HYDROCHEMISTRY OF MINE WATER DISCHARGES IN THE ABANDONED UPPER BAVARIAN PITCH COAL MINING DISTRICT/GERMANY

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ABSTRACT

Upper Bavaria hosts several dozen of abandoned underground pitch coal mines where mine water is discharging into the receiving steams. First mining activities in the Upper Bavarian pitch coal district date back to the end of the 16th century, but industrial coal mining started in the 19th century. In 1971 the last remaining pitch coal mine in Peißenberg closed after having produced 40 Mt of coal. None of the mine water discharges is currently treated and since its closure no scientific investigations have been conducted. The paper describes the location of the abandoned coal mines and the results of water analyses at 17 mine water discharges. At all locations also the flow was measured, which ranges between 1 and 2100 L/min. Because the coal mines are located in carbonate rich host rocks most of the sites cause no visible environmental impact to the receiving streams. Most of the pH-values range between 6.7 and 8.3 and therefore are an indication for the well buffered discharge waters. Electrical conductivities reaches values of up to 4.9 mS/cm and at least 6 discharges cause a local negative impact to the receiving streams. The most problematic discharge is that of the Friedrichstollen with a flow of 2 m³/min, an electrical conductivity of 4.9 mS/cm and an iron concentration of 13 mg/L. In general, all waters are Ca bi-carbonate waters with some Ca-Mg sulphate waters.

1. INTRODUCTION

In the southern part of Bavaria several dozen underground pitch coal mines have been mined on an industrial scale between the 19th and the 20th century (BALTHASAR 1975, ZORN 1981/1982). Yet, first reports of coal mining date back as early as the 16th century, but their use has been locally restricted (SCHMITZ 1840, BALTHASAR 1975). Due to political and economical reasons the Bavarian Government and the mine operators in the 1960ies decided to close down the remaining mining operations and consequently the last Bavarian pitch coal mine at the Hohenpeißenberg closed in 1971 (JUNCK 1975). During the industrial mining period, a total of 100 Mt has been mined and another 10–100 Mt of reserves is assumed to be available (SCHMID & WEINELT 1978).

Intensive geological investigations revealed that the coal is of tertiary age and that it was deposited in a near costal lacustrine environment. During the alpine orogenesis the deposits were folded and deeply buried under younger molasse sediments. Today the coal can be found in seven synclines of which the Peißenberg, Penzberg, Nonnenwald, Hausham and Miesbach synclines were the most productive ones with up to 31 coal seams of which more or less eight were mined (Figure 1; SCHMID & WEINELT 1978). All deposits can be found in the Faltenmolasse (folded molasses), a sequence of molasse sediments dominated by sandstones, carbonates, and marles (HARTMANN 1938). From its genesis, pitch coal is classified as lignite (AMMON 1909), but due to the orogenic processes the heat content equals that of a subbituminous coal. Total sulphur contents, of which ¹/₃ is pyrite sulphur, typically range between 5 and 7 % (GEISSLER 1975) and can be as high as 10 % (TEICHMÜLLER & TEICHMÜLLER 1975).

Since their closure the mines where allowed to flood and eventually discharged into the receiving streams within the Upper Bavarian foothills of the Alps. All mine water discharges are originating from dewatering adits which were also used during the active mining period. Several discharge locations of long abandoned mines are today hidden under vegetation and access is sometimes severely limited. Currently, none of the mine water discharges is treated or regularly monitored. Furthermore, the ownership of the mine water discharges seems to be somehow unclear. For most of the mines, the mining rights are owned by E.ON Bayern, but the dewatering adits are either used by historical mining associations or are located on private property. Because the mines are abandoned, the responsibility for the mine water, according to the German mining legislation, is by the owners of the property where the mine water discharges.



Figure 1. Location of the Southern Bavarian coal mining district south of Munich. Main locations: circles with red and orange crosses; the main syncline hosting the coal deposits is marked in brown.

2. METHODS

No database of Bavarian mine water discharges exists. Therefore, historical records of the southern Bavarian pitch coal mining district had to be studied to locate potential mine water adits (e.g. SCHMITZ 1840, HERTLE 1898, KORSCHELT 1890, records of the Bavarian State Archive and the Southern Bavarian Mining Authority). Based on the historical investigation, 44 abandoned mines in six of the seven synclines could be located and were visited in spring and summer 2008. Out of those 44 locations, 17 had mine water discharges and samples could be collected. At each of those 17 sites, the on site parameters (pH, redox potential, temperature, electrical conductivity, oxygen content, flow) were measured with a *MYRON* L Ultrameter 6P or WTW electrodes (CellOx 325, SenTix 91T, TetraCon 325) attached to a WTW multiline P4. Furthermore, a 500 mL water sample for the main ions and a 50 mL, acidified sample for the trace element analyses were taken. Base and acid capacity were analysed on site, using a WTW pH probe and the HACH digital titrator.

In the lab, main ions were analysed with a Perkin Elmer AAS 3300 (Na⁺, K⁺, Ca²⁺, Mg²⁺) and DIONEX-IC-DX-100 (F, Cl⁻, NO₃⁻, SO₄²⁻). Trace elements were analysed using a Perkin Elmer AAS 3300 (Fe, Mn, Zn, Al, Na, Sr) and a Perkin Elmer SIMAA 6000 (As, Cd, Cu, Ni, Pb, Cr, Co). Based on the results, the ion balance ranged between +6 and -10 % with a mean of -3 %. The negative ion balance might be due to two factors: the missing Li and Si analyses, as WAGNER *et al.* 2003 shows Li and Si values of 0.8—6 µg/L (10 and 90 % quartiles) and 0—3 mg/L (10 and 90 % quartiles) respectively and an over determination of the bicarbonate. Yet, a statistical investigation could not identify a potential error. If we assume an analytical error of +/- 5 % for all analyzed ions, we get a reasonable error range of +1 to -5 %, which indicates that the analyses seem to be correct.

All chemical analyses were thermodynamically modelled with PHREEQC (Version 2.15.0.2697) and the WATEQ4F database.

3. RESULTS AND DISCUSSION

Electrical conductivities of the mine waters range between 407 and 4884 μ S/cm with a mean of 1458 μ S/cm (Table 1) and therefore significantly exceed the maximum electrical conductivity of 207 μ S/cm reported for the hydrogeological subunit (Faltenmolasse) in which the mines occur (WAGNER *et al.* 2003). Also the temperature is slightly increased (a mean of 10.8 °C compared to 8.4 °C), whereas the pH shows no deviation from the normal hydrogeological situation (7.48 compared to 7.45). Those data are a clear indication for an alteration compared to the normal hydrogeological situation in the subunit.

Table 1. Water chemistry of the investigated southern Bavarian mine water discharges. EC: electrical conductivity; Fe is total iron filtered; n.n.: not detected or below detection limit. Statistical values exclude missing data or data below the detection limit.

Bezeichnung	T, °C	рН,	EC,	рE	Fe,	Na,	K,	Ca,	Mg,	Sr,	Ba,	HCO3,	Cl,	SO4,	NO3,	F,	As,
Friedrichstollen	14.5	6.68	/ 99/cm	nn	12.61	620 0	30.7	207	117 /	111g/L	0.22	850	12.8	2 22/	n n	1.2	μ <u>β</u> / L
Wassarstallan	11 5	0.08	4,004	n.n.	12.01	204 5	50.7	404	117.4	0.5	0.22	630	13.0	1 004	6.0	1.2	12.0
	11.5	7.24	3,474	11.11.	0.95	304.5	00.9	404	115.5	0.0	0.22	052	97.8	1,004	0.0	0.0	15.0
Pelisenberg Herstollen	16.8	7.13	3,200	2.81	0.11	351.8	16.7	342	92.8	8.5	<0.6	837	22.3	1,640	1.5	0.7	6.4
Peißenberg Mittelstollen	12.0	7.10	2,480	3.06	5.13	165.8	10.8	406	91.2	8.6	<0.6	577	12.6	1,543	n.n.	0.5	<3.8
Marienstein Halde	10.2	8.34	2,409	7.10	0.06	83.5	195.0	217	101.9	2.8	0.22	155	2.5	1,261	29.0	0.9	<2.4
Peißenberg Sulzer Stollen	8.5	7.60	1,007	4.56	0.05	15.6	2.3	147	41.5	1.4	<0.6	350	7.2	286	1.5	0.2	<3.8
Achtalschacht (lab results)	24.4	7.06	908	n.n.	< 0.05	113.1	4.2	65	21.9	1.0	< 0.1	n.n.	6.4	49	n.n.	0.7	< 2.1
Alter Auer Erbstollen	n.n.	7.47	849	2.75	<0.05	24.6	2.8	119	30.1	1.1	0.64	495	23.3	12	0.9	0.3	<2.4
Phillippstollen	9.4	7.12	773	n.n.	0.33	28.0	3.9	111	21.8	1.0	<0.2	333	8.8	94	1.4	0.3	<2.4
Auer Hauptstollen	9.9	7.10	748	1.86	0.25	22.7	2.5	106	23.7	1.0	<0.2	461	5.3	17	0.3	0.3	<2.4
Kemathstollen	9.6	7.75	675	5.21	0.06	7.9	2.6	106	24.6	0.9	0.38	431	10.8	14	0.4	0.2	<2.4
Marienstein Marienstollen	7.2	7.72	634	4.01	< 0.05	23.6	2.0	81	21.0	0.6	< 0.1	326	6.7	76	4.4	0.2	< 2.1
Deisenrieder Stollen	8.4	7.74	612	10.33	0.04	4.9	1.0	92	21.5	0.4	<0.6	398	3.8	25	6.4	0.2	<3.8
Eckersberger Stollen	7.4	7.71	603	5.83	<0.05	3.2	0.8	97	20.0	0.4	0.45	325	2.3	32	17.3	0.2	<2.4
Peißenberg Hauptstollen	8.0	8.28	568	8.89	< 0.04	9.4	0.9	82	18.3	0.2	<0.6	389	19.0	15	7.8	0.2	<3.8
Bärenschützstollen	9.5	7.09	560	3.50	0.82	2.5	1.3	101	14.4	0.7	0.26	359	1.5	42	0.3	0.2	<2.4
Leitsachstollen Querschlag	5.3	8.08	407	n.n.	0.06	1.0	0.7	65	13.9	0.2	0.27	243	1.2	17	7.5	n.n.	<2.4
Means of the above	10.8	7.48	1,458	4.99	1.70	104.8	19.9	173	46.4	2.6	0.33	448	14.4	549	6.1	0.4	14.5
Standard deviation	4.6	0.47	1,325	2.62	3.72	170.3	47.7	128	38.8	3.3	0.15	193	22.6	815	8.1	0.3	8.5
min	5.3	6.68	407	1.86	0.04	1.0	0.7	65	13.9	0.2	0.22	155	1.2	12	0.3	0.2	6.4
тах	24.4	8.34	4,884	10.33	12.61	620.0	195.0	406	117.4	8.6	0.64	850	97.8	2,334	29.0	1.2	23.3

Based on the FURTAK & LANGGUTH classification (FURTAK & LANGGUTH 1967) within the PIPER diagram (Figure 2), 10 waters are normal earth alkaline waters predominantly bicarbonatic, 5 are earth alkaline waters with higher alkali amounts predominantly sulphidic (MST, MSH, BS4, TST, FST), 1 is a normal earth alkaline water bicarbonatic-sulphidic (PSS), and another one is an earth alkaline water with higher alkali amounts predominantly bicarbonatic (AR1). All the mine waters falling into the predominantly sulphidic category are at the same time characterized by electrical conductivities above 2 mS/cm and elevated trace element contents. Those waters, emanating from the Marienstein pile, Peißenberg Mittelstollen, Peißenberg Tiefstollen, Wasserstollen, and Friedrichstollen can therefore be described as classical mine waters. Their As mass concentration reaches up to 23 μ g/L, Cr 6 μ g/L, Ni 23 μ g/L, Cu 5 μ g/L, and Co 8 μ g/L.

pH values range between 6.7 (Friedrichstollen: FST) and 8.3 (Marienstein pile: MST). While the pH of the Friedrichstollen is clearly influenced by pyrite oxidation, the Marienstein pile shows an influence from basic processing chemicals. All other pH-values range between 7.1 and 8.3, thus being well buffered in the bicarbonate buffer range, which might be expected from the local geological situation.

During the field investigation in spring and summer, the flows from the dewatering adits ranged between 1 and 2100 L/min with a mean of 180 L/min. The largest flow is that of the Friedrichstollen (FST), discharging into the river Leitzach, being also the dewatering adit with the highest electrical conductivity, sulphate, arsenic, cadmium, and iron concentrations. Its annual load is 14 t of Fe, 26 kg of As, 14 kg of Ni, 4 kg of Cu and approximately 1 kg of the before mentioned elements.

During the field investigation local informants reported about "red" water near the abandoned Achthal shaft (AR1). This shaft's pit head has an elevation of about 550 masl (meters above sea level) and is connected to the Auer dewatering adit (AHS) which discharges 1.7 km to the North-East at an elevation of 510 masl. At both locations the mine water had a noticeable H_2S smell and a low redox potential (110–170 mV). Due to the fact that the mine water discharges at the pit head of the Achthal shaft, it might be assumed that the Auer dewatering adit is broken in. Should the pressure behind the blockade further increase, an outburst at the Auer dewatering adit with an ensuing pollution of the receiving brook might not be excluded.



Figure 2. PIPER (PIPER 1944, 1953) diagram of the 17 mine water discharges in the Southern Bavarian pitch coal mining district. The labels are meant as an indication for the total water chemistry, not the chemistry of the single samples.

There are no special discharge criteria for mine waters in Germany or Europe. Yet, according to the EU Water Framework Directive (EUROPEAN COMMISSION 2000) those mine water discharges are point sources that are locally polluting the receiving streams and should be treated accordingly. Compared to other abandoned mining areas, the pollution of the receiving streams is locally restricted as their total flow is large compared to the mine water discharges. Furthermore, the pH values and the buffer capacity are relatively high resulting in a fast precipitation of the iron oxihydrates and a co-precipitation of the other metals and semi-metals.

Nonetheless, the discharges cause a visible staining of the receiving streams (Figure 3) and at least in one case informants reported an outburst of the Friedrichstollen with a subsequent fish dying. Therefore, the local authorities should ensure that the mine waters are treated accordingly, if possible with passive treatment systems which would suit to the touristic region of Upper Bavaria.

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Figure 3. Mine water discharge of the Friedrichstollen into the river Leitzach.

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