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Technical Article

Ground Water in Abandoned Mercury Mines: A Study from the Saar-Nahe Basin in Southwestern Germany

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Abstract. The abandoned Lemberg and Königsberg mines extracted mercury ore from the Saar-Nahe Basin in southwestern Germany. Mining ceased more than 70 years ago. Different hydrochemical types of mine- and ground water can be distinguished. Extremely acid water or high mercury concentrations are restricted to isolated insignificant local seepage, and so no negative environmental effects are anticipated. In fact, the underground Königsberg Mine has developed into an important potential water resource for the local area.

Key words: abandoned mercury mining, environmental effects, mine water, Saar-Nahe Basin, water resources

Introduction

There are a large number of previously mined mercury deposits in the Nordpfälzer Bergland area and the Saar-Nahe Basin. Although not as extensive as Idrija and Almanden, these were some of the most important mercury deposits of Europe. Obermoschel, Stahlberg, Wolfstein, Potzberg, Lemberg, Münsterappel, Orbis-Kirchheim-Bolanden and Mörsfeld-Niederwiesen-Kriegsfeld have all been centres of mining (Figure 1). After several hundred years of operation, mining ceased in 1942. Altogether, more than 180 abandoned mines are known (Neuhaus 1994).

The ore deposits are hosted by Permian rhyolithic vulcanites. The mineralization was dominated by HgS, though Hg^{o} and other primary metal sulphides are also present. During the development of the deposits, highly mineralized water ascended along fractures and altered the sediments and porous rocks for several metres on both sides of the fault zones.

Hydrogeological and hydrochemical investigations were made at the Schmittenstollen Mine (Lemberg) and the Königsberg mines near Wolfstein (Figure 1). The examined pits were closed down more than 70 years ago. The aim of the studies was to interpret the most important hydrogeochemical reactions, to develop strategies to control the mercury concentrations of the mine water, and to determine the environmental effects of the mines.

The Saar-Nahe Basin is mostly rural, with numerous small villages and single dwellings. The Glan and Nahe Rivers have eroded a wide valley and drain the area to the Rhine. Precipitation averages only about 500 mm/year. The geology consists of Carboniferous and Permian sedimentary and volcanic rocks. The rhyolitic massifs of the Königsberg (6 km^2) and the Lemberg (3 km^2) are wooded and rise about 300 m above the surrounding area.

The Schmittenstollen mercury mine

The Lemberg deposit, near Bad Münster am Stein, consisted of three important mercury ore veins: the Martinszug, the Treue Zuversichtszug and the Schmittenzug, which was investigated. The ore was mined by the upper Schmittenstollen and by the deeper Karls-Glück-Stollen (Figure 2). The tunnels are connected by a shaft with a depth of about 60 m. Ground water drains from the Karls-Glück-Stollen level at rates up to 2 L/sec. The adits under the drainage tunnel are flooded. In the unsaturated zone of the mine, the infiltration rate is very low. In the Schmittenstollen, there were only 2 locations where the seepage water could be sampled (P 201, P 309). In the mined vein area along the shaft, 3 small pools with dammed water were found (P 202-P 204). In contrast to the upper levels, the drainage tunnel is characterised by intensive water flow. The walls are covered by crusts of carbonates and amorphous FeOOH. Seepage, ground and mine water collect and flow in a channel on the tunnel floor (P 205-P 208). In addition to these analysed samples, other samples, collected at small seeps, were investigated for pH and conductivity. Three different types of ground and mine water can be distinguished.

The Schmittenstollen water is nearly neutral or mildly alkaline and has only a low salt content. The sums of the total dissolved solids (TDS) range from 3 to 3.6

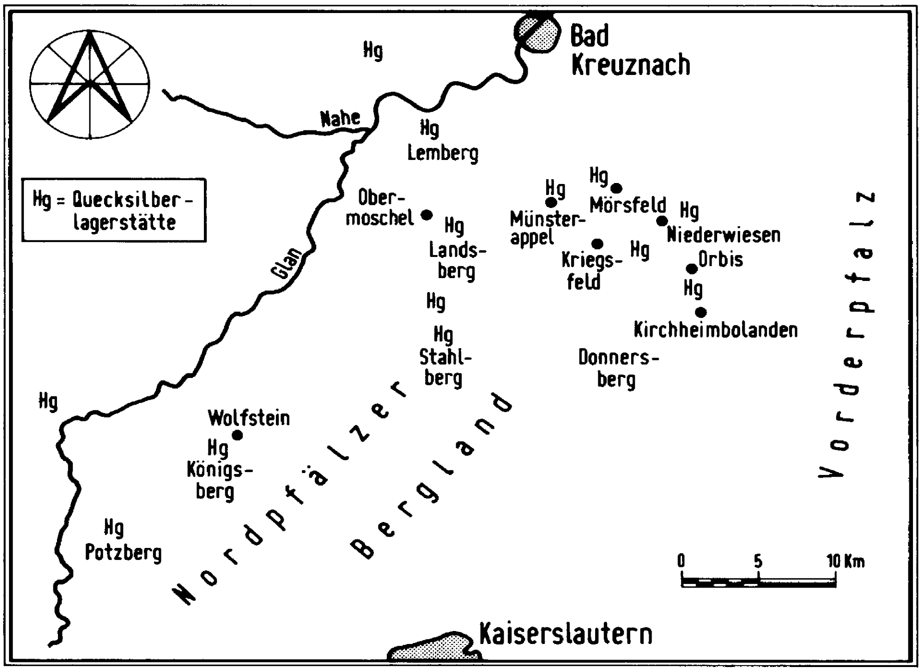

Figure 1. Mercury deposits of the Saar-Nahe Basin

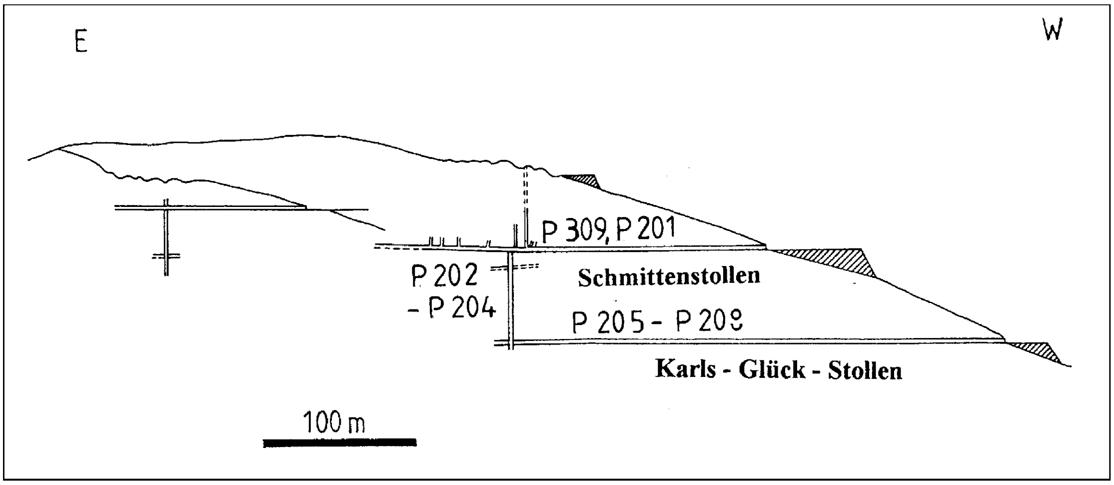

Figure 2. Cross section of the Schmittenstollen mine, Lemberg (Wieber 1999)

mmol(eq)/L. The water of P 201 is bicarbonate dominated; in P 309, sulphate dominates (63 ceq-%). The trace elements were analysed and determined to be at low concentrations (Table 1).

The water leakage of the mined area along the shaft is significantly more mineralized. TDS ranges from 14-24 mmol(eq)/L. Most pH values are alkaline. Only the mine water of location P 202 [on the Schmittenstollen level] was acid [pH: 3.9 and 4.4]. The dissolved anions consist mainly of sulphate (>70 ceq-%). Mercury could not be detected. The concentrations of Ba, Pb, Cr and Co were low. The mine water of P 203 and P 204 had low levels of Al, Cd, Fe, Cu, Ni, and Zn. These parameters are significantly more concentrated in the acidic water of P 202. The elevated levels of sulphate and acidity indicate that oxidation of sulphides continues. The H^+ ions have been buffered by clay minerals, Al-hydroxides, and Fe-oxides. The result of these reactions is the mobilisation of Al, Fe, and other ions.

The third type is the water of the Karls-Glück-Stollen. It has an alkaline pH and its TDS ranges from 13-15 mmol(eq)/L. HCO_3^- is the predominant anion (> 66 ceq-%). Due to the high pCO_2 of the drained upwelling groundwater and the atmospheric pCO_2 of the air of the tunnel, $CaCO_3$ crusts have developed on the walls and the water surface. As $CaCO_3$ precipitates, the ratio of Ca/Mg becomes <1. The concentrations of the trace elements are low (Table 1). The Fe concentrations exceed 1 mg/L.

The saturation indices (SI) of the different types of mine water (Table 2) were calculated by PHREEQC (Parkhurst and Appelo 1999). Important geochemical reactions include the dissolution of siliceous minerals, plagioclase (albite, anorthite) and K-feldspar (partly). The decay of feldspars mobilizes Al ions, and gibbsite [Equation 1] is generated [SI: –0.17 to +2.70]. The dissolution of silica causes gibbsite to dissolve and the minerals kaolinite [Equation 2], Ca-montmorillonite, and illite to form [SI> 0, Table 2]. For the ground water at the end of the drainage tunnel (P 205), oversaturation of chlorite (SI 2.64) and talc (SI 1.28) is indicated. The calculations for the other mine waters indicate negative saturation indices of these minerals. Intensive decomposition of the rocks and the genesis of clay minerals can be recognised all over the mine.

$$KAlSi_3O_8 + 7H_2O + H^+ \Rightarrow Al(OH)_{3(s)} + K^+ + 3H_4SiO_4 \quad (1)$$

$$Al(OH)_{3(s)} + 2H_4SiO_4 \Rightarrow Al_2Si_2O_5(OH)_4 \quad (2)$$

The mine water of the upper levels is undersaturated in carbonates. On the other hand, the upwelling groundwater of the flooded shaft and some cross cuts of the drainage tunnel is oversaturated in carbonates (Table 2). Carbonate crusts sometimes develop on the surface of the stagnant water.

The water of the non-flooded part of the mine is oversaturated with iron oxides and hydroxides due to the atmospheric environment. An exception is the acid mine water (P 202), with calculated saturation indices <0. The concentrations of aluminium are limited by the precipitation of secondary minerals like alunite and gibbsite (Table 2). Negative SI

Table 1. Chemical quality of the mine water

	Schmittenstollen (upper tunnel)	Mined vein area along the shaft	Karls-Glück-Stollen (drainage tunnel)
Drain [l/sec]	< 0.01	< 0.01	1.0
T [°C]	11.6 – 13.2	9.0 – 11.0	11.6 – 14.1
pH	7.3 – 8.0	3.9 – 8.2	7.1 – 8.3
Eh [mV]	240 – 301	106 – 466	0 – 255
Conductivity [µS/cm]	156 – 290	674 – 1459	886 – 1125
O_2 [mg/L]	6.2 – 9.6	3.9 – 6.1	0.7 – 7.5
CO_2 [mg/L]	2.2 – 6.1	n.n. – 6.6	1.7 – 79
Ca [mg/L]	18.0 – 24.0	111 – 129	18 – 54
Mg [mg/L]	3.9 – 4.0	55 – 57	39 – 71
Na [mg/L]	4.6 – 4.8	7.7 – 8.7	9.8 – 22.4
K [mg/L]	1.9 – 3.5	4.5 – 7.2	2.8 – 6.6
NH_4 [mg/L]	< 0.05 – 0.81	< 0.05 – 0.76	< 0.05 – 0.58
Si [mg/L]	3.6 – 8.3	0.64 – 3.4	2.4 – 3.1
Cl [mg/L]	5.8 – 12.5	8.5 – 9.6	11.7 – 14.3
SO_4 [mg/L]	15.5 – 52.2	376 – 497	44.7 – 121
HCO_3 [mg/L]	17.3 – 62.5	3.8 – 145	300 – 350
NO_3 [mg/L]	0.38 – 3.1	4.5 – 18.7	< 0.1 – 9.5
Al [µg/L]	160 – 220	3.0 – 12700	30 – 100
Sb [µg/L]	4.0 – 6.0	2.0 – 210	2.0 – 7.0
Ba [µg/L]	95 – 210	11 – 18	17 – 46
Pb [µg/L]	3.7 – 6.4	4.8 – 7.6	2.7 – 5.0
Cd [µg/L]	< 0.1	< 0.1 11	< 0.1
Cr [µg/L]	0.34 – 0.78	0.43 – 1.4	< 0.1 – 4.1
Co [µg/L]	< 2.0	< 2.0	< 2.0
Fe [µg/L]	390 – 400	100 – 2110	1300 – 2500
Cu [µg/L]	9.0 – 14	8.0 – 42	5.0 – 9.0
Mn [µg/L]	13 – 14	4.0 - 10200	28 – 104
Ni [µg/L]	2.0 – 3.0	2.0 – 46	1.0 – 36
Hg [µg/L]	0.26 – 2.6	< 0.05	< 0.05 – 0.96
Sr [µg/L]	55 – 79	130 – 170	327 – 626
Zn [µg/L]	10 - 40	6.0 - 730	< 6.0 – 10

Table 2. Saturation indices (SI) of the mine water

Mineral groups	Minerals	Schmitten-stollen		Mined vein area along the shaft		Karls-Glück-Stollen	
		min.	max.	min.	max.	min.	max.
SiO_2 modifications	Chalcedony	-0.18	0.19	-0.90	-0.17	-0.36	-0.25
	Quartz	0.29	0.66	-0.41	0.32	0.12	0.22
	$SiO_{2(a)}$	-1.07	-0.70	-1.79	-1.06	-1.24	-1.14
Silicates	Albite	-1.65	-0.67	-7.35	-4.22	-2.55	-1.67
	Anorthite	-1.38	-084	-12.7	-3.73	-3.38	-2.21
	Ca-Montmorillonite	5.40	6.64	-2.16	1.00	1.66	3.57
	Illite	4.41	5.33	-5.22	0.60	1.72	2.86
	K-feldspar	0.74	1.43	-5.04	-1.77	-0.27	0.29
	K-mica	11.7	12.3	0.13	7.51	7.66	9.70
	Kaolinite	6.74	7.40	1.03	3.68	3.43	5.43
Carbonates	Aragonite	-1.88	-1.31	-5.91	-0.17	-0.48	0.29
	Calcite	-1.73	-1.15	-5.75	-0.02	-0.33	0.44
	Dolomite	-4.08	-2.81	-11.7	-0.22	-0.55	1.40
	Rhodochrosite	-2.44	-1.81	-4.30	-1.92	-1.09	0.13
	Siderite	-4.62	-3.93	-5.43	-2.70	-2.20	0.47
Oxides/Hydroxides	$Al(OH)_{3(a)}$	-0.16	-0.12	-3.02	-0.97	-1.70	-0.62
	Alunite	0.34	1.29	0.08	3.46	-5.34	-0.04
	$Fe(OH)_{3(a)}$	3.13	3.15	-0.96	0.73	1.87	4.08
	Gibbsite	2.66	2.70	-0.18	1.88	1.11	2.22
	Goethite	9.02	9.04	6.62	8.66	7.76	9.98
	Hematite	19.0	19.0	14.0	18.1	16.5	21.0
	Jarosite-K	-1.82	-0.84	-1.13	2.27	-3.90	0.59
Sulphates	Gypsum	-2.77	-2.15	-0.97	-0.85	-2.41	-1.92
	Anhydrite	-3.02	-2.41	-1.23	-1.11	-2.66	-2.14

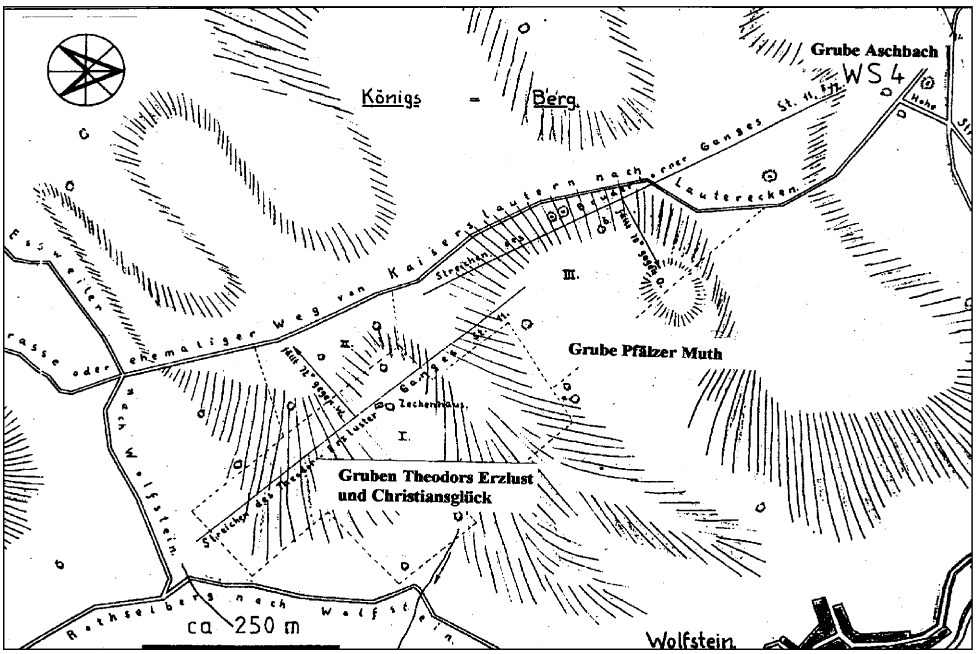

Figure 3. Historical map of the Königsberg mines near Wolfstein (1938, unpublished)

were calculated for gypsum and anhydrite, though water on the rock surfaces is oversaturated due to evaporation, and crystals of gypsum can be observed.

Initially, mining took place in independent pits: the Theodors Erzlust and Christiansglück Mines in the south, Pfälzer Muth in the middle of the area and Aschbach in the north (Figure 3). The Elias Tunnel connects the mines (Figure 4). Later, the Vereinigte Quecksilberbergwerke managed all the mines of the Königsberg. Besides cinnabar, barite was also obtained. Relics of the abandoned mining, like dumps, quarries and tunnels, are spread all over the rhyolite massif.

The mine water was sampled at the portals of the Eliasstollen (WS 3), the Tiefen Pfälzermuther Stollen (WS 1, WS 2), and the drainage tunnel (WS 4) of the Aschbach Mine (Figure 3). The water of the Tiefen Pfälzermuther Stollen flows through a pipe into the Eliasstollen. Therefore, the mine water of the Eliasstollen is a mixture of the two mine waters (Figure 4). Analytical results are shown in Table 3.

The saturation indices (Table 4) of amorphous SiO_2, albite, anorthite, (most) K-feldspar and carbonates are generally negative (indicating solution). The mine water of the Königsberg is nearly saturated to oversaturated relative to K-mica, Ca-montmorillonite, kaolinite and the iron- and aluminium-oxides and hydroxides, hematite, goethite, $Fe(OH)_{3(amorphous)}$, alunite and gibbsite (precipitation). The water is generally undersaturated in sulphate and non-ferrous metal minerals. The barium concentrations are limited by the solubility of barite (SI 0.54-1.38). The mines are not accessible because they are used as drinking water reservoirs. The abandoned pits, tunnels, shafts and mined veins drain the whole massif. Natural springs do not exist.

Table 3. Chemical quality of the mine water of the "Königsberg"

	Tiefer Pfälzermuther tunnel	Elias tunnel	Drainage tunnel Aschbach Mine
Number	WS 1. WS 2	WS 3	WS 4
Drain [l/sec]	ca. 2	ca. 8	ca. 5
T [°C]	9.7 – 11.9	9.5 – 10.0	9.3
pH	5.6 – 5.8	4.9 – 5.8	6.1
Eh [mV]	254-320	210 – 258	315
Conductivity [µS/cm]	83 – 118	76 – 101	212
O_2 [mg/L]	6.8 – 8.3	7.4 – 8.4	3.1
H_2CO_3 [mg/L]	15.4 – 45.7	14.3 – 35.8	24.8
Ca [mg/L]	5.2	4.2 – 4.5	7.2
Mg [mg/L]	2.2	1.3 – 1.8	2.9
Na [mg/L]	7.1	5.0 – 5.8	6.0
K [mg/L]	2.6	1.7 – 2.3	1.5
NH_4 [mg/L]	1.0	0.78 – 0.85	0.96
Si [mg/L]	13.1	8.8 – 11	8.4
Cl [mg/L]	3.5	4.2 – 5.4	3.9
SO_4 [mg/L]	13	15 – 20	21
HCO_3 [mg/L]	18.5	2.0 – 14.2	15
NO_3 [mg/L]	5.5	4.0 – 6.4	8.1
Al [µg/L]	42 – 64	60 – 289	88
As [µg/L]	< 5.0	< 5.0	<5.0
Ba [µg/L]	304 – 340	244 – 260	231
Pb [µg/L]	< 2.0 – 2.2	2.0 – 5.1	2.4
Cd [µg/L]	< 0.1	0.3	< 0.1
Cr [µg/L]	0.22 - 0.36	< 0.1	0.25
Co [µg/L]	< 2.0	< 2.0	< 2.0
Fe [µg/L]	134 – 141	169 – 332	23
Cu [µg/L]	< 10	10 – 15	12
Mn [µg/L]	1.0 – 47	43 – 62	3.0
Ni [µg/L]	< 1.0 – 1.0	< 1.0 – 1.0	6.0
Hg [µg/L]	0.07 – 0.09	0.14 – 0.41	0.05
Sr [µg/L]	29 – 54	32 – 45	21
Zn [µg/L]	49 - 50	121 – 131	41

Table 4. Saturation indices of the mine water "Königsberg"

Mineral groups	Minerals	Mine water of the drainage tunnels of the Pfälzer Muth, Aschbach and Theodors Erzlust and Christiansglück Mines variation	
		min.	max.
SiO_2 modifications	Chalcedony	0.22	0.41
	Quartz	0.70	0.89
	$SiO_{2(a)}$	-0.68	-0.49
Silicates	Albite	-5.58	-1.86
	Anorthite	-11.7	-4.18
	Ca-Montmorillonite	-0.08	5.92
	Illite	-3.28	3.66
	K-feldspar	-3.52	0.08
	K-mica	2.23	10.6
	Kaolinite	2.41	7.18
Carbonates	Aragonite	-7.63	-4.11
	Calcite	-7.48	-3.95
	Dolomite	-15.3	-8.20
	Rhodochrosite	-6.94	-3.95
	Siderite	-6.34	-3.81
Oxides/Hydroxides	$Al(OH)_{3(a)}$	-2.72	-0.33
	Alunite	0.49	3.78
	$Fe(OH)_{3(a)}$	-5.48	1.17
	Gibbsite	0.11	2.51
	Goethite	0.41	7.06
	Hematite	1.63	14.9
*	Jarosite-K	-20.1	-1.43
Sulphates	Gypsum	-3.30	-2.44
	Anhydrite	-3.56	-2.70
	Barite	0.54	1.38

Environmental effects and conclusions

Because of the abandoned underground mines, groundwater is lowered to the level of the drainage tunnels. For that reason, the upper part of the mine is relatively dry and different types of mine water develop: two types in the unsaturated zone, beyond sulphide veins and in the area of sulphide minerals and one additional type of mine water in the saturated zone (II). The compositions of the differentiated hydrochemical types are shown in Figure 5.

The geochemical environment of the unsaturated zone is aerobic. Nearly neutral, slightly mineralized alkaline-earth seepage water (Lemberg P201, P 309) develops. However, near the mined and backfilled sulphide veins, acid drainage is produced by the exposure of certain sulphide minerals to air and water, resulting in the production of acidity and elevated concentrations of metals and sulphate. Acid-consuming minerals can neutralise the water.

At the Schmittenstollen, most of the analysed samples have nearly neutral or alkaline pH. Extremely acid water is restricted to isolated, insignificant local seepage flows (Lemberg P 202). Altogether, the acid-consuming capability exceeds the acid-generating capability of the water draining from the rocks of the Lemberg. Additionally, the acid-producing sulphides are largely coated by iron oxides or hydroxides.

The mine water of the drainage tunnels consists mainly of upwelling groundwater, with contributions of seepage water from the unsaturated zone. The hydrochemical composition depends on the local/regional geological and hydrogeological situation. The water of the Schmittenstollen (Lemberg) is a nearly neutral or alkaline, highly mineralized alkaline-earth HCO_3-dominated mine water. In contrast, the Königsberg mine water is acidic and slightly mineralized.

The Hg concentrations of the two investigated mines are different. The Hg concentrations in most (70%) of the analysed samples of the Schmittenstollen pit were below the detection limit of 50 ng/l. Higher concentrations (260 ng/l-2600 ng/l) were restricted to isolated insignificant local seepage flows. Only one seepage water sample had a Hg concentration above the limiting value of the German Trinkwasserverordnung (1991) of 1 µg/L.

In contrast, all analysed water samples of the Königsberg had detectable Hg (50-410 ng/l). This corresponds to the higher Hg concentrations of uncontaminated ground water in Baden-Württemberg (Koch 1989; Merkel and Sperling 1998), in southern Germany. Up-gradient of the mine openings, the mine water of the Elias and the Aschbach Mine drainage tunnel infiltrates into dumps and then emerges below. Mercury was not detected in these samples, presumably due to vaporization.

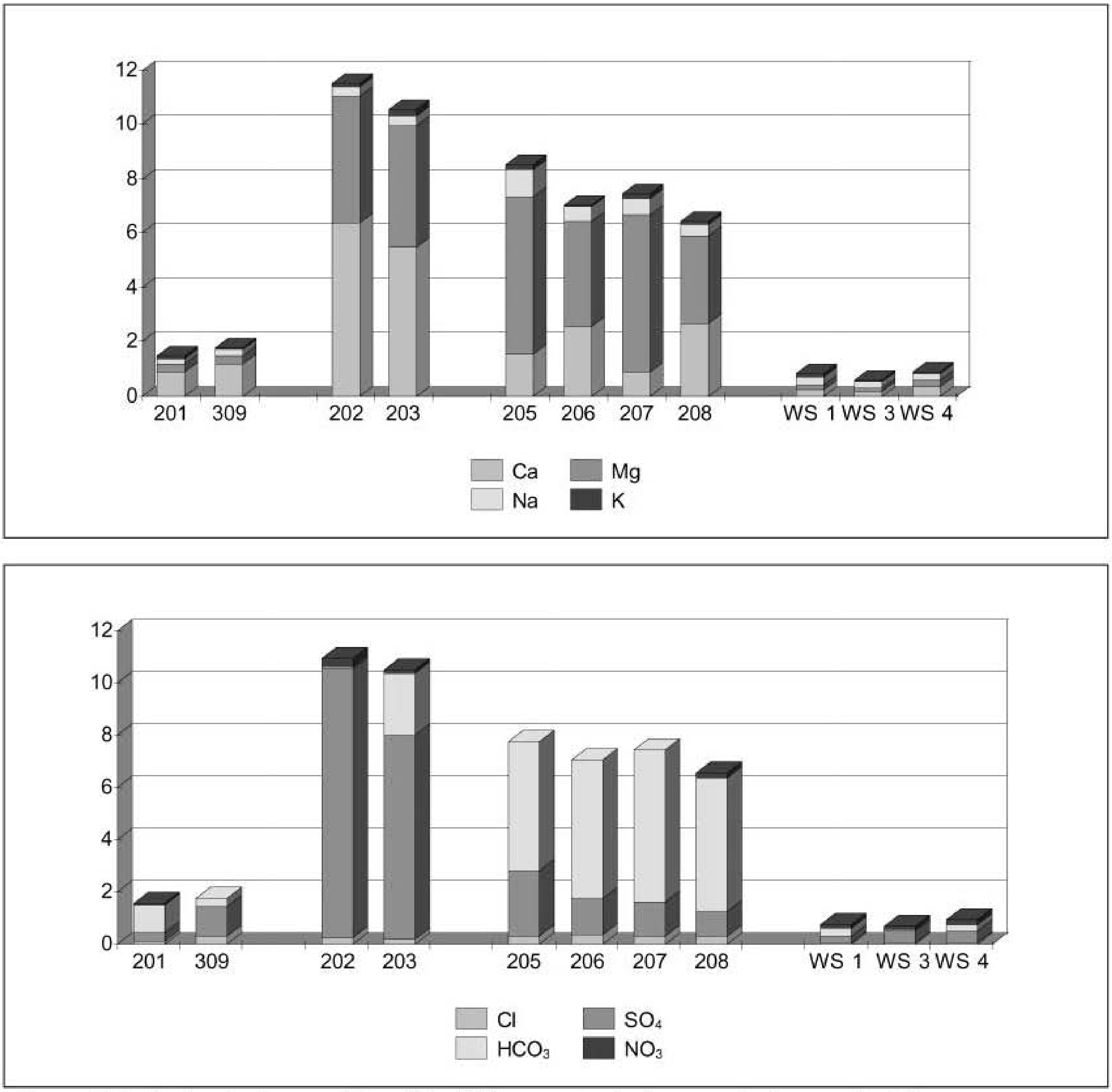

Figure 5. Hydrochemical composition of the different types of mine water (units: mmol(eq)/L)

No serious damage to ground and surface water was observed. In contrast, Dizdarevic and Rezun (1998) describe contamination of surface water up to 1140 ng/l Hg caused by discharges from the Idrija Mine (Slovenia).

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