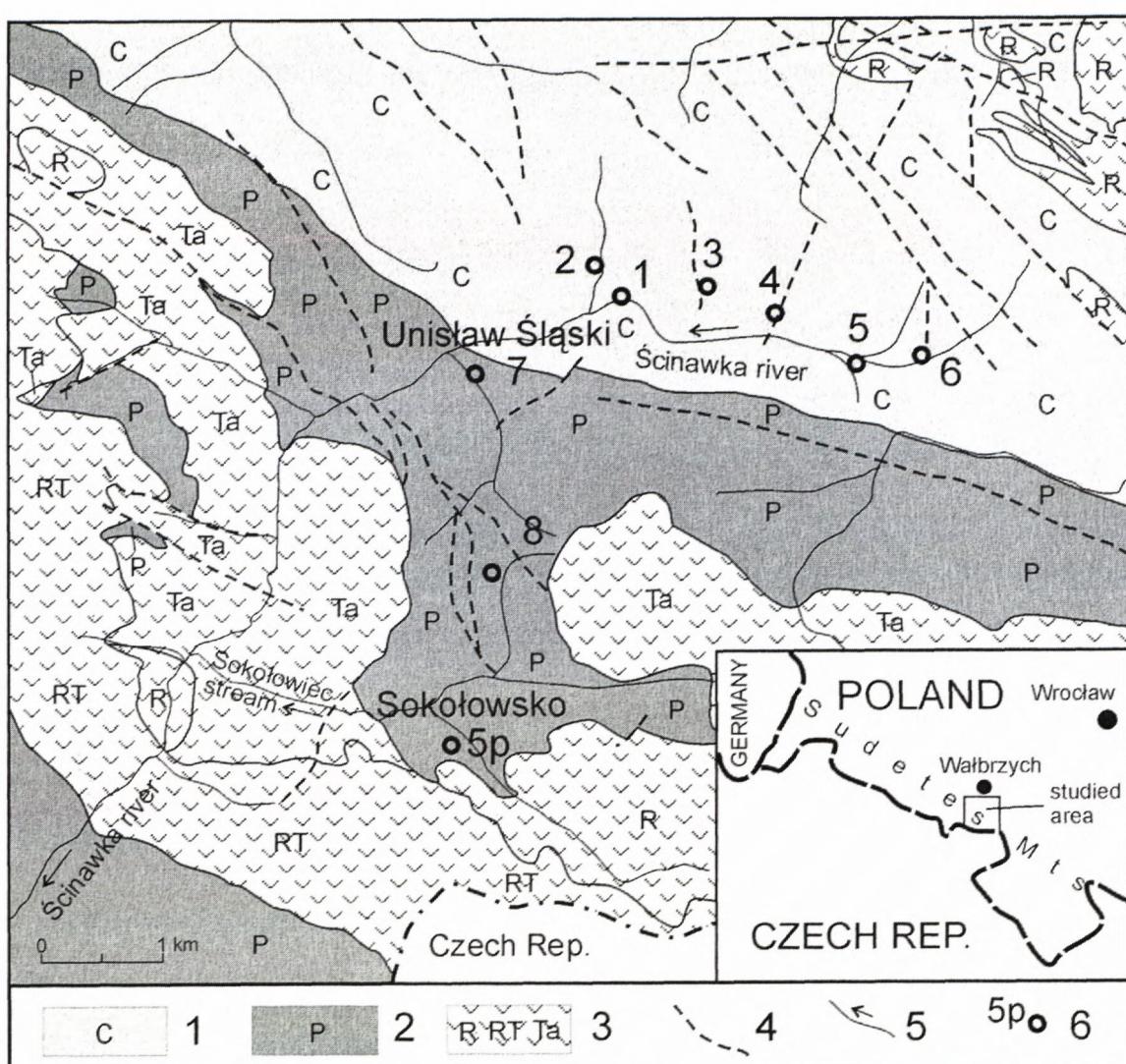


Fig. 1. Geological map of the studied area (after Grocholski, 1971; Bossowski et al., 1994; Awdankiewicz, 1999).
1 – Carboniferous sedimentary rocks, 2 – Permian sedimentary rocks, 3 – volcanic rocks: rhyolites, rhyolite tuffs, and trachyandesites, 4 – faults, 5 – waterways, 6 – wells.

Tab. 1. Mineralogical characteristics of sedimentary rocks in the Unisław Śląski – Sokołowsko area (after Bossowski, ed., 1996, 1997)

Lithostratigraphic units	Lithology	Main features of mineral composition
Zagórzyn Member (Autunian)	Mudstones and claystones with sandstones	Rare fragments of volcanic rocks and feldspars, argillaceous-siliceous and ferrous cement, xenomorphic calcite, dolomite, illite, kaolinite, rare dispersed pyrite and organic matter
Krajanów Member (Autunian)	Sandstones and mudstones with claystones, limestones, calcareous mudstones, bituminous limestones and mudstones at top	Fragments of volcanics and feldspars, chloritized clay schists, gypsum cement and covers, argillaceous-siliceous cement, ferrous pigment, siderite, bituminous mass, illite, calcite veins, dispersed pyrite and organic matter
Ludwikowice Member (Stephanian)	Polymict conglomerate sandstones, rarely mudstones and shales	Numerous fragments of volcanic rocks (rhyolites, trachytes) and feldspars, chloritized biotite, carbonates (mainly calcite), gypsum, sericitized and kaolinitized feldspars, argillaceous-siliceous cement with neogenic calcite, gypsum, and limonite

activated flow of sulphate groundwaters northwards. A first sign of this process was found in the chemistry of groundwater from wells 7 and 1 (Dobrzański & Mitrega, 2002; Wiśniewska, 2003).

Groundwater chemistry

Fresh groundwaters from wells (Nos. 1, 3-6) located in the upper part of Ścinawka catchment (Fig. 1) present similar composition (Wiśniewska, 2003). They are of low total dissolved solids, usually below 400 mg/L. Bicarbonate-calcium-magnesium and bicarbonate-sulphate-calcium-magnesium hydrochemical types prevail there.

The groundwaters from wells situated along the dip of beds (Fig. 1, Tab. 2) – i.e. from well No. 2 followed by Nos. 1, 7, 8 to well 5p – manifest different chemical features. Chemical composition gradually changes from the fresh water in unconfined part of the aquifer at the recharge area (well 2) to mineral sulphate water southwards (well 5p). The concentration of the most solutes (SO_4 , Ca, Mg, Na, Fe, Mn, Sr, B, As, NH_4 , Zn, Li, Mo) increases southwards. Only concentration of chloride, fluoride, nitrate and barium increases (Tab. 3). It causes gradual changes of hydrochemical types. Waters from “meridional” set of wells were the subject of geochemical modelling (Dobrzański, 2005).

Tab. 2. General characteristics of sampled wells

Well	Altitude, m a.s.l.	Well depth, m	Screened intervals (below the surface level, m)
2	582.1	96.5	32.5 - 86.7
1	582.5	88.8	43.5 - 47.5 60.7 - 67.7 75.7 - 77.7 81.0 - 86.0
7	569.8	100.0	60.0 - 85.0
8	620.0	220.0	71.9 - 102.5 160.5 - 197.7
5p	570.0	350.0	49.4 - 60.6 (fresh water) 72.3 - 92.2 (fresh water) 176.15 - 266.6 (sulphate mineral water) 305.6 - 314.3 (sulphate mineral water)

Groundwater chemistry is affected by the solubility products of gypsum (Fig. 2). Deviations from the regular pattern of gypsum dissolution are found both at the lowest and the highest calcium and sulphate concentrations. Bicarbonate and calcium concentration initially increases due to carbonate minerals. However, at the deeper part of the aquifer the inorganic carbon is immobilized (Fig. 3).

Increasing concentration of numerous trace elements (e.g. As, B, Sr, Zn) is interesting feature of the groundwater chemistry. Strontium surely originated by the gypsum/celestite dissolution. Arsenic is probably released from sulphides (pyrite) and also might come from organic matter both deposited in the deep lacustrine reduction environments. Iron and zinc can be related to pyrite and siderite dissolution.

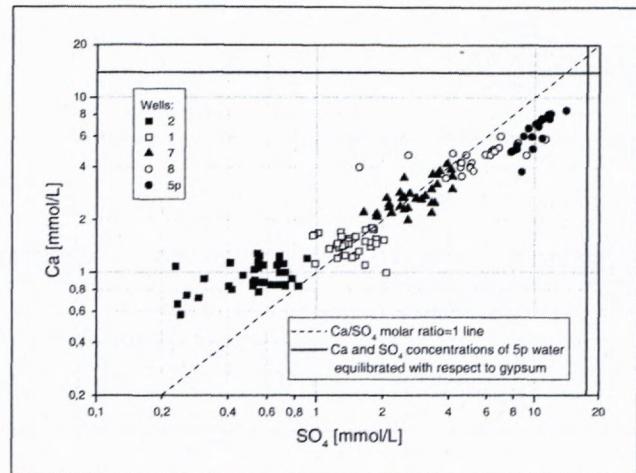


Fig. 2. Calcium vs. sulphate concentration in groundwater (after Dobrzański, 2005).

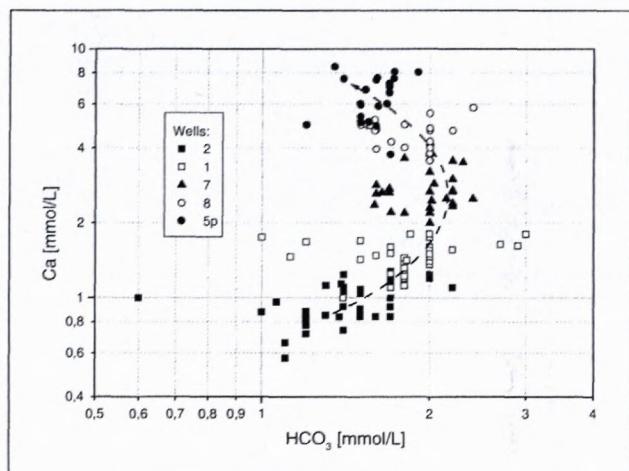


Fig. 3. Calcium vs. bicarbonate concentration in groundwater (after Dobrzański, 2005).

Mass balance modelling results. Effects of conceptual model assumptions

Groundwaters manifest the effects of gradual chemical evolution. However, one should mention that sampled wells (Nos. 2, 1, 7, 8, and 5p) are not situated in the same flow path. Waters from extreme wells (Nos. 2 and 5p) show the scale of present chemical evolution in the aquifer, and were assumed as the “end-member” waters. Inverse modelling was performed between these two wells. The model included gypsum, celestite, dolomite, siderite, rhodochrosite, smithsonite, pyrite, arsenopyrite, calcite, barite, chlorite, kaolinite, $\text{Fe(OH)}_{3(a)}$, CH_2O , gases (CO_2 , O_2 , N_2), and calcium, sodium, and potassium in cation exchange. The role of particular phases has been discussed by Dobrzański (2005). Results of speciation-saturation calculation and aquifer mineralogy data were used in constructing conceptual model(s). The saturation state of sulphate minerals (gypsum, celestite, and barite) approaches the equilibrium as sulphate concentration increases downwards the basin. At the same time

Tab. 3. Chemical composition of groundwater (after Dobrzyński, 2005). Concentrations in mg/L

Parameter	Well No. 2	Well No. 1	Well No. 7	Well No. 8	Well No. 5p ¹
T	11.2	9.3	10.1	15.46	15.3
pH	7.73	7.80	7.47	7.74	7.60
pe	6.373	6.151	5.969	5.556	1.278
SEC ₂₅ ² [μS/cm]	249	460	598	1230	2070
SiO ₂	17.0	18.0	17.3	30.4	19.8
SO ₄	38.8	126	205	625	1113
HCO ₃	84	111	123	95	116
Cl	7.12	9.5	2.4	<0.5	<0.5
F	0.11	0.10	0.10	0.01	0.01
NO ₃	8.11	8.9	4.46	1.94	0.00
Ca	33.5	56.5	98.4	197.7	322.9
Mg	5.8	16.6	9.4	25.9	20.2
Na	6.0	12.6	16.1	54.9	129.5
K	1.1	1.5	1.9	0.3	1.5
Al	<0.01	<0.01	0.02	<0.01	0.001
As	<0.01	<0.01	0.01	0.11	0.14
B ³	0.02	0.05	0.17	0.45	1.41
Ba	0.127	0.044	0.038	0.017	0.011
Fe	<0.01	<0.01	<0.01	0.06	0.66
Li ³	0.005	0.011	0.031	0.035	0.121
Mn	0.001	0.001	0.011	0.086	0.126
Mo ³	0.001	0.001	0.005	0.016	0.022
NH ₄	<0.05	<0.05	<0.05	<0.05	0.13
Sr	0.086	0.291	1.045	8.942	7.836
Zn	0.016	0.018	0.054	0.017	1.052
Hydrochemical type	HCO ₃ -SO ₄ -Ca	SO ₄ -HCO ₃ -Ca-Mg	SO ₄ -HCO ₃ -Ca	SO ₄ -Ca	SO ₄ -Ca-Na

1 – composition of water from the sulphate horizons in well 5p; 2 – specific electric conductivity compensated to 25 °C; 3 – element not included in geochemical models

Tab. 4. Mole transfers in found geochemical models

Phase	Models with minimum number of phases		Model without minimum number of phases
	1	2	
CO ₂ (g)		4.981E-04	
N ₂ (g)	-6.174E-05	-6.174E-05	-6.174E-05
Gypsum	1.077E-02	1.068E-02	1.075E-02
Celestite	8.861E-05	8.861E-05	8.861E-05
Dolomite	5.669E-04	7.168E-04	7.168E-04
Siderite	6.612E-04		5.747E-04
Pyrite		4.408E-05	5.765E-06
Rhodochrosite	2.279E-06	2.279E-06	2.279E-06
Smithsonite	1.588E-05	1.588E-05	1.588E-05
Arsenopyrite	1.805E-06	1.805E-06	1.805E-06
Calcite	-7.183E-04	-7.050E-04	-7.817E-04
Barite	-8.443E-07	-8.443E-07	-8.443E-07
Kaolinite	-6.199E-05	-4.700E-05	-4.700E-05
Chlorite	6.206E-05	4.708E-05	4.707E-05
Fe(OH) _{3(a)}	-6.512E-04	-3.413E-05	-5.705E-04
“Halite”	-1.951E-04	-1.951E-04	-1.951E-04
“Fluorite”	-1.576E-06	-1.576E-06	-1.576E-06
NaX	5.715E-03	5.715E-03	5.715E-03
KX	1.030E-05	1.030E-05	1.030E-05
CaX2	-2.863E-03	-2.863E-03	-2.863E-03
Sum of transfers	1.334E-02	1.391E-02	1.341E-02
Redox mole transfers			
As(3)	9.023E-07	9.023E-07	9.023E-07
Fe(3)	-6.511E-04	-3.407E-05	-5.704E-04
N(-3)	-7.152E-06	-7.152E-06	-7.152E-06
N(0)	-1.235E-04	-1.235E-04	-1.235E-04
O(0)	-3.610E-06	-3.610E-06	-3.610E-06
S(-2)	1.805E-06	8.996E-05	1.334E-05

also calcite and dolomite tends towards equilibrium. Saturation index of the latter minerals does not correlate with bicarbonate and pH (op.cit.).

Calculation by PHREEQCI code gave several mass balance models with minimum number of phases. Two of them were chosen (Tab. 4). The models mainly differ in mole transfer of: (1) gases (CO_2 , O_2) dissolution, (2) organic matter oxidation, (3) calcite precipitation, (4) iron source phase (siderite or pyrite), and (5) iron sink phase ($\text{Fe(OH)}_{3(a)}$). Gypsum and dolomite dissolution transfers differ slightly.

The models were selected as the ones that probably better describe the real system. Both models differ each other in term of iron source phase. Model No. 1 includes siderite, and model No. 2 – pyrite. In the real geochemical system the dissolution of both siderite and pyrite is surely taking place, what is illustrated by the model without minimum number of phases (model No. 3 – Tab. 4). Released iron can be immobilized at iron hydroxides and/or oxyhydroxides, like $\text{Fe(OH)}_{3(a)}$ or goethite. Selected models include decrease of Fe(3) and O(0) forms in redox transfer.

According to modelling results the chemistry of sulphate groundwater in Sokołowsko might be explained by congruent dissolution of gypsum and incongruent dissolution of dolomite with calcite precipitation. Increasing sulphate activity in water favours dolomite dissolution and MgSO_4^0 complex formation. It promotes further gypsum and dolomite dissolution and increase of magnesium concentration. Calcite precipitation is enhanced by the calcium common-ion effect among gypsum, dolomite, and calcite. Calcium also depends upon ion exchange with monovalent cations (Na^+ , K^+).

In the groundwaters at recharge area (well 2) the sulphate concentration is lower than conforms with gypsum solubility (Fig. 2). Gypsum in bedrock of recharge area is leached out already. Sulphates in fresh waters mainly come from biomass biodegradation and from atmospheric deposition, whereas calcium originates from carbonate minerals dissolution. Next, in sulphate mineral waters (wells Nos. 8 and 5p) the calcium concentration is lower than saturation with gypsum probably due to the cation exchange ($\text{Ca}^{2+} \leftrightarrow \text{Na}^+$ and K^+).

The barite precipitation causes the barium decrease, whereas celestite dissolution – strontium increase. Gypsum also can be the source of Sr. Mole transfer ratio of celestite to gypsum suggests that gypsum should contain about 0.8 % of Sr, what corresponds with reasonable level of the element content in gypsum.

Arsenic probably originated by the sulphide minerals dissolution. Iron can be released during both the siderite and pyrite dissolution. Sulphide dissolution promotes decrease of gypsum, siderite and calcite transfers. Pyrite oxidation does not bring the water acidification because groundwaters are efficiently neutralized by the carbonate dissolution.

Redox potential drops towards sulphate waters, from 357 mV (well 2) to 73 mV (well 5p). However, redox potential in sulphate groundwater remains still so high to reduce sulphates to sulphides.

The main features of aquifer mineralogy are known. However, some doubts arise during the modelling process because the absence of detailed data on bedrock mineralogy and chemistry.

Calcium geochemistry in groundwater depends upon gypsum dissolution and common-ion effects of several solid phases (gypsum, dolomite, calcite), and is strictly connected with other main solutes, like magnesium, sulphate and sodium.

Magnesium can originate from dolomite or Mg-calcite dissolution, but there is unknown chemical composition of carbonate minerals in aquifer. The former one was taken into account (Dobrzański, 2005) as magnesium solute source in the presented model. The calcite present in aquifer bedrock can also contain some amounts of magnesium. The application of Mg-calcite of different composition as a source of magnesium instead dolomite, extorts the higher mole transfer of dissolving Mg-calcite in groundwater mass balance than dolomite transfer, as well as increasing transfer of precipitated calcite. The lower content of Mg in incongruently dissolved Mg-calcite, the higher mole transfers (Fig. 4).

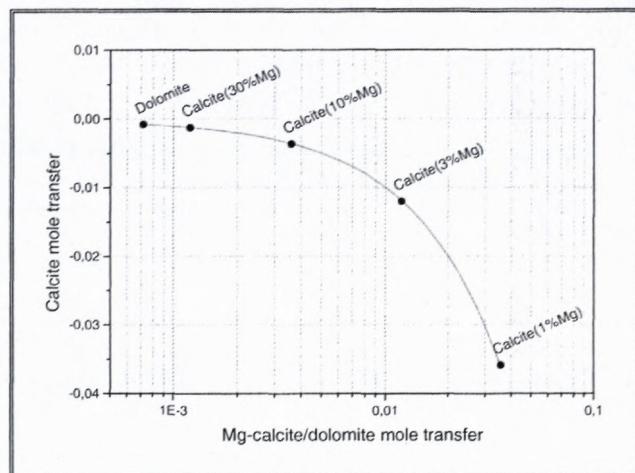


Fig. 4. Effect of magnesium content on Mg-calcite/dolomite and calcite mole transfers.

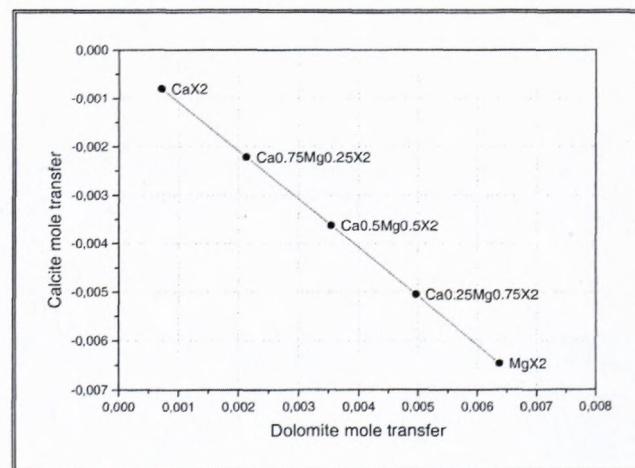


Fig. 5. Effect of magnesium sorption on dolomite and calcite mole transfers.

Magnesium together with calcium can take part in the cation exchange with monovalent cations (Na^+ , K^+). It affects transfer of carbonate minerals. Magnesium sorption causes the increased dolomite dissolution and resulting increased calcite precipitation. The higher magnesium adsorption, the higher transfer of dissolving dolomite (or Mg-calcite) as well as the higher calcite precipitation (Fig. 5).

Increase of pyrite dissolution promotes the decrease of siderite and gypsum transfer – source phases of iron and sulphate. Then, calcite precipitation transfer decreases (Tab. 4). Iron immobilizing in (oxy) hydroxides probably can take place mostly at recharge area where oxygen is available but the amount of organic matter is lower.

Obtained models suggest that the role of organic matter is probably negligible in the chemical evolution of the aquifer. Oxidation of organic matter can locally take place in the aquifer. It is more likely in recharge area where oxygen is more attainable.

Presented preliminary geochemical model fits with the main features of aquifer chemistry. Researches of tritium and stable isotopes (δD , $\delta^{18}\text{O}$, $\delta^{34}\text{S}$, $\delta^{13}\text{C}$) in groundwater are in progress (Dobrzański, 2005). It will allow the verification of the geochemical model. Detailed investigations of reactive minerals chemical composition in the bedrock are also necessary.

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References

- Awdankiewicz, M., 1999: Volcanism in a late Variscan intramontane trough: Carboniferous and Permian volcanic centres of the Intra-Sudetic Basin, SW Poland. *Geologia Sudetica*, vol. 32, 13–47.
- Bossowski, A., Cymerman, Z., Grocholski, A. & Ihnatowicz, A., 1994: Geological map of the Sudetes, 1:25 000, sheet Jedlina Zdrój. Wyd. Geol., Warsaw.
- Bossowski, A. & Ihnatowicz, A., 1994: Paleogeography of the uppermost Carboniferous and lowermost Permian deposits in the Intra-Sudetic Depression. *Geological Quarterly*, vol. 38, 709–726.
- Bossowski, A. (ed.), 1996: Grzedy IG1. *Profiles of deep boreholes*. Polish Geological Institute. No. 83, 57 p. (in Polish)
- Bossowski, A. (ed.), 1997: Unisław Śląski IG1. *Profiles of deep boreholes*. Polish Geological Institute. No. 88, 64 p. (in Polish)
- Dobrzański, D. & Mitrega, J.: 2002. Report on the KBN project 9 T12B 044 18: Origin of sulphate mineral waters in the Sokolowsko area (the Sudetes) on isotopic research and geochemical modelling. *Unpublished*. Institute of Hydrogeology and Engineering Geology, Warsaw University. (in Polish)
- Dobrzański, D., 2005: Chemical diversity of sulphate groundwater at Carboniferous-Permian aquifer in Sokolowsko-Unisław Śląski area (the Sudetes, Poland). Geochemical modelling approach. *Acta Geologica Polonica* (submitted)
- Dziedzic, K. & Teisseyre, A.K., 1990: The Hercynian molasse and younger deposits in the Intra-Sudetic Depression, SW Poland. *N. Jb. Geol. Paläont. Abh.*, vol. 179, no. 2/3, 285–305.
- Grocholski, A., 1971: Geological map of the Sudetes, 1:25 000, sheet Mieroszów. Wyd. Geol., Warsaw.
- Parkhurst, D. L. & Appelo, C. A. J., 1999: User's guide to PHREEQC (version 2): A computer model for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. *U. S. Geological Survey, WRI Report 99-4259*.
- Wiśniewska, M., 2003: Quality of groundwaters abstracted at intake in Unisław Śląski (the Sudetes) against hydrogeological conditions. *Unpublished*. M.Sc. thesis. Institute of Hydrogeology and Engineering Geology, Warsaw University. 184 p. (in Polish)