

Hydrogeochemistry of a deep gas-storage cavern, Czech Republic

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Abstract Groundwater was occasionally found during the construction of a deep gas-storage cavern at approximately 1 km below land surface near Příbram, Czech Republic. The individual groundwater seeps, with a discharge not exceeding 0.01 l/s and $T=23^{\circ}\text{C}$, were usually a strongly alkali natural solution with maximum pH values of 9.9 and TDS concentrations from 0.2 to 0.86 g/l; Na^+ , HCO_3^- , and Cl^- ions were the major dissolved chemical constituents. Two main groundwater quality groups were defined: Na–Cl and Na– HCO_3 . Based on the stable isotope ($^{18}\text{O}/^{16}\text{O}$, D/H), tritium and radiocarbon analyses, some groundwater originated from rainwater infiltrating during the Upper Pleistocene Epoch. Strontium in the groundwater of the crystalline aquifer was isotopically homogenous and equilibrates with strontium in the granite and granodiorite of the gas-storage cavern. Based on the information, the deep groundwater seeps were associated with slow or ‘stagnant’ groundwater circulation, without direct relation to the recent groundwater of faster circulation near the surface, which is periodically recharged by precipitation. The results of the water-quality monitoring of the deep groundwater seeps have been used in estimating the insulating properties of the neighboring rocks near the gas-storage cavern. This information will be important in the safe operation of the gas-storage cavern.

Résumé A l’occasion de la construction d’une cavité profonde de stockage de gaz à proximité de Příbram (République Tchèque), de l’eau souterraine a été trouvée fortuitement, environ 1 km sous la surface. Chaque suintement produisait un débit inférieur à 0.01 l/s, à une température de 23°C au maximum, et les solutions présentaient une alcalinité élevée, avec un pH de 9.9 et des concentrations en solides dissous comprises entre 0.2 et 0.86 g/l. Les constituants dissous majoritaires étaient les

ions Na^+ , HCO_3^- , et Cl^- . Deux groupes basés sur la qualité des eaux furent définis: eaux chlorurées sodiques et eaux bicarbonatées sodiques. D’après les analyses des isotopes stables ($^{18}\text{O}/^{16}\text{O}$, D/H), du tritium et du ^{14}C , certaines eaux souterraines sont issues de l’infiltration d’eau de pluie au cours du Pléistocène supérieur. Le strontium présent dans les eaux des aquifères cristallins montrait une grande homogénéité isotopique, en équilibre avec le strontium présent dans les granites et granodiorites de la cavité de stockage de gaz. D’après ces informations, les suintements ont été associés à des circulations lentes voire ‘stagnantes’, sans relation directe avec les circulations rapides d’eaux souterraines à proximité de la surface, qui sont réalimentées périodiquement par les précipitations. Les résultats du suivi qualitatif de l’eau des suintements profonds ont été utilisés pour estimer les propriétés isolantes des roches voisines de la cavité considérée. Cette information sera importante pour le bon fonctionnement du stockage.

Resumen Se encontró agua subterránea ocasionalmente durante la construcción de una caverna profunda de almacenamiento de gas, a aproximadamente 1 km debajo de la superficie de la tierra, cerca de Příbram, República Checa. Las filtraciones individuales de agua subterránea, con una descarga menor a 0.01 l/s y $T=23^{\circ}\text{C}$, normalmente eran una solución natural fuertemente alcalina, con valores máximos de pH de 9.9 y concentraciones de SDT desde 0.2 a 0.86 g/l; los iones Na^+ , HCO_3^- , y Cl^- eran los mayores constituyentes químicos disueltos. Se definieron dos grupos principales de calidad de agua subterránea: Na–Cl y Na– HCO_3 . Con base en los isótopos estables ($^{18}\text{O}/^{16}\text{O}$, D/H), análisis de tritio y radiocarbon, se estableció que alguna agua subterránea se originó a partir de agua lluvia infiltrada durante la Época del Pleistoceno Superior. El estroncio en el agua subterránea del acuífero cristalino, era isotópicamente homogéneo y se equilibria con el estroncio en el granito y la granodiorita de la caverna para almacenamiento de gas. Con base en la información, las filtraciones de agua subterránea profunda fueron asociadas con circulación lenta de agua subterránea o ‘estancada’, sin una relación directa con el agua subterránea reciente, de circulación más rápida cerca de la superficie, que se recarga periódicamente por la precipitación. Los resultados del monitoreo de la calidad de agua de las filtraciones profundas de agua subterránea,

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han sido usadas para estimar las propiedades aislantes de las rocas vecinas cerca de la caverna de almacenamiento del gas. Esta información será importante en el funcionamiento seguro de la caverna de almacenamiento de gas.

Keywords Gas-storage cavern · Groundwater monitoring · Hydrochemistry · Groundwater age · Stable isotopes

Introduction

The gas-storage cavern (GSC), with a volume of 660,000 m³ used for natural methane accumulation, was built approximately 60 km to the south of Prague, Czech Republic (Fig. 1), in the years 1990–1997 by the firm Plynoprojekt s.c. Stavebni geologie-Geotechnika, a.s. was contracted for the geological and geotechnical survey work during mining, and AQUATEST a.s., as subcontractor for Stavebni geologie-Geotechnika, a.s., investigated hydrogeological conditions in the GSC. The GSC is located approximately 5 km to the southeast of the city

of Pribram, south of the village of Buk, at the depth of 1,000 m (altitude of approximately 409 m above sea level (m asl)). The region is well known for its mining of silver ore in the Middle Ages, and mining of polymetallic and mainly uranium ore in the 1960s, which stopped in 1991. The hoisting shaft No. 16 of the former uranium ore field was used as the entrance at the land surface to the cavern. Access to the GSC entrance leads along the former main haulage road between shaft No. 16 and shaft No. 13 on the 21st floor (approximately 1 km in distance), and round the corner of shaft No. 13 along the new haulage road in a southeastern direction at a length of approximately 1 km. The GSC was built in the Central Czech Pluton. No mining that could negatively affect the insulation of the GSC was done in this area.

Groundwater seeps flowing from bedrock and ceiling dripping seeps were found inside the GSC while it was being constructed (Figs. 2, 3 and 4). The groundwater was sampled and chemical and isotopic analyses were performed. The results of the analyses have been used for solving the relation between the deep crystalline aquifer open to the GSC, and groundwater circulation

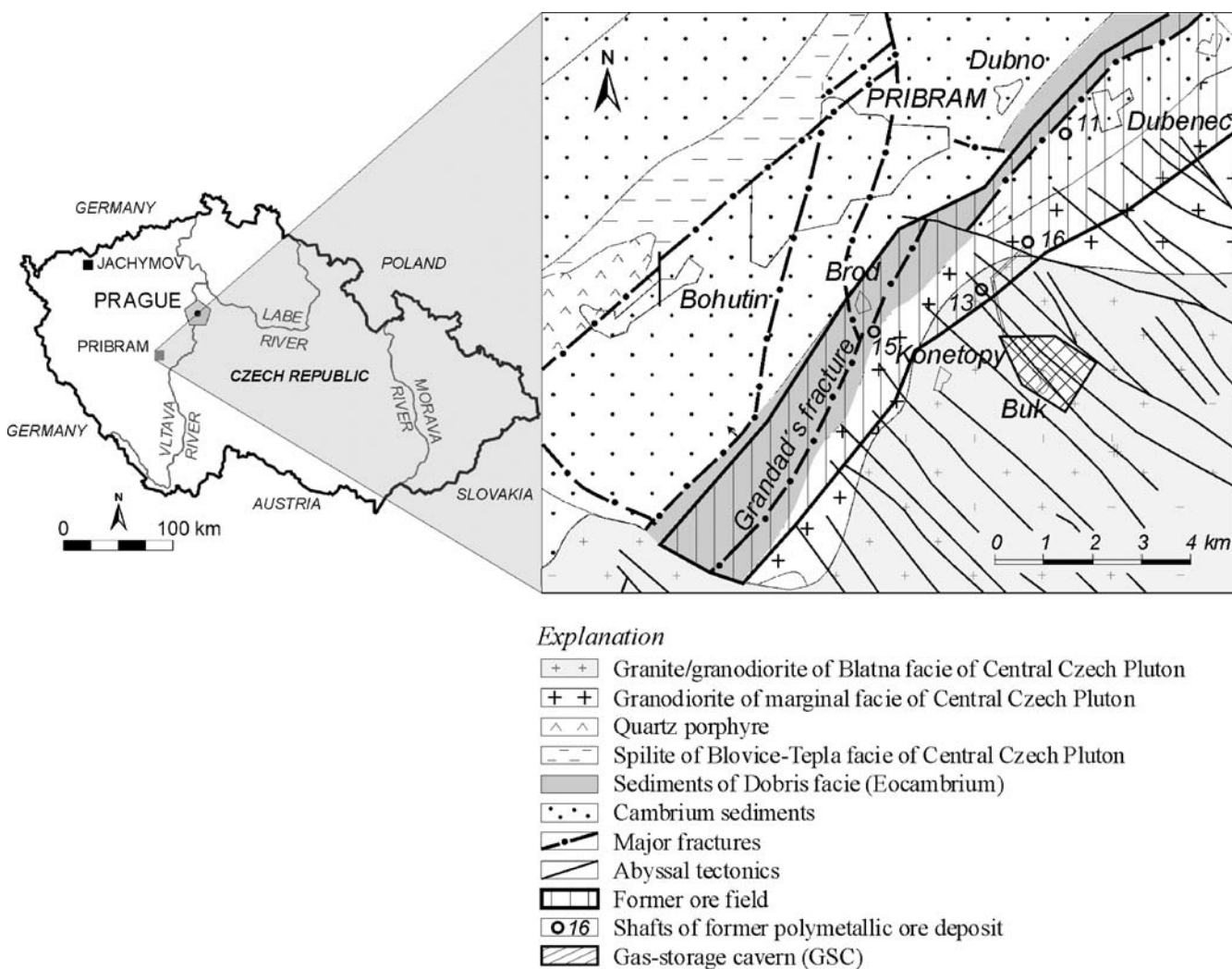


Fig. 1 Location of gas-storage cavern in the Czech Republic and surrounding geology

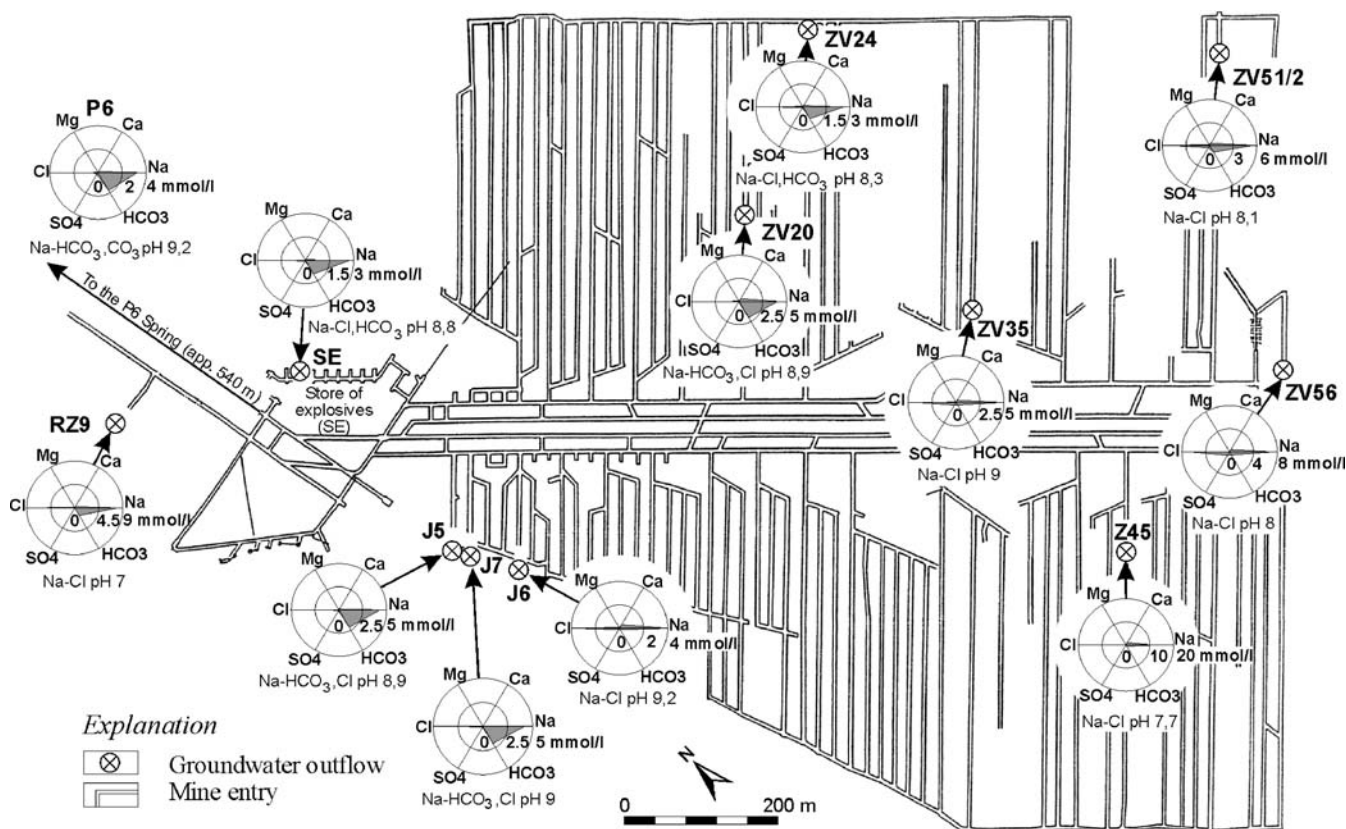


Fig. 2 Gas-storage cavern and sampling point locations (ground plan)

near land surface above the GSC. Evaluation of the groundwater outflows in the GSC with regard to the geohydrodynamic regime was used for classification of the GSC insulation. This evaluation will be useful for the safe operation of the GSC.

Methodology

Groundwater outflows in the GSC and in front of the GSC mouth were found while the GSC was being constructed. These groundwater outflows have been monitored both on a one-time basis and periodically. The mine water was pumped from the former ore field next to the GSC, and the shallow groundwater in the Quaternary aquifer above the GSC was sampled and used as reference samples for the GSC groundwater outflows. Special containers with a dual-protection cap preventing secondary evaporation [D/H (dual inlet/hydrogen) analysis], and two-way glass bottles (²²²Rn analysis) were used along with standard polyethylene bottles for the groundwater sampling. To gather the groundwater volume required for analysis from seeps slowly dripping from the ceiling, the polyethylene bottles were placed under the seep and collected the next day. No special chemical pretreatment of the water samples was performed in situ. The barium carbonate precipitation was prepared in situ using BaCl₂ solution for the ¹⁴C analysis.

Chemical analysis of the groundwater was completed in regards to common dissolved solids and constituents were recorded: Ca²⁺, Mg²⁺, Na⁺, K⁺, Fe, Mn, Li, NH₄⁺, Cl⁻, NO₃⁻, NO₂⁻, alkalinity (HCO₃⁻, CO₃²⁻), SO₄²⁻, F⁻, HPO₄²⁻, SiO₂, acidity (CO₂ free), pH, chemical oxygen demand (COD). Differences between the amount of cations and anions (charge balance) did not exceed the acceptable level of 5% with the exception of the RZ9 sample which had a pink color. Groundwater was located and sampled next to the former ore field, trace elements (Cu, Zn, Cr, Pb, Ni, Ag, As, Se, Cd, V, Al, Be, Co, Mo, Ba, Sr, B, Br, I, Hg) and radiochemical components (²²⁶Ra, ²²²Rn, U_{nat}, gross α-activity) were added to the monitored constituents. These constituents were analyzed in the certified laboratory of AQUATEST a.s., Prague, using operating procedures standardized in CSN EN ISO Nos. 7150-1, 10304, 8467, 6878, 9963-1, 10523, 11885, and CSN Nos. 757611, 757614, 757622, 757624 (the Czech State Standard, the European Standard, the International Organization for Standardization). The pH was measured simultaneously in the laboratory and in situ during monitoring of the groundwater during 1990–1991. A portable Wissenschaftlich-Technische Werkstätten (WTW) pH meter was used for measuring. The irregular difference between in situ and laboratory results was as much as 3%. Additional pH measurements were performed only in the laboratory about 3 h after groundwater sampling.

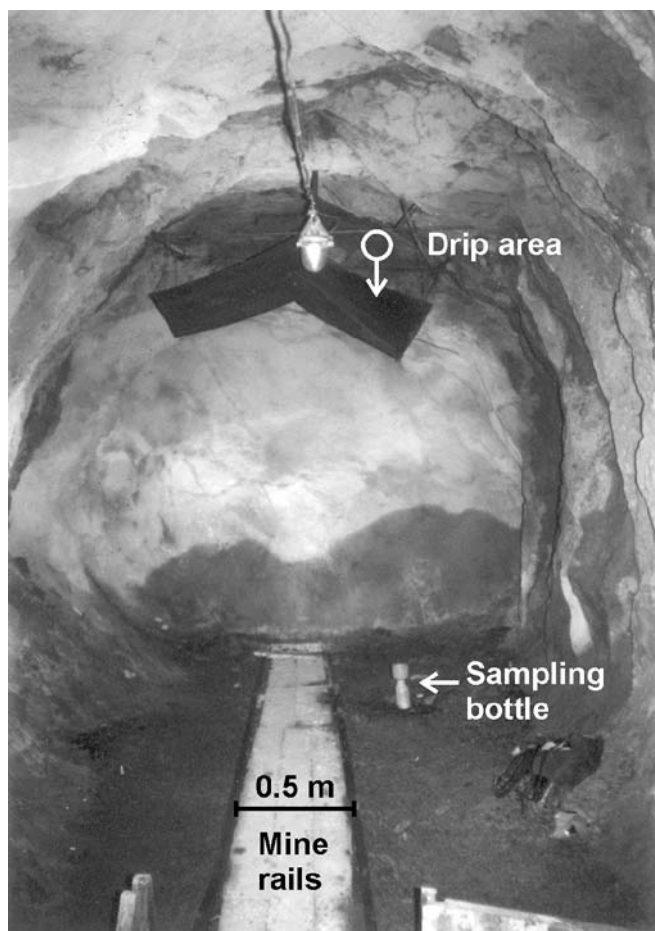


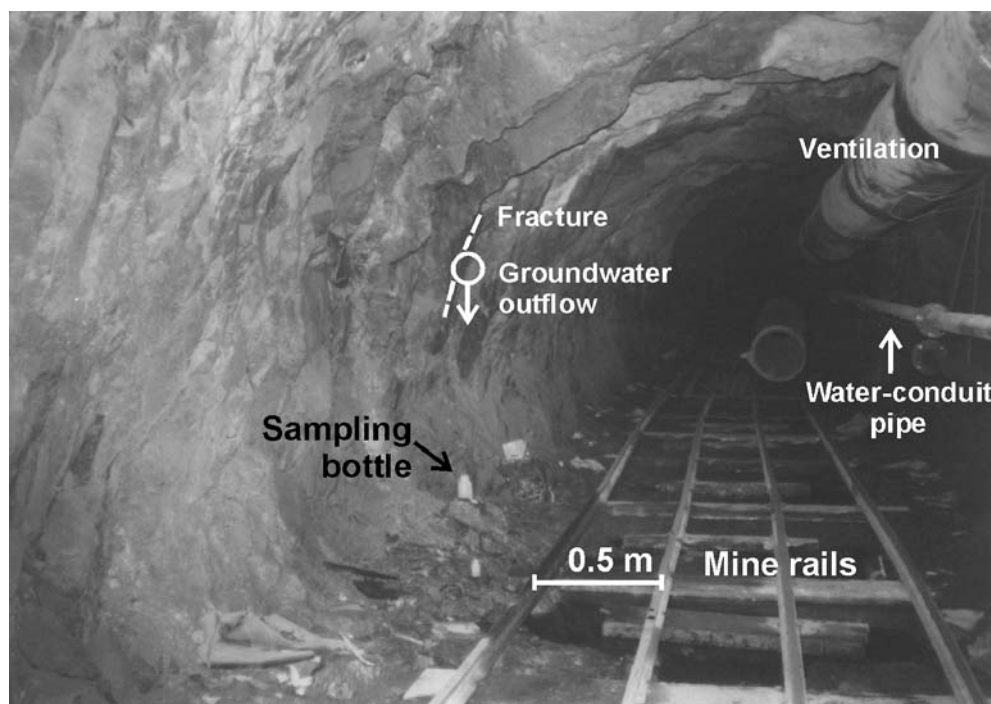
Fig. 3 Sample point in the store of explosives (SE)

Isotopic analysis focused on the following environmental isotopes: $^{18}\text{O}/^{16}\text{O}$, D/H , $^{34}\text{S}/^{32}\text{S}$, $^{13}\text{C}/^{12}\text{C}$, $^{87}\text{Sr}/^{86}\text{Sr}$, ^3H (tritium), and ^{14}C . Analysis of stable isotopes was performed at the Czech Geological Survey of Prague. The tritium activity was analyzed at the Brown Coal Research Institute, Most, and the TG Masaryk Water Research Institute, Prague. The ^{14}C activity was analyzed at Charles University in Prague, Faculty of Science, and at the Laboratory of Hydrology and Isotopic Geochemistry at the University Paris-South (Laboratoire d'Hydrologie et de Géochimie Isotopique, Université de Paris-Sud). Major rock types and mineral fillings of fractures in the GSC also were analyzed isotopically along with groundwater. The isotopic composition of carbon and strontium was investigated in the rocks and minerals.

Possible thermodynamic processes of the chemical composition evolution of the groundwater discharging to the GSC were tested based on saturation indexes (SI). The programs PHREEQC Interactive v.2.8.0.0. (USGS 2003), and AquaChem v.3.7 (Waterloo Hydrogeologic, Inc. 1998–1999) were used for calculating SI values. The saturation state of the groundwater to rock-forming minerals (albite, anorthite, K-feldspar, quartz), potential products of the silicate weathering (chlorite, kaolinite, Ca-montmorillonite, illite), and accessory minerals (fluorite, calcite) were determined.

Relations among monitored groundwater constituents were tested based on the correlation analysis. The correlation coefficient r is computed in this analysis. The closer r is to ± 1 , the stronger is the correlation among constituents. When $r > \pm 0.8$, parameters are strongly correlated. The coefficient correlation was computed at the 95% confidence level.

Fig. 4 ZV35 sampling point



Geology, hydrogeology, and hydrochemistry in vicinity of the gas-storage cavern

GSC was mined at the Central Czech Pluton, built up by a large spectrum of abyssal igneous rocks (Fig. 1). Younger tectonics in the northwestern–southeastern direction, and older tectonics in the northeastern–southwestern direction are present in the Pluton. The same tectonics have also been mapped in the GSC. The mouth of the GSC was approximately 300 m from the contact of the Central Czech Pluton–the Central Czech Algonkian. The Central Czech Algonkian is formed by shale, siltstone, graywacke, conglomerate, arkose, and quartz sandstone. This geological unit, next to the GSC, is petrographically uniform, formed by grey-black shale. Contact between the Central Czech Pluton and the Central Czech Algonkian is in a northeastern–southwestern direction; fault dip is of about 70° to the northwest.

Hydrogeological conditions in the GSC vicinity are naturally affected by fracturing resulting in block building of the geological structures mentioned previously and by past mining activity of the polymetallic ore field. Three types of the natural groundwater circulation were identified at the former ore field formed by sedimentary rocks of the Central Czech Algonkian near to the northwestern edge of the GSC (Kotovym et al. 1954):

1. The pore groundwater of the Quaternary aquifer
2. The shallow fracture water
3. The deep fracture water

The *Quaternary aquifer* in the region under study is formed by alluvial and deluvial deposits approximately 2–20 m thick. The aquifer is recharged by rainwater (annual precipitation of 613 mm based on 30-year monitoring). Groundwater saturates approximately 4 m of the area above the GSC (the Konetopy and Buk Villages). The groundwater level was measured in dug wells in 1994 (well bottoms were between 2 and 11 m) open to alluvial and deluvial deposits because of the potential effect of GSC underground construction on the Quaternary aquifer. The groundwater level fluctuated from 0 to 9.5 m under the surface only for a short period of a few weeks. Results of this monitoring indicated that mining at GSC had no effect on the shallow groundwater supply.

The *shallow fracture water* could be recognized based on physical properties of rocks constituting the aquifer up to a depth of approximately 100 m (Karcev et al. 1972). In the ore field neighboring the GSC, it was previously confirmed that intensively fractured sedimentary rocks (shale, siltstone, graywacke of Proterozoic age) had ‘opened’ fissures up to the depth of approximately 150 m under the surface. Also, the sedimentary rocks communicated locally with the Quaternary aquifer (the highest discharge of groundwater was found on the 3rd floor of the ore deposit at an altitude of approximately 110 m asl, resulting in all the wells open to the Quaternary aquifer being dry in the mining area (Ambra et al. 1967; Petroš et al. 1984). The fissures were closed by clay

minerals below the depth of 150 m below land surface and these fissures became nonconductive. *Granitoid* in the vicinity of the GSC has been weathered, and is potentially conductive up to a depth of 20 m below land surface, and in some places up to 50 m below land surface. Granitoid including vein rocks were nonconductive below the depth of 100 m because of sealing by clay minerals (Petroš et al. 1984).

The *deep fracture water* next to the GSC moved along mineral veins, and tectonics in northwestern–southeastern direction. The groundwater was found in the mine at an altitude between +360 and +430 m asl; thus, groundwater was found at a depth of more than 150 m below the surface. The groundwater in the fissure-mineral vein could be hydraulically connected with the upper aquifer that is above in a zone of fissured rocks near to the surface, and possibly with the Quaternary aquifer (Milovanov et al. 1958; Kotovym et al. 1954).

From a groundwater dynamics basis, two different zones were identified in the area under study (Kotovym et al. 1954):

1. Zone of intensive (active) groundwater movement
2. Zone of slow (stagnant) groundwater movement

Dynamic groundwater sources can be found in a zone of intensive groundwater movement because of periodically recharging by the rainwater and steady groundwater flow. Based on an observation from the Příbram ore field next to the GSC, the zone was at altitudes between 360 and 430 m asl (for example, to the depth of approximately 150 m under land surface). The pore water of the Quaternary aquifer, the shallow fracture groundwater of fissured rocks near to the surface, and the upper parts of the deep fracture groundwater are part of the overall groundwater system in the zone. Groundwater flow in this zone is generally assumed to be towards the Vltava River in a southeastern direction. Typical markers of Quaternary groundwater in a zone of intensive groundwater circulation include: an average groundwater temperature near the yearly average air temperature; groundwater chemical composition defined by mild acid-neutral reaction; alkaline earth ions ($\text{Ca}^{2+} + \text{Mg}^{2+}$) content exceeding the alkali metals ($\text{Na}^+ + \text{K}^+$); and bicarbonate, and, alternatively, sulfate being the dominant anion. The concentration of uranium ($^{235}\text{U} + ^{238}\text{U}$) was about 0.04 mg/l and the radium (^{226}Ra) concentration was approximately 0.03 Becquerel per liter (Bq/l; Škvor et al. 1992).

Stagnant groundwater is contained in the zone of slow groundwater movement. The upper boundary of the zone of slow groundwater movement is delineated in the area under study by the maximum depth of rock weathering observed in the former Příbram ore field (approximately 150 m in the proterozoic sediments, and approximately 50 m in the granitoid). Thus, a different groundwater regime is expected at a depth of 150 m below land surface. Based on experience from past mining activity, the groundwater outflow at depth below 150 m was limited to tectonic features and mineral veins, and their

individual yield was approximately 0.1 l/s and less. The humid spots, and dripping groundwater from the ceiling of openings was observed at depths more than 150 m below land surface. Higher groundwater temperature resulting from the thermal activity of rocks, and the groundwater chemical composition defined by the neutral-alkaline reaction were typical indicators of a zone of slow groundwater circulation. Also typical of slow circulation were sodium concentration exceeding alkaline earth ions ($\text{Ca}^{2+} + \text{Mg}^{2+}$) content and bicarbonate, and, alternatively, chloride being the dominant anion.

Locally, the total dissolved solids (TDS) content of the slowly moving groundwater at the former Příbram ore field near the GSC was as high as 1.7 g/l, and the Na^+ and HCO_3^- ions were dominant. The ^{226}Ra activity reached 0.5 Bq/l, and the uranium concentration was 1.5 mg/l (Škvor et al. 1992). Ion exchange and hydrothermal alteration of crushed minerals resulting in Cl^- being released into the groundwater could be important in the groundwater chemical composition evolution; chloride concentration of 717 mg/l (HCO_3^- 457 mg/l, Ca^{2+} 236 mg/l, traces of CH_4) were found in the groundwater outflows in mineral veins that are intensively fractured (Petroš et al. 1984).

Geology and hydrogeology of the gas-storage cavern

Rocks and minerals of the crystalline aquifer

Granite and granodiorite of the Central Czech Pluton are predominant rock types in the GSC area. The rocks have been affected in the GSC area by younger tectonic events in the northwestern–southeastern direction, and older tectonics in the northeastern–southwestern direction. The water-pressure test performed near the entry to the GSC at sub-horizontal and vertical boreholes, using the water pressure of approximately 12.5 MPa (the gas pressure in the GSC during future processing), indicated that the rock matrix is almost impermeable. Hydraulic conductivity at most tested locations ranged from 1×10^{-10} to 4.3×10^{-12} m/s (mean hydraulic conductivity of 3.4×10^{-11} m/s); however, higher hydraulic conductivity of strongly fractured and weathered rocks was measured (J5, J6, and J7 sub-horizontal boreholes, see Fig. 2). The highest hydraulic conductivity of 9.5×10^{-9} m/s was found in the J7 borehole.

Based on microscopic investigation the GSC granitoid-forming minerals are quartz, K-feldspar, plagioclase (oligoclase-andesine), biotite, and amphibole. Chemical weathering was observed locally in altered zones of granite (the J5 borehole): plagioclase → unidentified clay mineral, biotite → chlorite + Fe-mineral, amphibole → carbonate + chlorite. Ore minerals (Fe-sulfide), chlorite, apatite, and zircon have formed accessory minerals. According to a field study performed by the author, clay minerals, quartz, and calcite have been observed as predominant vein fillings at the GSC. Calcite crystals as high as about 20 cm were observed in the wide fracture

developed at the RZ9 lateral opening. Pyrite and chalcopyrite, approximately 2 mm high, often was observed growing on calcite crystals.

Groundwater

The groundwater in the GSC area was observed and monitored as permanent ceiling outflows (or dripping sources), and short-term outflows (naturally drying up soon after they have been developed). There have only been 12 instances of leaks observed in the GSC area during the course of this study. The groundwater outflows have been correlated with the main tectonic features. Total groundwater discharge has not exceeded 0.02 l/s. Groundwater temperature (permanent outflows) was about 23°C, and was slightly lower than normal temperatures because of the intensive ventilation of the working area.

Results of the hydrochemical monitoring

Groundwater in the Quaternary aquifer

The shallow groundwater is an important reference source with regard to solving potential communication of the deeply discharging groundwater in the GSC to land surface. The shallow groundwater was monitored just above the GSC, and next to the area potentially connected with the underground mine. A public well located at the Buk Village (well bottom at a depth of 5 m under land surface), and the spring near to the Konetopy Village was sampled (Fig. 1). Both samples of the shallow groundwater had a common chemical composition reflecting the shallow aquifer groundwater in a regional context (Včislavá et al. 1987; Table 1).

A mildly acid reaction of the water (pH 6.7–6.9), a medium TDS concentration (0.35–0.57 g/l), and major cation of Ca^{2+} and anion of HCO_3^- , and SO_4^{2-} are typical markers of the shallow groundwater in the area above the GSC. Principal ions of the shallow groundwater have been arranged in succession as follows (constituents in mmol/l):

- Public well in Buk Village:
TDS (11.05), pH (6.8)
 Ca^{2+} (2.4), K^+ (0.8), Na^+ (0.7), Mg^{2+} (0.5), HCO_3^- (4.2), SO_4^{2-} (1), Cl^- (0.6), NO_3^- (0.45)
- Spring next to Konetopy Village:
TDS (7.4), pH (6.9)
 Ca^{2+} (1.3), Na^+ (1.1), Mg^{2+} (0.4), K^+ (0.2), HCO_3^- (1.4), Cl^- (1.2), SO_4^{2-} (0.8), NO_3^- (0.5)

The K^+ concentration of 0.8 mmol/l and nitrate concentration of 0.45–0.54 mmol/l found in groundwater in the Quaternary aquifer indicated human impact on the groundwater chemical composition in and near the monitoring locations. Common, natural chemical reactions in the groundwater-soil gas-rock system usually are included in the processes of chemical composition evolution of the shallow groundwater: dissolving of

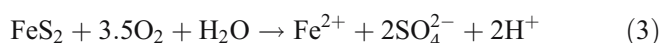
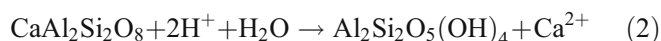
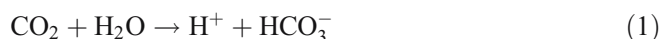
Table 1 Water samples used as reference to the GSC groundwater

Water	Mine water pumped from shafts (static level)		Mine water (drainage)			Groundwater		
	No. 15	No. 16	Floor No. 21, Shaft No. 16			Konetopy	Buk	Southern Czech ^a
Date	11/3/94	22/6/93	24/3/93	7/4/94	24/8/94	16/7/93	27/8/95	1987
pH	7.27	7.8	7.79	8.24	7.53	6.88	6.7	6.27
Na ⁺	389	270	210.3	325	314	25	15.4	13.3
K ⁺	13.9	7.4	6.6	8.9	8.9	6.4	33	4.7
Li	0.04	0.02	0.03	0.04	0.03	0.01	<0.01	<0.01
Ca ²⁺	402	173.8	258.5	374.8	364.7	52.1	94.6	41.6
Mg ²⁺	79	27.4	51.1	68.1	70.5	10.3	13.1	10.5
Fe	15.7	0.54	0.26	0.19	0.21	0.28	1.02	0.16
Mn	5.3	0.03	0.01	0.02	0.02	0.04	0.06	0.03
Al	—	—	—	—	—	0.02	0.02	—
NH ₄ ⁺	0.42	0.2	0.44	<0.01	<0.01	0.27	0.13	0.01
Cl ⁻	74	62	191.5	297.8	297	42.9	21.4	32.7
NO ₂ ⁻	0.02	<0.01	0.04	0.05	2.02	<0.01	0.13	0.01
NO ₃ ⁻	0.02	1.99	14.8	62	46.15	33.5	28.1	36.8
HCO ₃ ⁻	469.85	177	152.6	143.4	152.55	85.4	255.7	67.4
SO ₄ ²⁻	1721	878	878	1240	1275	78.3	97.6	48.5
HPO ₄ ²⁻	0.02	0.13	0.11	0.15	0.13	<0.01	0.38	0.02
F ⁻	0.51	0.29	0.27	0.23	0.09	0.22	0.12	0.07
SiO ₂	8.6	5.35	8.21	6.6	6.6	12.9	11.1	16.7
COD	4.72	3.4	2.16	1.56	7.84	2.8	3.7	2.7
TDS	3.2	1.6	1.8	2.5	2.5	0.35	0.57	0.28

^a12 springs (average of year 1987)

Constituents and COD in mg/l, TDS in g/l; — no data

carbon dioxide of biogenic origin (Eq. 1), hydrolysis of weathered silicates, predominantly anorthite portion of plagioclase (Eq. 2), and oxidation of ubiquitous pyrite (Eq. 3).



The chemical composition of the shallow groundwater evolved in an “open hydrogeological structure” that is periodically recharged by rainwater and has fast groundwater circulation. In accordance with the spatial hydrochemical zoning of the Czech Massif, groundwater of the Ca–C, and Ca–S type originates in the open hydrogeological structure. Dominant chemical groundwater components could be indicated as “exogenous-hydrolytic” (Ca–C) and “exogenous-oxidizing (Ca–S).

The shallow groundwater mineralized at the CO₂ partial pressure (P_{CO2} of 1×10^{−3}–5×10^{−3} MPa. These values were similar to the p_{CO2} of the soil atmosphere environment of Central Europe resulting from the organic material degradation and evapotranspiration in the soil zone of given climatic conditions (Appelo and Postma 1994).

Groundwater of the deep crystalline aquifer

The chemical, radiochemical, and isotopic composition of the groundwater outflows (12 sampling points) sampled over the GSC area were used to define the groundwater of the deep crystalline aquifer (Table 2). Permanent long-term (years) outflows (the P6 spring, the spring inside the explosives store, the ZV35 lateral opening spring, and the water flowing from sub-horizontal boreholes), and the groundwater outflows (slowly dripping sources), which dried out after approximately 5–10 days have been studied during GSC construction.

Chemical composition of the continual underground springs (P6, ZV35 and the spring inside the explosives store) was semi-stable during monitoring; the TDS value changed between 0.20 and 0.42 g/l (P6), and between 0.26 and 0.39 g/l (ZV35). The concentrations of all constituents see Tables 3 and 4. Based on this stability, and assuming that these springs have drained the largest groundwater volume compared to the other hydrogeologic features, such groundwater outflows are taken as representative of the crystalline aquifer.

Major cations and anions

Distinct differences were found between the deeply discharged groundwater compared to groundwater in the Quaternary aquifer and the mine water of the adjacent ore field based on the results of analysis of groundwater constituents. Sodium, either HCO₃[−] (+CO₃^{2−} if the pH values >>8.3), or Cl[−], were found as predominant ions in the groundwater contained in granite and granodiorite of the GSC area. Based on the concentrations of predominant ions, two general hydrochemical types of GSC ground-

Table 2 Results of the chemical and radiochemical analysis of groundwater at sampling locations in the GSC

Sample	P6	SE	J5	J7	J6	ZV20	ZV24	ZV35	Z45	ZV51/ 2	ZV56	RZ9
Count	1–20	1–4	2	2	2	1	1	1–12	1	1–6	1	1
Date	1990– 1996	1996	1992– 1994	1993– 1994	1993	10/5/ 94	3/5/96	94–96	14/9/ 94	94–96	6/11/ 95	31/8/ 95
Seep	LTO	LTO	B	B	B	DS	DS	LTO	DS	DS	DS	STO
pH	9.1	8.8	8.9	9	9.15	8.9	8.3	9	7.7	8.1	8	7
Na ⁺	77	63	99	96	90	93	60	109	261	125	166	187
K ⁺	0.5	0.25	0.5	10.8	0.89	0.62	0.5	0.5	3.1	0.75	5.1	1.2
Li	0.01	<0.01	0.015	0.015	0.01	0.01	0.01	0.01	0.01	0.014	0.01	0.02
Ca ²⁺	3.9	1.5	4	2.8	13.7	13	4	11	44.7	14	20	10.8
Mg ²⁺	0.6	0.27	0.61	0.425	1.75	0.61	1.22	1.1	4.4	2.5	1.8	2.43
Fe	0.11	0.4	0.095	0.155	0.065	0.32	0.06	0.07	6.1	0.9	0.32	1.17
Mn	0.01	<0.01	0.015	0.15	0.005	0.13	<0.01	0.01	0.99	0.65	0.17	0.06
NH ₄ ⁺	0.08	0.05	0.115	0.125	0.73	3.94	1.84	0.14	1.7	0.6	1.16	0.09
Cl ⁻	15	57	62.9	58.5	118.8	58.5	59.7	145	487.2	159	231	298
NO ₂ ⁻	0.002	<0.01	<0.01	<0.01	0.01	1.07	0.99	0.007	0.02	0.12	0.44	<0.01
NO ₃ ⁻	0.4	0.31	0.705	0.62	0.66	0.81	0.7	0.33	2.22	0.78	2.2	0.52
HCO ₃ ⁻	110	61.5	132.9	123.6	9.15	122	54.3	22	39.7	62	39.7	103.7
CO ₃ ²⁻	28	7.5	9	21	24	3	12	7.5	–	–	–	–
SO ₄ ²⁻	18	2.9	8.75	7.98	14.2	54.3	6	31	4.2	31.2	69.7	2.8
HPO ₄ ²⁻	0.06	0.02	0.065	0.055	0.015	0.41	0.03	0.1	0.16	0.1	0.02	<0.01
F ⁻	2.5	1.8	2	2	4.025	1.3	1.55	1.3	0.95	1.8	2.5	3.48
SiO ₂	9.4	12	9.2	9.5	12	6.9	10.4	9.7	5.6	10	1.8	7.6
COD	0.7	0.7	0.68	0.46	0.98	1.04	1.56	0.6	2.9	1.1	1.8	2.12
TDS	0.26	0.21	0.33	0.33	0.29	0.36	0.21	0.34	0.86	0.41	0.55	0.62
Cu	0.04	<0.01	–	–	–	–	–	<0.01	–	<0.01	<0.01	<0.01
Zn	<0.01	0.014	–	–	–	–	–	<0.01	–	0.014	<0.01	0.02
Pb	<0.01	<0.01	–	–	–	–	–	<0.01	–	<0.01	<0.01	<0.01
Ni	0.02	<0.01	–	–	–	–	–	<0.01	–	<0.01	<0.01	<0.01
As	0.023	<0.01	–	–	–	–	–	0.017	–	<0.01	0.098	0.065
V	<0.01	<0.01	–	–	–	–	–	0.026	–	<0.01	0.02	<0.01
Al	0.005	0.006	–	–	–	–	<0.001	0.0163	–	<0.01	0.01	0.003
Mo	0.006	<0.01	–	–	–	–	–	0.011	–	0.006	<0.01	0.006
Ba	<0.01	0.023	–	–	–	–	–	0.011	–	0.048	0.081	0.38
Sr	0.07	0.033	–	–	–	–	0.07	0.15	–	0.19	0.15	0.13
B	–	0.1	–	–	–	–	0.082	–	–	<0.5	0.72	0.45
Br ⁻	1.09	0.6	–	–	–	–	0.37	0.91	–	4.25	2.42	2.87
I ⁻	0.23	0.045	–	–	–	–	0.014	0.22	–	0.73	0.04	0.088
²²² Rn	660	–	–	–	–	–	–	50	–	5.85	–	–
²²⁶ Ra	0.05	<0.01	–	–	–	–	–	0.05	–	<0.01	<0.01	0.41
U _{nat}	0.0001	0.0005	–	–	–	–	–	0.02	–	0.005	0.0015	0.045

DS dripping source; LTO long-term outflows; STO short-term outflows; B sub-horizontal borehole; SE store of explosives; – no data

²²⁶Ra, ²²²Rn in Bq/l, TDS in g/l, other constituents in mg/l

water have been recognized: Na⁺, HCO₃⁻+CO₃²⁻ (the Na–C type, the J5, J7, ZV20, P6 sampling points), and Na⁺, Cl⁻ (the Na–Cl type, the J6, RZ9, explosives store, Z45, ZV24, ZV35, ZV51/2, ZV56 sampling points).

The concentration of major ions mentioned above produces a substantial portion of the TDS value that varied between 0.2 and 0.86 g/l. The TDS values of the Na–C group changed between 0.26 and 0.36 g/l and the TDS values of the Na–Cl group varied between 0.21 and 0.86 g/l. A strong positive statistical correlation among the concentrations of TDS, chloride, and sodium was developed in both groups ($r > +0.8$).

Relatively high pH values are typical for both groundwater groups. The pH values of the Na–C group ranged in a relatively narrow interval between 8.9 and 9.2. The pH values of the Na–Cl group fluctuated in a larger range between 6.99 and 9.15. The lowest pH values, between 6.99 and 7.7, were correlated with the high iron

concentrations in the samples (1.2, 6.1 mg/l, respectively). The actual pH value of these samples is expected to be higher (the measured pH value could be modified because of the Fe(OH)₃ precipitating in the time between groundwater sampling and laboratory analysis-Hem 1970).

A strong positive correlation was observed between chloride and sodium ions (“the Na–Cl component”) in all groundwater samples in the Na–C and Na–Cl groups ($r = +0.97$). This relation indicates the presence of the two end members. The P6 spring of the lowest concentration of the Na–Cl component and the Z45 outflow (dripping source) of the highest concentration of the Na–Cl component can be taken for end members. The other samples are assumed to be intermediate that probably originated by the mixing of these two members (see the tri-linear diagram in Fig. 5). The Na–Cl component concentration increases systematically approximately in the northwestern–southeastern direction.

Table 3 Chemical composition of the P6 spring groundwater over time

Date	pH	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Fe	Cl ⁻	F ⁻	HCO ₃ ⁻	CO ₃ ²⁻	SO ₄ ²⁻	SiO ₂	TDS
4/12/90	8.9	128.6	1.1	3	0.4	0.21	73	6.5	181	7	3.4	16	0.42
8/11/90	8.9	84	0.8	2	0.7	0.29	17.7	4.3	151	12	14.4	9	0.30
5/4/91	9.4	81	0.4	2	0.6	0.09	13.8	4	107	27	19	12	0.27
9/8/91	9.7	71	0.4	15.2	0.2	0.06	17.7	2.7	106	35	17	9	0.28
7/10/91	8.8	76	0.4	5.2	1.3	0.03	16	2.7	119	24	16	7.8	0.27
14/4/93	9.5	71	0.85	3	1.22	0.24	13.1	2.2	97.6	30	19.2	13.6	0.25
21/7/93	9.2	79.4	1.05	2.61	0.24	0.11	9.22	2.5	123.9	24	21.6	8.5	0.27
8/11/93	9.1	82	0.41	3	0.36	0.06	14.2	2.6	97.6	36	19.2	8.7	0.27
4/2/94	9.6	79.1	0.98	5	0.61	0.08	12.4	2.3	115.9	30	18.7	8.5	0.27
9/5/94	9.1	79.6	0.2	3	0.4	0.02	14.2	1.4	94.6	36	19.2	8.4	0.26
24/8/94	9.2	65.6	0.2	2	<0.1	0.2	8.3	2.1	58	39	15.9	8.9	0.2
31/3/95	7.1	83.3	0.3	5.6	0.24	0.03	12.1	0.68	181.2	<2	17.8	8.05	0.31
13/6/95	9.3	62	0.4	3.61	1.46	0.09	9.29	2.32	38.4	54	16.2	8.2	0.20
17/10/95	9.1	70.1	0.42	6	3	0.34	7.45	4	91.5	36	28.8	12.8	0.26
23/11/95	9.3	65.5	0.32	4	0.6	0.06	11.5	2.88	95.2	24	20.3	7.1	0.23
7/2/96	9.3	71	0.44	3	0.36	0.05	9.4	1.15	91.5	36	18	9.5	0.24
7/3/96	9.3	72.7	0.45	1	<0.1	0.09	9.72	2.5	130.6	18	21.8	8.2	0.27
23/4/96	9.3	70.9	0.33	4.61	0.49	0.07	8.44	0.96	104.3	30	20.6	7.9	0.25
24/5/96	9.4	70.4	0.33	3.81	0.73	<0.01	17.2	1.1	79.3	40.2	18	8.3	0.24
2/8/96	9.0	76	0.7	1	0.24	0.15	7	1.85	129.4	24	17.5	7.9	0.27

Constituents in mg/l, TDS in g/l

Ion successions of the end members and intermediate members represented by long-term groundwater outflows in the GSC area are as follows (values are in mmol/l):

– P6 (end member, 20 average samples):

1. TDS (6.5), pH (9.2)
2. Na⁺ (3.3), Ca²⁺ (0.1), Mg²⁺ (0.02), K⁺ (0.01), HCO₃⁻ (1.8), Cl⁻ (0.6), SO₄²⁻ (0.2)

– *Store of explosives* (intermediate member, 4 samples, on average):

1. TDS (5.8), pH (8.8)
2. Na⁺ (2.7), Ca²⁺ (0.04), Mg²⁺ (0.01), K⁺ (0.006), Cl⁻ (1.6), HCO₃⁻ (1.0), SO₄²⁻ (0.03)

– ZV35 (intermediate member, 12 samples, on average):

1. TDS (10.15), pH (9)

2. Na⁺ (4.8), Ca²⁺ (0.28), Mg²⁺ (0.04), K⁺ (0.01), Cl⁻ (4.1), HCO₃⁻ (0.3), SO₄²⁻ (0.3)

– Z45 (end member, 1 sample):

1. TDS (27.25), pH (7.7)
2. Na⁺ (11.35), Ca²⁺ (1.1), Mg²⁺ (0.18), K⁺ (0.08), Cl⁻ (13.7), HCO₃⁻ (0.65), SO₄²⁻ (0.04)

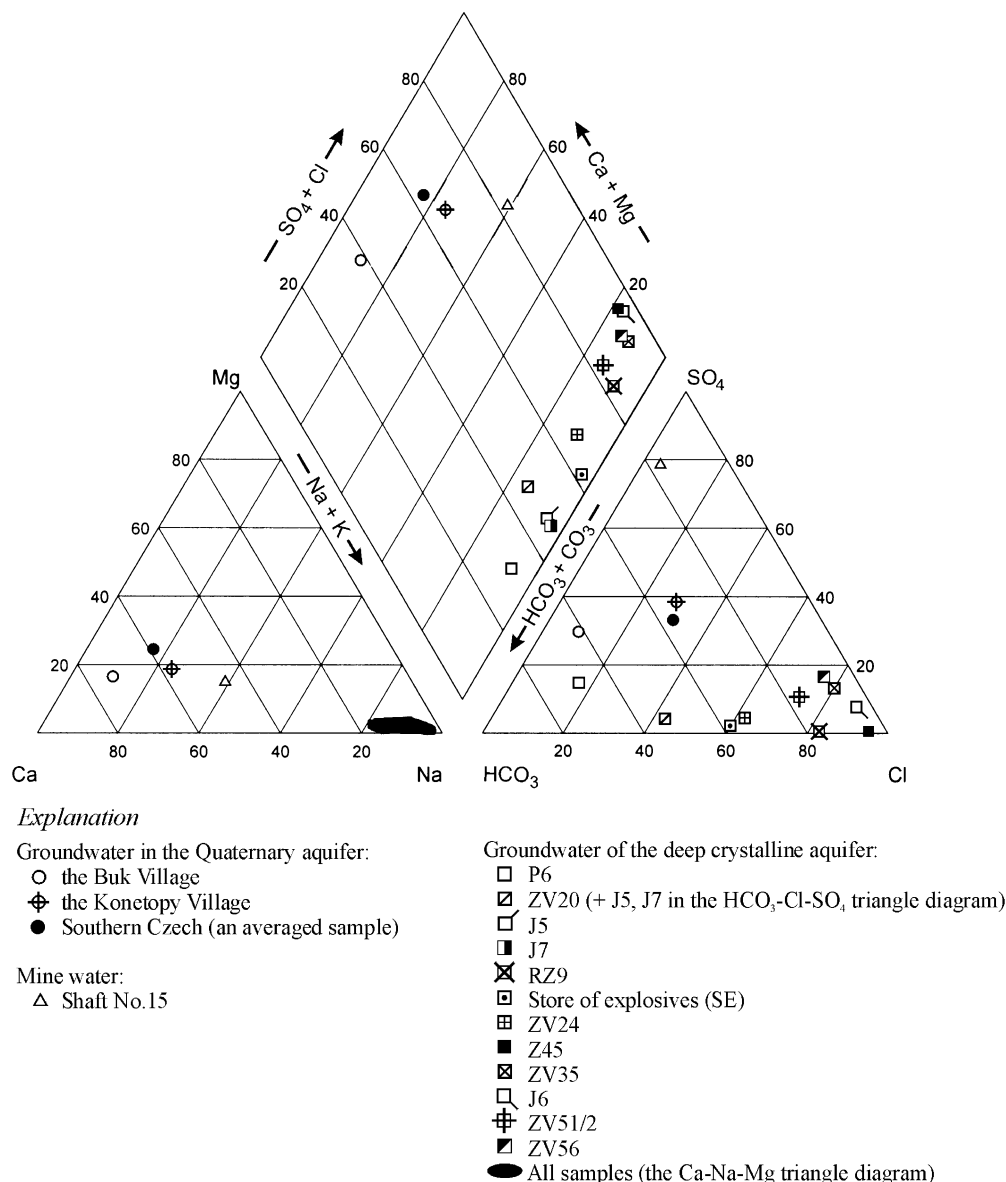
Comparison of all groundwater samples collected in the GSC based on the constituent concentration in mg/l is shown in Table 2. The groundwater of interest is contained in an almost impermeable crystalline aquifer with a mean hydraulic conductivity of 3.4×10^{-11} m/s. Based on this result, the groundwater in the aquifer can be considered as a “closed hydrogeological structure”. The Na–C component of the groundwater can be indicated as being “endogenous-hydrolytic” and the Na–Cl component of the groundwater as being “halide”. The predominant groundwater component, Na–C, could be explained by hydrolysis of the Na-feldspar Eq. (4), and by dissolving of

Table 4 Chemical composition of the ZV35 spring groundwater over time

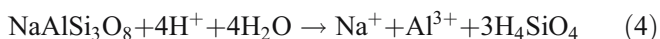
Date	pH	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Fe	Cl ⁻	F ⁻	HCO ₃ ⁻	CO ₃ ²⁻	SO ₄ ²⁻	SiO ₂	TDS
23/2/94	9.7	92	0.27	6	0.61	0.12	127	1.75	5.5	16.2	4.8	7.9	0.26
11/3/94	9.7	110	0.4	9	0.61	0.1	142	1.46	2	12	36	11.4	0.33
28/3/94	9.9	95	0.51	8.82	2.9	0.05	155	2.05	2	3	17.3	12	0.3
4/5/94	9.9	111.7	0.35	9	1.2	0.15	151	2.45	2	6	31.2	11	0.33
17/10/94	9.7	108	0.6	10.4	0.97	0.18	137	1.95	12.2	12	38	2.4	0.32
31/3/95	6.4	125	0.6	15	<0.1	0.02	163	0.45	41.5	<2	34.3	9.98	0.39
4/10/95	7.0	106	0.6	9.62	2.2	<0.01	158	0.75	32.3	<2	27.6	10.6	0.35
12/12/95	9.6	114	0.5	20	0.73	0.03	156	1.05	42.7	6	25	11.1	0.38
19/3/96	9.5	126	0.6	10	0.36	0.1	129	0.74	26.9	13.2	41	14.6	0.36
23/4/96	9.5	102	0.56	10	0.61	0.11	112	0.62	21.4	15	45.5	8.5	0.32
2/5/96	8.9	123	0.4	12.6	1.5	<0.01	154	0.84	30.5	6	48.6	8.3	0.39
19/6/96	7.9	98	0.59	11	1.22	0.02	151	1.2	39.7	<2	25.2	8.3	0.34

Constituents in mg/l, TDS in g/l

Fig. 5 Groundwater analyses represented by three points plotted in a tri-linear diagram (meq‰)



biogenic CO_2 , when the groundwater infiltrated in the past through the soil zone Eq. (1). The solution was predominately enriched by sodium and bicarbonate, whereas aluminum remained conserved in clay mineral. Because this deep hydrogeological system is closed to biogenic CO_2 , the H^+ ions originated by dissolving biogenic CO_2 were almost consumed during hydrolysis, and probably without recharge with endogenous CO_2 in this part of the Czech Massif. The result is mostly alkaline groundwater with a maximum pH of 9.9. The Na-Cl component is explained by the presence of the fossil water.



The idea of the chemical composition evolution of the groundwater is supported by the results of microscopic analysis of the granite sampled from the core of the J5 sub-horizontal borehole located in an intensively fractured

zone in the GSC. Indication of silicate weathering (clay mineral, chloritized biotite, relicts of amphibole totally weathered to chlorite, and carbonate) was recognized in this analysis.

Sodium is the only major cation found in the groundwater. In all of the groundwater samples, the Na^+ ion concentration was an order of magnitude higher than that of the K^+ ions, even though the average concentration of these elements in the upper continental crust is almost equal—Na 2.89, K 2.8% (Taylor and McLennan 1985). This relation between the concentrations of dissolved alkaline metals generally validates that groundwater is unaffected by human activity. This result is explained by the loose bond of K^+ ions with an advantageous ionic radius (1.33 Å) in structures of clay minerals and the higher resistance of the K-feldspar than Na-Ca feldspars to weathering processes. However, the individual clay mineral illite $\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$, a possible product of K-

feldspar weathering, probably does not lower the K^+ concentration in the groundwater; a negative value of the saturation index indicates the groundwater was subsaturated to this clay mineral and dissolving of this mineral is expected (Table 5).

The concentration of alkaline earth ions (Ca^{2+} , Mg^{2+}) is unimportant in comparison to sodium. This result could be explained based on (1) aquifer rock composition (plagioclase is one of predominant granite component, the volume of carbonate is neglected compared to this silicate), (2) chemical weathering is limited in the closed hydrogeological structure without a CO_2 source and slow groundwater circulation. Under these conditions, the groundwater is enriched due to incongruent dissolving of silicate by weakly bonded alkali metals having a charge of +1 prior to the alkaline earth ions having a charge of +2. When alkaline earth ions are released by solution, these ions would be fixed in clay minerals preferentially to Na^+ . Moreover, the groundwater in this closed hydrogeological structure is in equilibrium, and near equilibrium, with calcite already at low Ca^{2+} concentrations (ZV35-0.3, P6-0.1 mmol/l).

Major anions are either bicarbonate or chloride. Bicarbonate predominately originated by the previous dissolving of biogenic CO_2 when the groundwater infiltrated through the soil zone (see $\delta^{13}C$ values in Table 6). The chloride source is generally mineral apatite and mica (both minerals are present in the GSC granitoid). Chloride concentrations of more than 1 mmol/l (all samples except for the P6 sampling location of 0.4 mmol/l) probably do not come from minerals forming rocks in the aquifer neighboring the GSC and are explained by the presence of the fossil water in the deep crystalline aquifer (the Na-Cl component in the groundwater). Based on the molar ratio between Na^+ and Cl^- , varying from 0.8 to 1.2 in the groundwater, where Na^+ and Cl^- have been recognized as major ions (the J6, RZ9, ZV35, ZV56 sampling points), sodium chloride is dissolved in the groundwater.

Table 6 Results of analyses of $^{18}O/^{16}O$, D/H, $^{13}C/^{12}C$, and $^{34}S/^{32}S$ (‰)

Sample location	$\delta^{18}O$	δD	$\delta^{34}S$	$\delta^{13}C$
P6	-10.2	-69.0	+3.8	-21.4
J-6	-8.2	-61.4	—	—
J-7	-8.8	-61.0	—	—
ZV56	-6.8	—	—	—
ZV35	-8.0	—	+27.0	-28.6
Store of explosives	-9.1	—	—	—
ZV51/2	-10.1	—	—	—
Calcite (Z45)	—	—	—	-7.7

General reproducibility $\pm 0.2\%$

— no data

Different sulfate sources in the GSC groundwater are assumed. Accessory pyrite in the adjacent granitoid is estimated as a potential source. Probably because the groundwater is in contact with this mineral in anoxic conditions deep under land surface, the sulfate concentration in the groundwater was often below ~ 0.2 mmol/l (this is the SO_4^{2-} concentration determined from Eq. (3), assuming air-saturated water concentrations in the oxygen of ~ 0.72 mmol/l at $9^\circ C$). The rainwater infiltrated to the deep crystalline aquifer in the past could be another source of sulfate in the groundwater. Relatively high sulfate concentrations of 0.3–0.7 mmol/l (ZV35, ZV51/2, ZV56) correlated positively with the chloride concentration. Then, the fossil water in the deep hydrogeological structure is assumed to be another sulfate source in some samples of GSC groundwater (see also isotopic composition of S – SO_4^{2-} in the P6 and ZV35 seeps).

A low concentration of bicarbonates and high pH values reflect limited influence of CO_2 on groundwater based on the environment in the GSC area. This result suggested a natural insulation around the GSC from the shallow zone where continuous CO_2 generation resulting from bioactivity is present. The H^+ ions produced by the dissolving CO_2 were consumed by hydrolysis of the

Table 5 Saturation indexes (SI) and partial pressure of CO_2 of the Quaternary and deep crystalline aquifers

Sample location	Buk	Konetopy	P6	Store of explosives	ZV24	ZV35	ZV56
Phase	The Quaternary aquifer (5 m under surface)		The crystalline aquifer (1,000 m under surface)				
Albite	-2.5	-2.2	-2.95	-2.5	-3.4	-2.1	-4.3
Anorthite	-3	-3.1	-5.8	-5.7	-6.9	-4.2	-5.8
Calcite	-0.4	-0.9	0.4	-0.6	-0.6	-0.05	-0.6
Chlorite	-10.5	-9.2	1.45	-2.6	-4.7	2.2	-7.3
Fluorite	-2.8	-2.4	-1.45	-2.05	-1.75	-1.5	-0.8
Illite	2.2	1.7	-4.1	-3.1	-4.2	-2.5	-3.55
K-feldspar	0.2	-0.5	-2.8	-2.55	-3.1	-2.1	-3.4
Kaolinite	4.6	4.35	-1.8	-0.5	-1.3	-0.3	-0.1
Quartz	0.3	0.3	0.09	0.2	0.2	0.1	-0.6
Ca-montmorillonite	3.1	2.8	-4.1	-2.6	-3.6	-2.3	-3.3
p CO_2 (MPa)	0.0049	0.0011	7.08E-06	0.00001	3.16E-05	2.24E-06	3.7E-05
Major ions	Ca,HCO ₃	Ca,SO ₄	Na,HCO ₃	Na,Cl	Na,Cl	Na,Cl	Na,Cl
TDS (g/l)	0.57	0.35	0.29	0.21	0.21	0.34	0.55

SI $\approx$ 0 $\rightarrow$ the groundwater is in chemical equilibrium with the mineral.

SI<0 $\rightarrow$ the groundwater is subsaturated to the mineral (dissolution is expected).

SI>0 $\rightarrow$ the groundwater is supersaturated to the mineral (precipitation is expected).

silicate phases of the GSC granitoid; groundwater reached a maximum pH of 9.9. Assuming that the anomalous RZ9 outflow with a low pH value is not representative (or the anomalous value resulted from analytical problems), the CO_2 partial pressure of the GSC groundwater outflows was at an extremely low level between 3.5×10^{-5} and 2.2×10^{-6} MPa. Compared to the environments found at land surface, the CO_2 partial pressure of the soil gas, resulting from climatic conditions in Central Europe, varies because of the decay of organic material and root respiration near $10^{-2.8}$ MPa. The p_{CO_2} in the present atmosphere at land surface is near $10^{-4.5}$ MPa (Appelo and Postma 1994). The partial pressure of CO_2 in the mineral water forming in the environments of the higher CO_2 activity of abyssal origin exceeds 0.1 MPa.

It is possible to recognize from the SI values (Table 5), in spite of assumed long-term groundwater/rock interaction, the groundwater discharged to the GSC was appreciably subsaturated to prime silicate phases formed by plagioclase and K-feldspar. Thus, the minerals could still be dissolved in the groundwater. Such SI values reflect a very low capacity of groundwater to leach minerals where groundwater is depleted of the CO_2 that brings the H^+ ions to the water–rock system. The closed groundwater system probably without endogenous CO_2 supply, and the lack of calcite in granitoid resulting in the groundwater, was mostly undersaturated to calcite (explosives store, ZV24, ZV56 sampling points), seldom in equilibrium (ZV35 spring), and near to equilibrium with the mineral (P6 spring). The groundwater was mostly far from equilibrium with the clay minerals. The groundwater was always subsaturated to illite and Ca-montmorillonite, and subsaturated (P6, explosives store, ZV24 sampling points), and almost in equilibrium (ZV35, ZV56) with kaolinite. Kaolinite is a more probable weathering product of primary silicate compared to illite and montmorillonite. Moreover, the groundwater was subsaturated with respect to fluorite and seldom in equilibrium with quartz (P6, ZV35 sampling points).

Comparing the deeply discharged groundwater to the shallow groundwater of the local Quaternary aquifer using selected SI values, the main difference in SI values was found in the silicate system (the groundwater–primary silicates, and the groundwater–clay minerals, Table 5). Thus, the different evolution of the groundwater chemical composition in the Quaternary and crystalline aquifers was assumed, reflecting a strong difference in shallow and deep groundwater movement.

The Bowers Mansion Spring in Nevada, USA (White et al. 1963 in Pačes 1983) could be an example of the deep groundwater in the acid igneous rock, insulated from CO_2 supply, where the pH 9.3 was found because of hydrolysis of granodiorite feldspars (TDS 0.2 g/l, Na^+ , HCO_3^- major ions, $p_{\text{CO}_2} = 4.4 \times 10^{-6}$ MPa). The deep groundwater of similar chemical type to the GSC groundwater (Na–C, Na–Cl), however, with higher TDS (in units of grams per litre) and p_{CO_2} , as high as 0.9×10^{-1} MPa is found, for example, in granitoid in the western part of the Czech

Massif with high activity of endogenous CO_2 . Vertical hydrochemical zoning was studied at the former Jachymov ore field in Western Bohemia (Pačes 1969). Distinct differences were found between the chemical composition of the groundwater with fast groundwater circulation in the zone of metamorphic cover affected by mining activity (Ca^{2+} , SO_4^{2-}), and subjacent, hydraulically separated granite not affected by mining activity, where the groundwater circulates very slowly (Na^+ , HCO_3^-). The sodium concentration was chosen as the measure of time and intensity of the physical–chemical interaction in the water–rock system containing sodium feldspars.

Trace elements

The trace elements Al, Be, Sr, Ba, Li, Rb, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, Ag, Cd, Hg, Pb, B, As, Se, F, I, Br, and P (as HPO_4^{2-}) have been analyzed in some groundwater samples. The concentrations of most trace elements were usually below the detection limit (Li, Cu, Zn, Cr, Pb, Ni, Ag, V, Rb, Mo, $\text{Co} < 0.01$ mg/l; Se, Cd < 0.001 mg/l; Be, Hg < 0.0001 mg/l), or near the limit. Iron concentrations were some of the highest among the elements under investigation (maximum of 6.1 mg/l), followed by manganese (maximum of 0.99 mg/l), and boron (maximum of 0.72 mg/l; Table 2). Fluoride, iodide, and bromide also were found at a relatively high concentrations in trace elements; fluoride and bromide were found at similar concentrations (F^- 0.95–4 mg/l; Br^- 0.6–4.25 mg/l). Both F^- and Br^- exceeded iodide concentrations in the same samples (0.014–0.73 mg/l). The mass ratio between bromide and iodide varied largely in the GSC groundwater from 4 (ZV35 sampling point) to 60 (ZV56 sampling point), and thus, different to seawater ($\text{Br}^-/\text{I}^- = 1.083$, Hem 1970). No important statistical correlation among all analyzed halogens (Cl^- , F^- , Br^- , I^-) was determined ($r < +0.8$). Phosphate concentrations (HPO_4^{2-}) ranged from 0.02 to 0.41 mg/l, and reached higher levels in only one sample. No correlation between phosphate and fluoride or chloride concentration indicates that apatite (having fluorine or chlorine in its mineral structure) is important as the source of these elements in the groundwater.

Results of the analysis of the trace elements listed above are consistent with the chemical composition of the groundwater originating in aquifers containing acid igneous rocks. The granite-forming mineral (feldspars and biotite), and accessory minerals (carbonate, apatite, fluorite, pyrite) undergoing hydrolysis are sources of the elements that form the fundamental mineral portion and/or that substitute other elements in a mineral structure. Fluoride found at a higher concentration than in the Quaternary aquifer (maximum of 4 mg/l) indicates long-term retardation of groundwater in the crystalline aquifer. Although fluoride was found at higher concentrations, only lithium concentrations (another indicator of water/silicate rock interaction) were near the detection limit of 0.01 mg/l. This result is explained by the absence of muscovite, the mineral that is a common source of this

alkali metal (lithium) in the groundwater. Based on the very low concentration of trace metals forming polymetallic ores (Cu, Pb, Zn, and others), any effect on the chemical composition of the GSC groundwater outflows by the mine water potentially coming from the Příbram ore fields next to the GSC was eliminated.

Nitrogen analyzed as NO_3^- , NO_2^- , and NH_4^+ ions was found in the GSC groundwater generally in trace concentrations. Nitrogen compounds in the groundwater discharging to the GSC probably originated in the dissolving of nitrogenous oxides (N_2O , NO), and ammonia (NH_3) formed by burning explosives during mining, and persisted in the underground atmosphere of badly ventilated mine gateways. That is why the higher concentrations of nitrogenous compounds were observed in the slowly dripping groundwater (ZV20: NH_4^+ , 3.9 mg/l, NO_2^- , 1.1 mg/l; ZV24: NH_4^+ , 1.8 mg/l; NO_2^- , 1 mg/l). These sources are located far from the main haulage road at the GSC. Only one source could possibly be ventilated from the land surface.

Radioactivity and radioactive substances

The natural uranium ($^{238}\text{U}+^{235}\text{U}$), ^{226}Ra , ^{222}Rn , and gross alpha activity were measured during monitoring in some of the groundwater outflows at the GSC (Table 2). Low uranium concentration between 0.0001 and 0.02 mg/l, the ^{226}Ra activity between <0.01 and 0.05 Bq/l, and the changing of gross alpha activity from <0.01 to 0.1 Bq/l indicate that there is no connection between the GSC area and the neighboring polymetallic ore field. Maximum values of radioactive substances were ascertained in the RZ9 groundwater sample (the outflow stopped immediately after opening the weathered cavern at the RZ9 lateral opening): U_{nat} 0.045 mg/l, ^{226}Ra 0.41 Bq/l, gross alpha activity 1.46 Bq/l. For comparison, the mine water sampled at the bottom of shaft No. 11 (Fig. 1) in the former polymetallic ore field had a concentration of U_{nat} 3.6 mg/l, activity of ^{226}Ra 0.26 Bq/l, and gross alpha activity of 106 Bq/l.

The maximum ^{222}Rn activity was measured in P6 spring (2.6.1993: 564–607 Bq/l; 12.12.1995: 683–785 Bq/l), the ^{222}Rn activity at average levels was found in ZV35 spring (12.12.1995: 51.2–48.6 Bq/l), and the minimum ^{222}Rn activity was found at the ZV51/2 dripping source (5.85 Bq/l). Differences observed in the radon activity could be explained by differences in the groundwater discharges (Q) of the monitored sources: the P6 spring with Q approximately 0.01 l/s, the ZV35 spring with Q approximately 0.001 l/s, and the ZV51/2 dripping source with the lowest discharge (the discharge was estimated and not measured). This result supports the similar radioactive activity found in the aquifer rocks. The increased Rn concentration in the groundwater probably indicates more permeable zones in the aquifer (Magri and Tazioli 1970). Volatilization losses during sampling could also explain the lowest Rn concentration at the ZV51/2 dripping outflow.

Oxygen and hydrogen isotopes

Indication of the genetic type of the groundwater under investigation, and the physical-chemical condition of the groundwater was the goal of stable isotope analysis. The $\delta^{18}\text{O}$ values in the GSC groundwater varied from –6.8 to –10.2‰. Additionally, analyses of the D/H ratio were performed for some of the water samples; the δD values varied between –69 and –61‰. Groundwater at the GSC was indicated genetically to be the same as rainwater based on the relation between the isotope ratio $^{18}\text{O}/^{16}\text{O}$, and D/H (the P6 spring, the J6 and J7 sub-horizontal boreholes) followed the world meteoric water line: $\delta\text{D}=8\delta^{18}\text{O}+10$ (Craig 1961).

Assuming that a larger portion of the Czech Massif groundwater could be formed from rainwater of the cold Pleistocene Epoch (Šilar 1988), the $\delta^{18}\text{O}$ values of the samples of the ZV51/2 spring and the P6 spring ($\delta^{18}\text{O}=-10.1$ to -10.2 ‰) are only slightly lighter isotopically compared to present rainwater ($\delta^{18}\text{O}=-10$ ‰). Despite this result, the oxygen and hydrogen isotopic composition combined with other results of hydrogeochemical monitoring does not exclude the possible effect to the groundwater system at the GSC that is within a closed hydrogeological structure. These $\delta^{18}\text{O}$ values can be explained, for example, by the rainwater forming during warmer interglacial periods. Other groundwater samples collected at the GSC are distinctly isotopically heavier ($\delta^{18}\text{O}=-6.8$ to -9.1 ‰). These values correlate with the presence of the Na–Cl groundwater component, which probably naturally evaporated (the oxygen of the sample ZV56 with relatively high sodium and chloride concentrations is isotopically the heaviest). However, these samples could be also be affected by secondary evaporation and/or dissolving of the oxygen, which may result from mine ventilation, and affect the mainly slowly dripping groundwater discharges.

Sulfur isotopes of dissolved sulfate

Sulfur isotope analysis of sulfate dissolved in the GSC groundwater was used for indication of a source of this anion in the groundwater. Sulfate was analyzed at sampling points P6 and ZV35, with $\delta^{34}\text{S}$ values of +3.8 and +27‰, respectively. These results correlate with the chemical composition of the groundwater. The isotopically lighter sulfur was found in the P6 seep of the Na– HCO_3 chemical type, and of lower SO_4^{2-} concentration (0.2 mmol/l), whereas heavier sulfur was measured in the ZV35 seep of the Na–Cl chemical type and of higher SO_4^{2-} concentration (0.3 mmol/l). Moreover, a $\delta^{34}\text{S}$ value from the P6 sample correlates with $\delta^{34}\text{S}$ values of accessory sulfides in granitoid bodies of the Central Czech Pluton that are close to 0‰ (Žák and Dobeš 1991). That is why different sources of dissolved sulfate are assumed based on isotopic composition of S – SO_4^{2-} in the GSC groundwater. Accessory sulfides of the adjacent granite (P6) and probably naturally evaporated sulfate of fossil water were contained in groundwater with higher concentration of the Na–Cl component (ZV35).

Carbon isotopes of dissolved bicarbonate

Because bicarbonate is a major anion in the GSC groundwater, analysis of $^{13}\text{C}/^{12}\text{C}$ was performed to accurately pinpoint the source of this anion. The isotopic composition of bicarbonate in the groundwater of the P6 and ZV35 seep and carbonate from the carbonate-quartz vein near the sampling location Z45 were analyzed. The similar source of bicarbonate dissolved in the groundwater was estimated based on the results obtained: the P6 spring: $\delta^{13}\text{C} = -21.4\text{‰}$; the ZV35 spring: $\delta^{13}\text{C} = -28.6\text{‰}$. Measured values are close to that of biogenic CO_2 of the $\delta^{13}\text{C}$ value (about -22‰ ; Moser and Rauert 1980), and differ from those of the carbonate-forming local mineral vein ($\delta^{13}\text{C} = -7.69\text{‰}$). Based on these results, previous dissolving of biogenic CO_2 , when the groundwater infiltrated through the soil zone, is assumed as the probable source of most bicarbonate ions in the GSC groundwater. Because the groundwater was interacting with predominately rock-forming silicate, the ratio $^{13}\text{C}/^{12}\text{C}$ in bicarbonate was conserved. Isotopically lighter carbon in the ZV35 groundwater, which is in chemical equilibrium with calcite, could result because of precipitation of carbonate before the groundwater reached equilibrium with the calcite.

Strontium isotopes

The principal sources of strontium in igneous rocks are plagioclase feldspar and apatite, where Sr^{2+} can replace Ca^{2+} ions. Chemical weathering of rocks releases strontium, which is isotopically indistinguishable from that remaining in the silicate rock fragments (Faure 1972). The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in the GSC groundwater varied in a very narrow interval from 0.7069 to 0.7093. This result indicates isotopic homogeneity in the GSC area, and in the P6 spring with respect to time. The groundwater of all analyzed seeps is in isotope equilibrium with adjacent granite and granodiorite, resulting in values of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.7093 and 0.7134, respectively, (Table 7). These results support the idea that the GSC is a part of a closed hydrogeological structure, insulated from land surface, where isotopic equilibration of strontium between rock and water is unlikely. Strontium isotope disequilibrium was found between the GSC groundwater and the carbonate (calcite) of the vein fillings ($^{87}\text{Sr}/^{86}\text{Sr} = 0.7345$). Based on this result, carbonate (calcite) is not assumed to be important during the evolution of groundwater chemical composition, probably because a negligible volume of calcite is required as compared to the rock-forming silicates.

Tritium

Tritium activity (T, the ^3H isotope) was monitored both one-time and periodically at selected groundwater sources over the GSC area between 1990 and 1996 (Table 8). Determination of the relative groundwater age was the goal of this monitoring. The tritium activity of the groundwater was always below the detection limit of 3–6 TU (tritium units), or 2.4 TU (the P6 spring, May 24,

Table 7 Results of strontium isotope analysis

Sample location	$^{87}\text{Sr}/^{86}\text{Sr}$
P6	0.708099(93)–0.708620 (60)
J-5	0.708507 (30)
J-7	0.708560 (45)
Z45	0.706902 (67)
ZV51/2	0.707851 (30)
ZV35	0.708040 (45)
ZV49	0.707669 (40)
Store of explosives	0.709334 (50)
RZ9	0.708684 (122)
Granite	0.709264 (207)
Granodiorite	0.713431 (39)
Carbonate	0.734529 (41)

Values in brackets express 2σ -error in the last decimal place.

1996). The average tritium activity of rainwater in Europe before 1952 was 5 ± 5 TU (Moser and Rauert 1980). The tritium activity of rainwater of the Czech Republic was between 7 and 20 TU ± 5 TU in 1992 (Trýzna 1992). Therefore, all of the groundwater sources of the GSC were eliminated based on tritium activity, and the relative age of the groundwater in the GSC was higher than approximately 45 years (related to the time of the GSC groundwater investigation). This finding is of great importance regarding the future usage of the mine for gas storage (the groundwater discharged to the GSC probably had no direct connection to the recent shallow groundwater). The results of the ^3H activity measurements correlated with the results of the standard chemical analysis and supported the hypothesis about the lack of interaction of the deep groundwater with groundwater in the shallow aquifer, and the neighboring, flooded fields. The mine water had tritium activity between 8 and 21 TU and can be classified as “young” water.

Radioactive carbon

The ^{14}C activity was measured in the most important groundwater source—the P6 spring (highest permanent underground discharge). Based on the results of the ^{14}C

Table 8 Tritium activity (TU) of the waters in the GSC and vicinity

Sampling location	Date	^3H
P6	1990–1993	<3
P6	1994–1995	<5
P6	24/5/1996	2.4 ± 0.2
Z45	14/9/1994	<6
J-5	30/8/1994	<6
J-6	30/8/1994	<6
J-7	13/5/1993	<3
J-7	30/8/1994	<6
ZV35	28/3/1994	<5
ZV56	3/11/1995	<5
ZV51/2	13/6/1995	<5
RZ9	31/8/1995	<5
Store of explosives	11/3/1996	<5
ZV24	3/5/1996	<5
ZV20	4/5/1994–19/5/1994	<6
Mine water in the GSC	24/3/1993–30/8/1994	$16–21 \pm 5$
Mine water (Shaft No. 16)	22/6/1993	9 ± 5
Mine water (Shaft No. 15)	12/4/1994	8 ± 5

activity performed at two independent isotopic laboratories—Charles University in Prague, Faculty of Science, analyst Mrs. Z. Melkova (1994): 8.69 ± 0.6 percent modern carbon (pmc); the Laboratory of Hydrology and Isotopic Geochemistry at the University Paris-South, analyst Mr. J.L. Michelot (1996): 8.0 ± 0.3 pmc—a mean residence time of the groundwater was estimated as being from 18,869 to 19,001 years. Thus, rainwater forming the P6 spring probably infiltrated during the Upper Pleistocene Epoch. These results agree well with the groundwater dating in the Czech Massif (Šilar 1988). The low ^{14}C activity level agrees well with the results of groundwater analysis presented here, at least concerning the P6 spring (see Tables 3 and 8). Also, these results support the idea of no direct relation between the deep crystalline aquifer and the shallow Quaternary aquifer above the GSC, and neighboring flooded mine area.

Conclusions

A gas-storage cavern was constructed near the city of Příbram in Central Czech, Czech Republic during 1990–1996. Outflows of free-flowing groundwater developed in the mining space at a depth of 1,000 m below land surface. Mining was completed in the granite and granodiorite of the Czech Massif. The discharge of all groundwater outflows (12 locations over an area of approximately 1.2 km^2) did not exceed 0.01 l/s , and the groundwater temperature was about 23°C .

Sodium cations, and either HCO_3^- or Cl^- anions are the dominant ions in the deep groundwater. TDS concentration varies from 0.21 to 0.86 g/l , with an average of 0.4 g/l . The deep groundwater outflows were predominately alkaline; the pH exceeded a value of 8, with a maximum of 9.9. The chemical composition of steady groundwater seeps in the gas-storage cavern was relatively stable in time and appreciably different compared to the chemical composition of the groundwater contained in the shallow Quaternary aquifer (TDS concentration of 0.35 – 0.57 g/l , dominant Ca^{2+} ions, and either SO_4^{2-} or HCO_3^- , pH values of 6.7 – 6.9). Additionally, the groundwater discharged to the gas-storage cavern (dominant Na^+ ions, and either HCO_3^- or Cl^- , TDS 0.21 – 0.86 g/l , $\text{pH} > 8$) was distinctly different compared to the mine water of the neighboring polymetallic ore field (dominant Ca^{2+} ions, and SO_4^{2-} , TDS 2 – 3 g/l , pH 7.3 – 7.8).

The fundamental chemical composition of the deep groundwater is in agreement with the specific environments of the area under investigation. The specific environments determined during this investigation are the following:

1. The presence of deep groundwater outflows
2. Very low permeability of the rock matrix containing the groundwater: hydraulic conductivity of $3.4 \times 10^{-11} \text{ m/s}$
3. Silicates that are potentially hydrolyzed forming the host granitoid rocks

4. Ore mineral presented only as accessories
5. CO_2 activity at a very low level from about 3.5×10^{-5} to $2.2 \times 10^{-6} \text{ MPa}$, when compared to the soil environment and regions with higher CO_2 activity of abyssal origin
6. An anoxic environment with groundwater moving in granitoid

The groundwater chemical composition of the gas-storage cavern is generally similar to the environment of the closed hydrogeological structure or the zone of slow or stagnant groundwater movement. These indicated conditions also were based on strontium isotope ($^{87}\text{Sr}/^{86}\text{Sr}$) homogeneity in time and space and isotopic equilibration between the groundwater and adjacent granite and granodiorite. The isotopic composition of the groundwater ($^{18}\text{O}/^{16}\text{O}$, D/H) indicated that it was formed from rainwater. Based on tritium dating, all of the groundwater outflows were formed from rainwater older than 45 years.

Based on the ^{14}C activity, the rainwater probably infiltrated during the Upper Pleistocene Epoch (approximately 19,000 years ago). However, the isotopic composition of oxygen of the groundwater molecules ($\delta^{18}\text{O} = -7$ to -10‰) indicates that the rainwater condensed at a relatively high air temperature of about 7°C ; thus, the water probably infiltrated during a relatively warmer interglacial period.

The results of long-term monitoring strongly support the idea of flowing groundwater seeps disconnected from groundwater contained in the shallow Quaternary aquifer above the gas-storage cavern. Geotechnically, these conclusions support the insulation properties of the gas-storage cavern and indicated that the gas-storage cavern can be operated safely in the future. Even so, all fractures developed in the gas-storage cavern have been packed to prevent leakage and a monitoring system for CH_4 concentration in the soil air at land surface has been completed. The original results of groundwater chemical composition in the gas-storage cavern added general information on the groundwater of the deep zone of silicate rocks. Thus, these results are important in the fundamental hydrogeochemical investigation of the Czech Massif.

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