Hydrogen sulphide (H₂S) migration in groundwater of the Zechstein strata in the Legnica-Głogów Copper Basin and its vicinity, SW Poland

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Hydrogen sulphide (H₂S) occurs in groundwater in various lithostratigraphic units of the Zechstein Basin in the Legnica-Głogów Copper Basin (SW Poland). This region is located in the Fore-Sudetic Monocline within which, several tens of kilometres NE of the study area, at greater depths, natural gas fields with hydrogen sulphide (H₂S) occur. The Main Dolomite (Ca2), in which H₂S-containing natural gas has accumulated, is younger than the Zechstein Limestone (Ca1), which is actively mined. The Ca2 and Ca1 formations are separated by a thick anhydrite succession including a wedge-shaped salt body. Hydrochemical analyses of 18 groundwater samples taken from different horizons within the Zechstein strata showed spatial variability of H₂S and chloride concentrations. A conceptual model of groundwater flow with dissolved H₂S in the Zechstein formations was developed. H₂S migration is associated with groundwater flow between the Ca2 and Ca1 aquifers through fissures in the anhydrite strata that separate them. Hydraulic contact through fissures in the anhydrite layers is the result of long-term exploitation of the underground copper deposit. Groundwater flow between the layers is influenced by a large change in the piezometric pressure of the groundwater in the depression cone caused by mining drainage.

Key words: hydrogen sulphide, chlorides, groundwater, mining impact, Zechstein Basin, Legnica-Głogów Copper Basin.

INTRODUCTION

The occurrence of hydrogen sulphide (H₂S) in geological strata results from redox reactions that involve sulphates and hydrocarbons, as the association of these is thermodynamically unstable in most geological settings involving diagenesis, catagenesis and metagenesis (Machel, 2001). Hydrogen sulphide can be produced by various geochemical and geological processes including:
- thermochemical sulphate reduction – TSR,
- microbial sulphate reduction – MSR,
- thermal decomposition of sulphur-containing organic compounds of oil and organic matter,
- reaction of elemental sulphur with hydrocarbons,
- volcanic and plutonic processes (Orr, 1977; Krouse et al., 1988; Machel et al., 1995; Worden et al., 1995; Worden and Smalley, 1996; Machel, 2001; Zhu et al., 2005; Zhang et al., 2008).

This gas is commonly found associated with sulphate and carbonate rock units forming sour natural gas reservoirs (Worden and Smalley, 1996; Aali and Rahmani, 2012; Liu et al., 2014; Bilkiewicz and Kowalski, 2020; Kotarba et al., 2020; Torghabeh et al., 2021; Cheng et al., 2022). Besides its occurrence in these natural gas reservoirs, the origin, migration and accumulation of H₂S has been also studied in connection with coal seams (Liu et al., 2012; Deng et al., 2014; Tan et al., 2020; Xie et al., 2021), petroleum fields (Kotarba et al., 2017b) and the exploration, design and operation of geothermal facilities (D'Amore et al., 1990; Mayrhofer et al., 2014; Jácome Paz et al., 2022).

The occurrence of H₂S in Poland is mainly associated with oil and natural gas fields accumulated in the Zechstein Main Dolomite (Ca2) (Karnkowski, 1999; Bilkiewicz and Kowalski, 2020; Kotarba et al., 2020), of the Fore-Sudetic Monocline (also referred to as the Fore-Sudetic Homocline – Żelaźniewicz and Aleksandrowski, 2008), though also in Upper Jurassic and Cenomanian strata of the Paleozoic-Mesozoic basement of the Carpathian Foredeep and in the Upper Paleozoic strata of the Lublin Basin (Karnkowski, 1999).

The presence of H₂S in areas other than volcanically active zones and sulphate and sour gas accumulations associated with carbonate rock formations is generally rare. The Legnica-Głogów Copper Basin (LGCB), SW Poland, had not been considered as an area where H₂S may occur. However, H₂S was unexpectedly detected in 2010 in the Lower Anhydrite (A1d) strata of the LGCB (Kijewski et al., 2012). Thereafter, this gas occurring in A1d and Zechstein Limestone (Ca1) strata may cause potential risks in mining operations. Kotarba et al.

(2017a, 2020), based on preliminary isotopic and mineralogical studies, inferred that such local occurrences of H_2S dissolved in groundwater of Ca1 strata may be sourced from natural gas accumulations in the Zechstein Main Dolomite (Ca2). However, the path and manner in which H_2S migrates from the Ca2 strata to the older and deeper Ca1 strata is still unknown. Establishing the origin of H_2S in the LGCB area and its vicinity is difficult because of a complex pattern of gas migration dissolved in groundwater where flow paths are determined both by the geological structure of the monocline in this area and by mining operation impacts.

This study explores (i) the spatial occurrence of H_2S dissolved in groundwater of the geological structure of the LGCB and its surroundings, and (ii) the path and manner of migration of H_2S to the Ca1 strata in the LGCB area located between Głogów city in the north and Polkowice city in the south (Fig. 1) based on the chemical composition of 18 groundwater samples in relation to the geological setting and hydrogeological conditions of the Fore-Sudetic Monocline.

GEOLOGICAL AND HYDROGEOLOGICAL SETTING

The LGCB is located in the SW part of the Polish Zechstein Basin, in the western part of the Fore-Sudetic Monocline. The Zechstein strata of the Fore-Sudetic Monocline are developed as megafacies that make up four major carbonate-evaporitic cycles (PZ1, PZ2, PZ3 and PZ4) that originated mainly during transgressive-regressive periods with thick successions of carbonates, sulphates and salts representing climatic changes from humid to arid (Wagner and Peryt, 1997). These strata developed in the Polish Zechstein Basin, which was a part of the epicontinental marine sedimentary basin known as the Southern Permian Basin (Peryt et al., 2010). The first three cycles are widely developed across the Polish Zechstein Basin and each of them starts with a basal carbonate unit which precipitated from water of raised salinity and is overlain by evaporites formed during progressive evaporation resulting from deficiency of new seawater (Wagner, 1994; Wagner and Peryt, 1997).
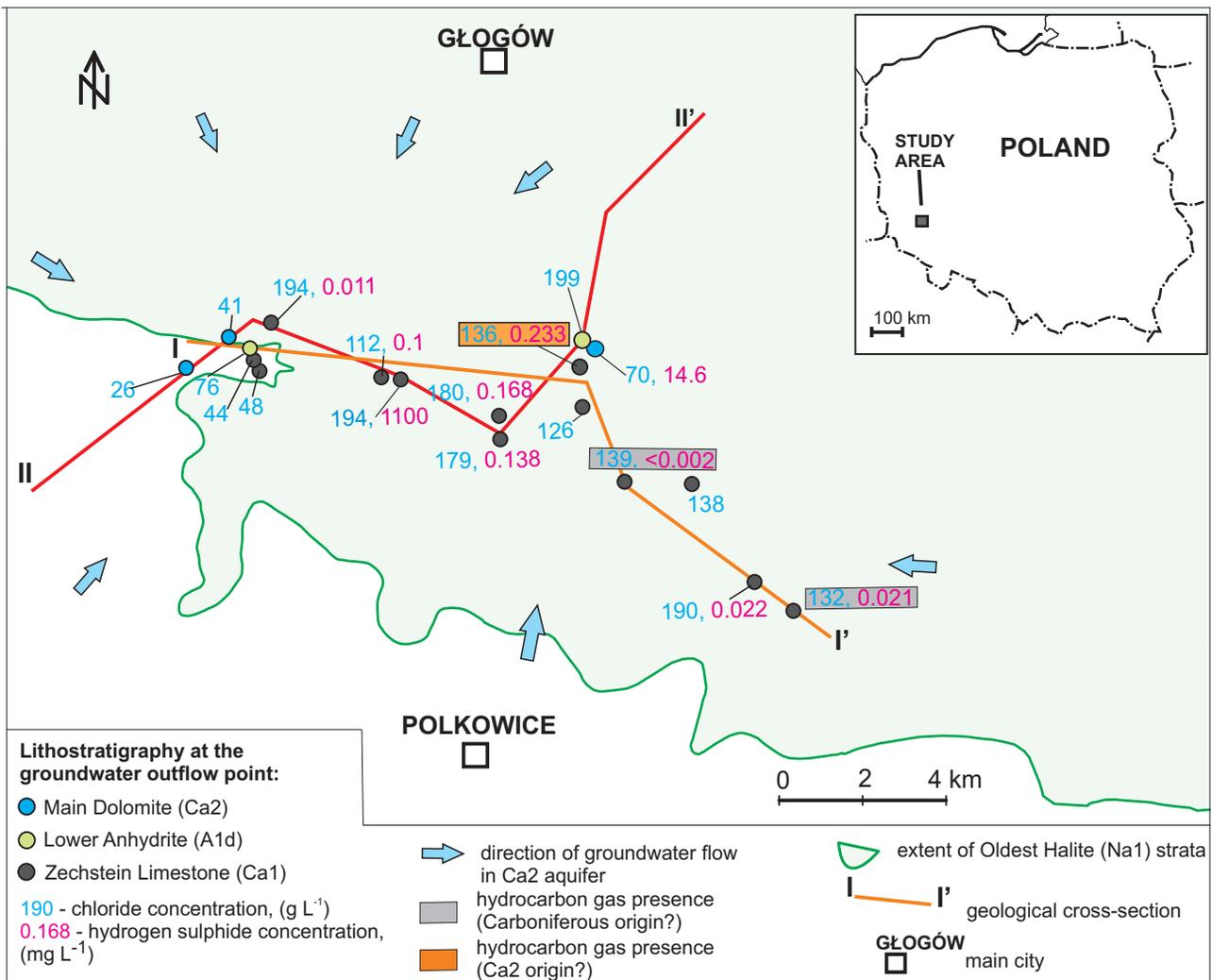
Fig. 1. Sketch-map of the study area showing the location of the groundwater samples studied, the extent of the Oldest Halite (Na1) strata, and chloride and H_2S concentrations

The Zechstein strata in the LGCB are monoclinal, dipping 3–6° NE (Fig. 2). Locally these strata are bent into steeper flexures with dips up to 30°. In the study area there are faults that dip at 30–90°, most being steep. The throws on the faults reach 70–100 m (Markiewicz, 2007). The fault planes are usually filled with breccia, gypsum, calcite or barite, so faults can form hydraulic connections between aquifers in the LGCB.

In the Zechstein strata of the LGCB area there are two aquifers: Ca2 and Ca1 (Bocheńska, 1988, 2003). Both aquifers are recharged from Paleogene sands on outcrop located SW of the LGCB. The Ca2 confined aquifer is formed by karstic and fissured dolomites 10–30 m thick (Becker et al., 2007). Before mining operations were started in this area the groundwater piezometric pressure in the Ca2 aquifer was 5–9 MPa depending on the location of the measurement point on the monocline. The rock hydraulic conductivity ranged from $9 \cdot 10^{-8}$ to $9 \cdot 10^{-6}$ m s^{-1} (Bocheńska, 1988, 2003). The Ca1 aquifer comprises fissured-karstic limestone and dolomite from a few to >30 m thick. Under natural conditions before mining, the hydraulic conductivity of these rocks ranged from $2 \cdot 10^{-8}$ to $2 \cdot 10^{-7}$ m s^{-1}, and the groundwater piezometric pressure was 4–10 MPa (Bocheńska, 1988, 2003).

The Ca2 aquifer is separated from the Ca1 rocks by a succession of anhydrites (Lower Anhydrite A1d and Upper Anhydrite A1g), and the Oldest Halite (Na1) of the PZ1. The average thickness of the evaporite rock package is ~130 m (Kłapciński et al., 1984; Kłapciński and Peryt, 2007).

In the LGCB area there exist also extensive hydrodynamic and structural effects related to decades-old mining operations appearing as: (i) a depression cone, which causes reversal of the natural piezometric pressure head in the aquifers (Fig. 2) and (ii) numerous and widespread cracks and fissures in the rock mass that create new and privileged flow paths for groundwater (Becker et al., 2007). In the Ca1 unit, within the range of the depression cone, groundwater flows to its centre not only from the S, i.e. from the outcrop beneath the Paleogene sands, but also from the W, N and E. In central region of the LGCB, there are vertical relaxation fractures in the A1d and A1g strata.

Vertical rock fractures above the copper-bearing layer in the LGCB are the result of mining activities, seismic tremors and rock bursts (Burtan, 2017; Gogolewska and Strzeszyńska, 2019). Some seismic events in the study area are high-energy (Szczerbowski, 2019). As a result, cracks were created in the evaporite rock package, which is impermeable under natural conditions, enabling the flow of groundwater from the Ca2 to the Ca1 strata. Confirmation of the hydraulic connection between both aquifers is the lowering of the groundwater pressure in the Ca2 succession – by the year 2022 the pressure had decreased by 600 m as compared to the original pressure from ~1970 (Fig. 2). The large difference in the groundwater pressure generated in the Ca2 succession caused a reversal of the original regional groundwater flow direction in this strata. Currently, within the range of the depression cone in the LGCB, part of the groundwater in Ca2 flows from the N and NE, i.e. from the zone where Ca2 is more deeply buried (Figs. 1 and 2).

GROUNDWATER SAMPLING AND ANALYTICAL STUDY METHODS

Groundwater samples were collected at water outflow points located in Ca2 (3 samples), A1d (2 samples) and Ca1 (13 samples) strata (Table 1). In total 18 groundwater samples were collected, determined by the availability of water outflow points and the technical possibilities of sampling during underground mining excavations. Groundwater samples were collected directly either from a borehole head in an excavation sidewall or roof, or outflows from a rock fissure, into glass bottles and PET containers, and immediately transferred to the laboratory. Samples intended for H$_2$S concentration analysis were collected into dark glass bottles and prepared for analysis by adding 5 ml of 10% zinc acetate followed by adding NaOH to bring pH to the range of 8.5–9.0. Chemical analyses of samples were performed by Quality Research Centre Laboratory (CBJ) in Lubin, Poland, in accordance with the procedures applicable
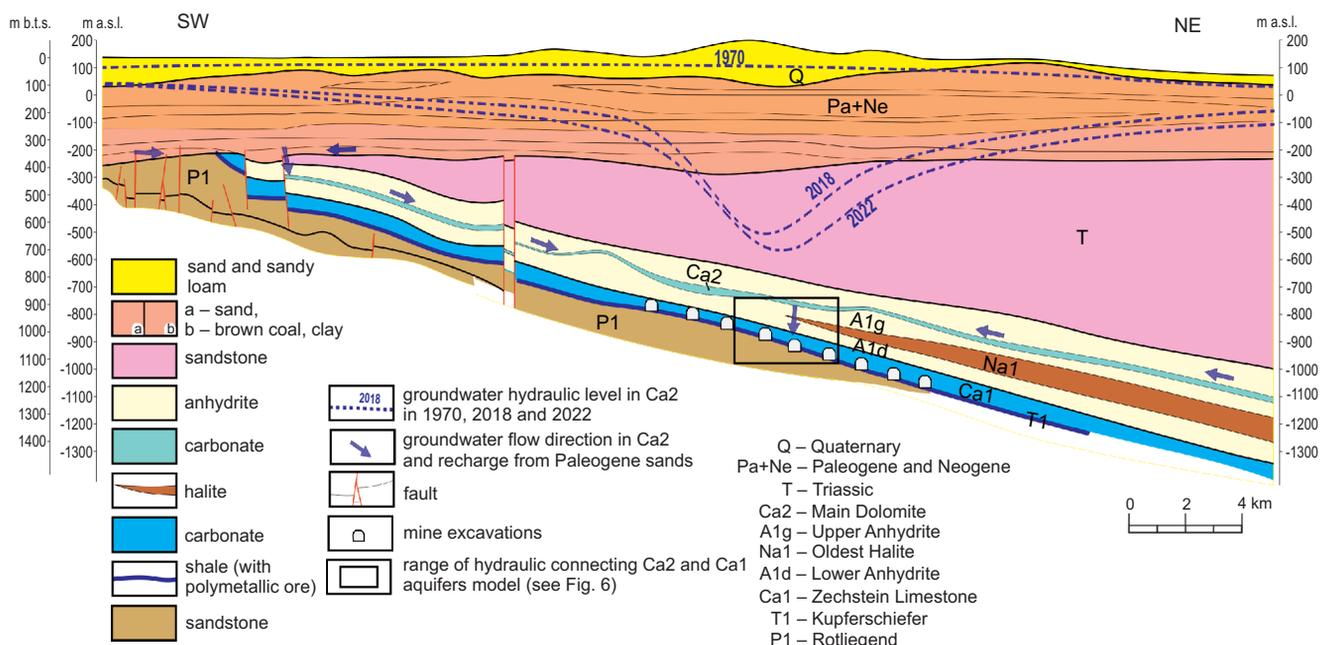
Fig. 2. Hydrogeological cross-section through the LGCB (Kłapciński et al., 1984, modified)

**Lithostratigraphy at the sampling point, chemical composition and pH
of the groundwater samples analysed**

Sample code	Lith.	H_2S	TDS	Cl	Na	SO_4	Ca	Mg	pH
					$(mg\ L^{-1})$				
1	Ca1	0.1	208 550	112 153	73 000	3 672	n.a.	n.a.	7.4
2	Ca1	0.011	335 250	194 351	130 625	2 620	n.a.	n.a.	6.5
3	Ca1	0.021	242 250	132 354	72 790	1 636	n.a.	n.a.	7.0
4	Ca1	<0.002	259 600	138 623	65 740	762	14 451	1 993	6.2
5	Ca2	14.6	126 950	69 795	37 100	2 462	4 672	1033	6.7
6	Ca1	0.168	298 250	179 781	115 000	2 722	2 885	731	7.2
7	Ca1	0.138	292 100	179 073	117 000	3 252	2 581	768	7.0
8	A1d	n.a.	315 250	198 892	124 000	943	8 220	465	8.6
9	Ca1	n.a.	229 400	126 144	71 500	1 032	10 670	873	5.7
10	Ca1	2.22	347 850	193 421	123 700	1 531	4 026	1003	5.8
11	Ca1	n.a.	85 900	48 215	n.a.	3 883	n.a.	n.a.	6.6
12	Ca2	n.a.	53 000	25 719	14 750	3 871	1 775	466	6.6
13	A1d	n.a.	133 350	75 929	48 190	4 261	2 595	1144	7.0
14	Ca1	n.a.	83 250	43 746	25 300	3 871	2 295	1130	7.0
15	Ca1	1 100	326 650	193 937	127 400	4 477	2 022	1 256	7.3
16	Ca2	n.a.	81 850	40 832	25 500	3 672	2 637	693	6.5
17	Ca1	n.a.	283 250	138 204	69 500	983	12 136	1 920	6.8
18	Ca1	0.233	313 850	136 110	58 400	614	18 762	2 284	5.5

Lith. – lithostratigraphy; TDS – total dissolved solids; n.a. – not analysed

in the lab. Individual determinations were made in accordance with the following methods and standards: H_2S – spectrophotometric method according to internal norm WKJ-4/IB/123, chloride – titration method according to PN-ISO 9297:1994, sodium – spectrometric AAS method in accordance with internal norm WKJ-4/IB/118, sulphates – gravimetric method in accordance with PN-ISO 9280:2002, calcium – titration method according to PN-ISO 6058:1999a, magnesium – calculation method in accordance with PN-C-04554-4:1999b, total dissolved solids (TDS) – gravimetric method in accordance with PN-EN 15216: 2010, pH – potentiometric method in accordance with PN-EN ISO 10523:2012.

For a better understanding of H_2S origin and its migration and for determining groundwater flow, stable hydrogen isotope composition data of groundwater samples published by Duda et al. (2023), were also used for interpretation.

RESULTS AND DISCUSSION

The chemical composition of groundwater in the LGCB, including the concentrations of hydrogen sulphide and chlorides, varies spatially depending on the lithostratigraphic unit from which the sample was taken and the lithostratigraphic unit from which the water studied genetically originates. Total dissolved solids (TDS) content in the samples analysed varies from

53,000 mg L^{-1} in groundwater from Ca2 strata to 347,850 mg L^{-1} in groundwater from Ca1 strata (Table 1). The H_2S concentration was found to range from <0.002 mg L^{-1} to 1,100 mg L^{-1} in samples of water flowing out in the Ca1 unit, and 14.6 mg L^{-1} in water sampled in the Ca2 strata (Table 1, Figs. 1 and 3). Measured groundwater pH values in the Ca2 unit do not differ significantly (6.5–6.7) and range from 5.5 to 7.4 in groundwater from Ca1. In the A1d strata groundwater pH values reached 7.0 and 8.6.

Groundwater in the Zechstein aquifers of the LGCB are mixtures of waters of different origins and residence times in the rock mass. In the Ca2 strata, groundwater has significantly lower salinity than the brines flowing out of the Ca1 strata (Figs. 3 and 4A). The Ca2 unit contains water of the chloride-calcium type (Cl-Ca), which, according to a classification proposed by Sulin (1948), may be related to hydrocarbon accumulations (Fig. 4B).

In the Ca1 unit brines occur with chloride concentrations varying from about 45,000 mg L^{-1} up to about 190,000 mg L^{-1} and waters containing H_2S occur locally in this horizon. The area of occurrence of more concentrated brines and H_2S is generally spatially correlated with the wedging zone of the Na1 salt seam (Figs. 2 and 3). Concentrations of H_2S in the groundwater samples analysed typically show slightly higher values in the central part of the study area, which is consistent with the centre of the depression cone into which the groundwater flows.
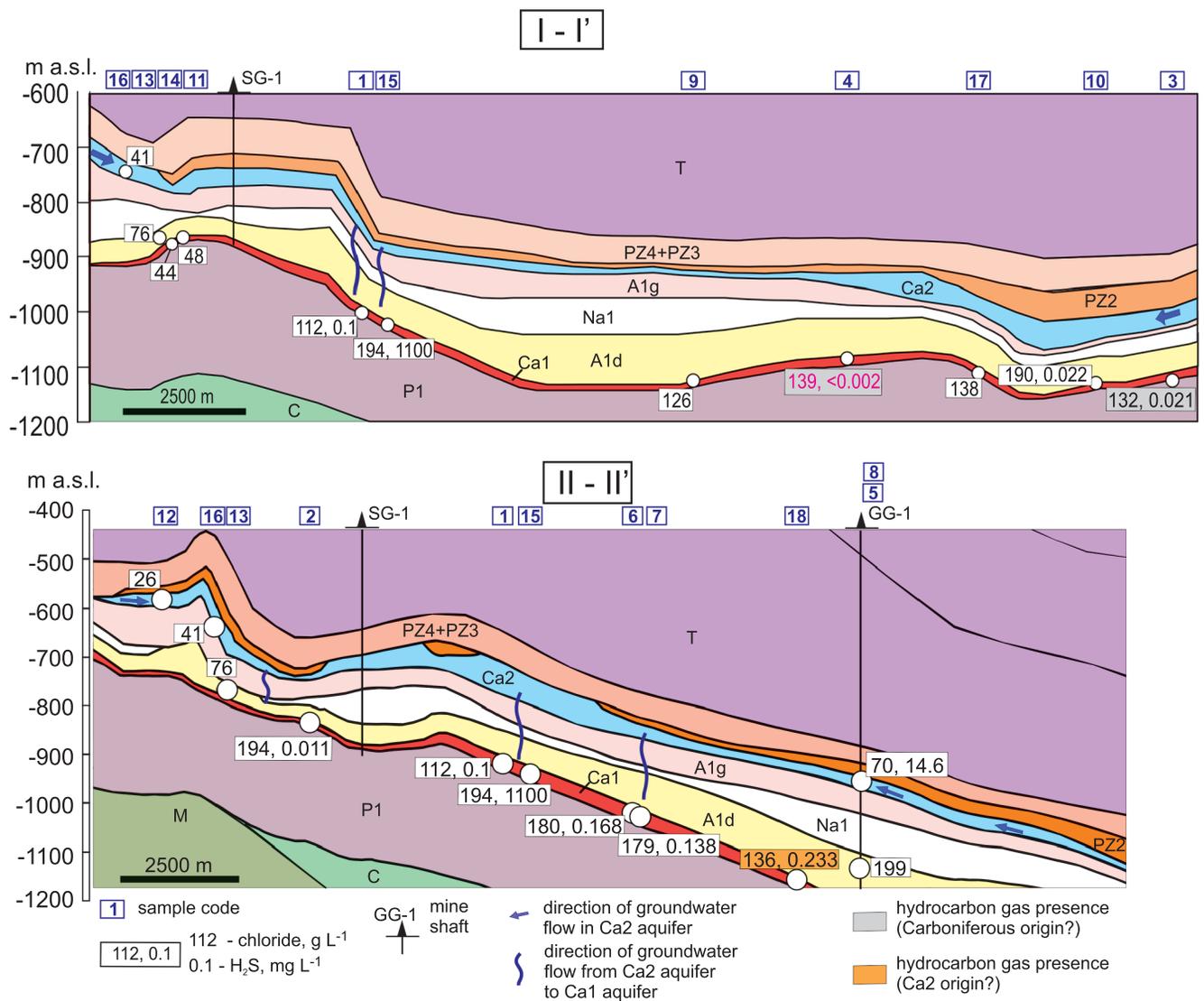
Fig. 3. Spatial variability of H₂S and chloride concentrations in the LGCB groundwater along the lines of geological cross-sections indicated in Figure 2 (cross-sections courtesy of Stanisław Mazur, Institute of Geological Sciences, Polish Academy of Sciences)

The increased salinity of the groundwater from Ca2 flowing into Ca1 strata results from leaching of the Na1 seam in the zone of its wedging. This seam is deformed by internal tectonics and intersected by a salt-anhydrite breccia (Markiewicz and Banaszak, 2005; Garlicki et al., 2007). On the basis of the correlation of rock temperature and its depth in the LGCB shown by Speczik et al. (2007) it was estimated that at the depth of 950–1050 m, where halite Na1 occurs, the temperature of rocks and groundwater is 37–40°C, which facilitates the leaching process.

In the Ca1 unit there occurs also groundwater with a higher salinity than water in the Ca2 strata, though not as high as groundwater from Ca2 in the contact zone with Na1 (Figs. 3 and 4A). Typical chloride-magnesium (Cl-Mg) groundwater is associated with the Ca1 strata (Fig. 4B). The groundwater is of palaeoinfiltration origin and contains a component indicative of the longest residence time in the rock mass, as demonstrated by the location of samples in the diagram plotting the ^2H values

against the concentration of chlorides in the samples analysed (Fig. 5). The area of Ca1 where these groundwaters occur is in the centre of the LGCB, where the thickness of the Na1 seam is already large enough to significantly limit the hydraulic connectivity between Ca1 and Ca2.

In the LGCB region hydrogen sulphide occurs both as gas dissolved in groundwater and free gas associated with small-scale, low-pressure nitrogen-dominated gas accumulations containing hydrocarbon gases, mainly methane (Kotarba et al., 2017a). Gases constituting these accumulations are of various origin, related to different formation processes and different sources, eventually reaching the same trap. Hydrocarbon gases on the Fore-Sudetic Monocline are believed to be linked both to the Carboniferous and the Ca2 source rocks (Kotarba et al., 2017b, 2020; Bilkiewicz and Kowalski, 2020). Our current research on the origin of natural gas in the LGCB area indicates that gases occurring in the Zechstein strata show various molecular and isotopic compositions suggesting the ex-
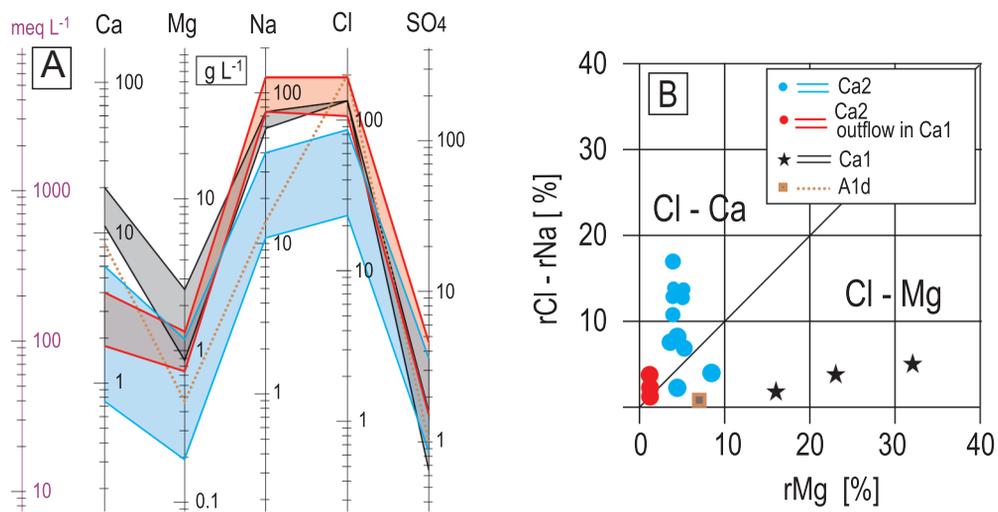
Fig. 4A – concentration ranges of the main chemical components of groundwater from the Zechstein lithostratigraphic units in the LGCB, g L^{-1}; B – identification of the hydrogeochemical type of groundwater based on Sulin's (1948) classification
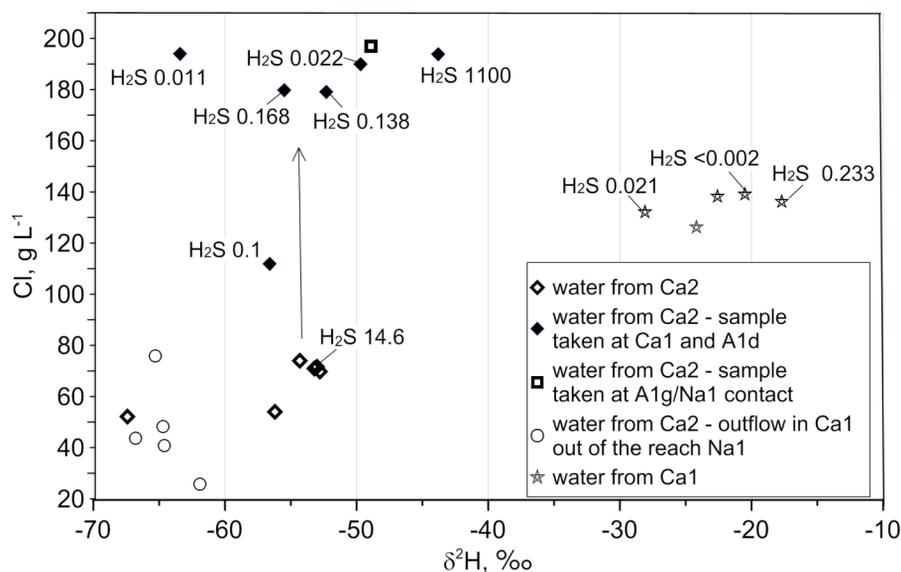
Fig. 5. Concentration of chloride (g L^{-1}) *versus* stable hydrogen isotope values (‰) of the groundwater samples analysed, showing groundwater salinity changes during flow from Ca2 to Ca1 (arrow)

H$_2$S – mg L^{-1} (δ^2H data of groundwater samples courtesy of Marek Duliński, Faculty of Physics and Applied Computer Science, AGH University of Science and Technology)

istence of different genetic groups of natural gas. Hydrocarbon gases from natural gas sampled from borehole heads in Ca1 strata together with groundwater samples 4 and 3 exhibit stable isotopic compositions characteristic of thermogenic gas generated from type III kerogen of higher maturity corresponding to a Carboniferous source rock, while hydrocarbon gas collected from a borehole head in Ca1 strata together with the groundwater sample 18 shows a different stable isotopic signature, indicating thermogenic generation from type II kerogen of lower

maturity, which is similar to gases generated from the Ca2 source rock (Figs. 2 and 3). This indicates that in the LGCB area there have been active migration paths for gas from both the Carboniferous and the Ca2 strata.

Hydrogen sulphide is a common component of natural gas in hydrocarbon deposits developed in the Ca2 strata of the Fore-Sudetic Monocline located tens of kilometres N and NE of the LGCB (Kotarba et al., 2000, 2020; Bilkiewicz and Kowalski, 2020). Previous studies (Bilkiewicz and Kowalski, 2020;

Kotarba et al., 2020) indicated that H₂S in these gas accumulations was produced mainly as a result of (i) thermochemical sulphate reduction (TSR) of anhydrites of the PZ1 cycle as supplying the highest amounts of H₂S, (ii) thermal decomposition of organic matter containing sulphur compounds and (iii) microbial sulphate reduction (MSR) of anhydrites of the PZ1 cycle. This suggests that one of the main sources of H₂S in the LGCB region is Ca2 strata from which H₂S can migrate to the Ca1 unit as gas dissolved in groundwater, using the same available migration routes as hydrocarbon gas of Ca2 origin.

Other important sources of H₂S are connected with the anhydrite strata of PZ1, especially those enriched in organic matter (Kijewski et al., 2012), where hydrocarbons necessary for sulphate reduction in TSR/MSR processes are present and may lead to H₂S production. H₂S in these strata has been also observed as minor manifestations in cores from boreholes drilled in order to explore the copper deposit in the LGCB region. This horizon can act rather as a local source for H₂S and may contribute to current MSR processes.

A consequence of the hydrogeological conditions that occurred in the LGCB as a result of long-term mining operations could be changes to the path and manner of H₂S migration through the strata in this area. In the Ca2 aquifer, H₂S dissolved in groundwater can probably migrate across a distance of several tens of kilometres from the natural gas fields in the Ca2 strata which on the Fore-Sudetic Monocline are located deeper than in the LGCB area, where mining drainage occurs (Fig. 2). Furthermore, in the LGCB and its vicinity, gas can migrate not only upwards along the natural lithostratigraphic profile, but also in the opposite direction, e.g. from the Ca2 aquifer downwards into the older and deeper Ca1 succession. Hydrogen sulphide dissolved in the groundwater of the Ca2 succession most likely reaches Ca1 through fissures in the PZ1 anhydrites and salt breccia in the wedging zone of the Na1 seam (Fig. 6).

Groundwater flowing downwards in fissures through both anhydrite units (A1d and A1g) may become enriched in H₂S, resulting in enormous H₂S concentrations reaching 1,100 mg L⁻¹ (Table 1). Such a large accumulation of gas is not possible in the carbonate Ca2 aquifer. However, it is possible in an insulated pocket in the A1d unit that has subsequently been opened up through a fracture created by mining or by seismic tremor. However, H₂S during migration is usually subjected to processes changing its concentration in groundwater, such as precipitation, degassing and re-dissolution.

This interpretation, due to limited dataset discussed, is treated as a preliminary study for more advanced research – including isotopic, mineralogical and microbiological studies – on the origin of H₂S in the deposit zone of the LGCB which, due to the specificity of the area affected by mining, should be regarded as of high priority. Further studies on the origin of H₂S should include genetic consideration of the likely processes responsible for its generation, which is crucial in the light of the threat posed by the occurrence of this gas.

CONCLUSIONS

Based on the interpretation of the results of hydrochemical analyses of groundwater samples in relation to geological and hydrogeological conditions in the LGCB, the following conclusions were drawn:

1. The main source of H₂S in groundwater in the LGCB area is most likely the Zechstein Main Dolomite strata. Another, local, source of H₂S is organic matter-rich anhydrites of the PZ1 cycle.
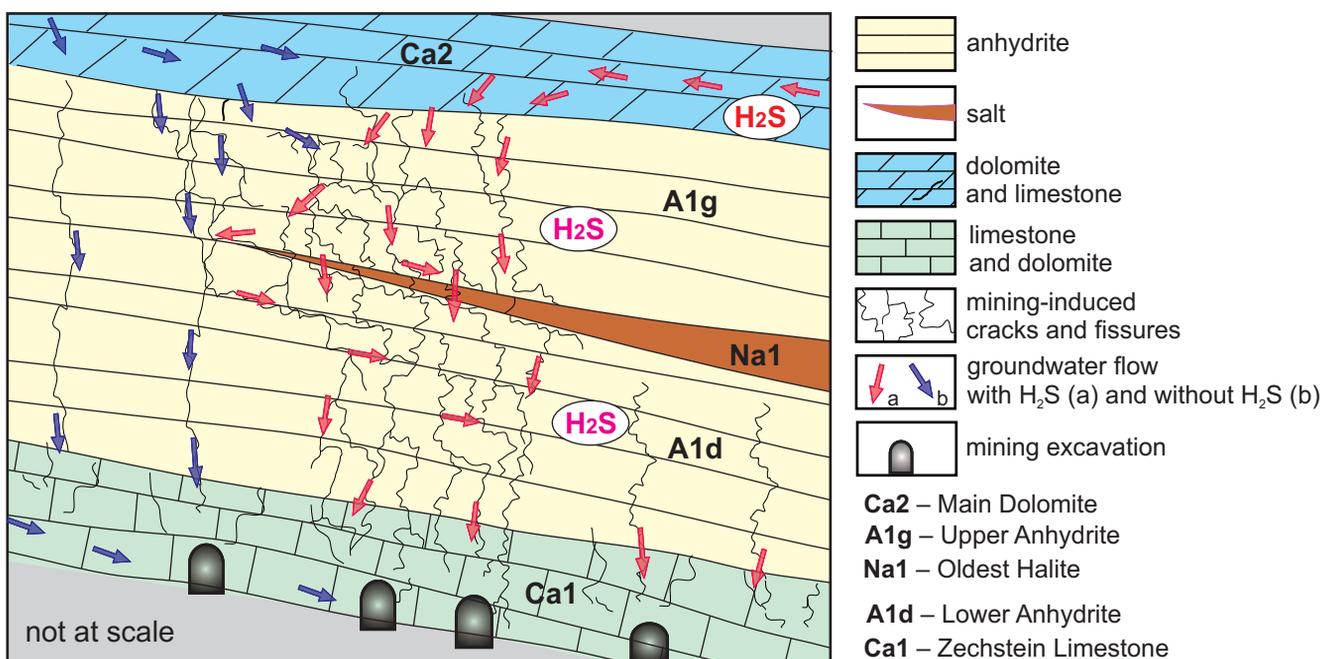
**Fig. 6. Conceptual model of hydraulic connection of Ca2 with Ca1 and groundwater flow
through fissures in the anhydrites (A1d, A1g) and Na1**

2. The effects of deep mining operations may lead to inevitable changes in hydrogeological conditions. In some cases, these changes may have a large spatial range propagating from the exploited deposit.

3. It is advisable to take into account the geological conditions, including gas conditions, in the further vicinity of the deposit already at the stage of exploration of raw material deposits. Gas migrating in aquifers and through mining-induced cracks and fissures may cause potential risk to mining staff. Therefore the spatial extent of exploration and analysis of the effects of deposit exploitation should be supra-local, especially if hydrocarbon gas accumulations are located in a given region.

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