Estimation of pyrite weathering in Lusatian lignite open cast mines using geochemical investigation methods

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Abstract

In this paper the procedure of geochemical investigations in Lusatian lignite open cast mines is described. It is distinguished between geochemical investigations in the forefront of the mine and in dumps. Geochemical investigations in the forefront focus on the sediments above the lignite seam. Investigations in the dumps determine the geochemistry in the complete overburden of the open cast mine. Investigations in the forefront serve two purposes: 1) to predict the geochemical composition of the dumps in the lignite open cast mines and 2) to estimate hydrogeochemical processes in drained aquifers surrounding the mines.

Based on the investigations in the forefront the mean content of pyrite, calcite and other geochemical parameters in the future dump is estimated. Furthermore the acidification potential may be predicted. These data are used in models of different spatial discretisation to estimate the pyrite weathering. These estimations are verified by geochemical investigations in the dump. In already existing dumps the effective pyrite weathering rate is estimated using the analysed sulphur species. Often the zones of primary and secondary pyrite weathering may be defined. For this case the rate of pyrite weathering can be quantified separately.

In dumps in the Lusatian lignite mines the mean pyrite content is between 0.05 and 0.5 mass-%. Recent investigations estimate a profile-averaged pyrite weathering rate between 6 % and 18 %. The pyrite weathering rate is about 5 % in the zone of primary weathering and mostly above 25 % in the zone of secondary weathering. The thickness of the zone of secondary weathering is between 5 and 40 meter.

Key words: acid-base-accounting, rate of pyrite weathering, lignite mining, geochemical investigation

1 Introduction

Lignite is a main primary energy source in Germany and from the recent point of view of energy still necessary. Mineable lignite seams can be found in Germany only in unconsolidated rocks of tertiary age between 50 and 400 meter below the terrain. The lignite is mined in open cast mines using excavators. Therefore it is necessary to dewater the open cast mine. Dewatering of the open cast mines is often realised by screen wells.

In the Lusatian lignite mining area the Tertiary is between 150 and 200 meter thick. In the tertiary profile terrestrial and marine sediments alternates (Nowel et al. 1994). It consists of a series of fine sands, silt, clay and lignite seams. Altogether there are five important lignite seams in the tertiary profile in Lusatia. Mainly the 2^{nd} Lusatian lignite seam (2. LFH) is mined.

In Quaternary there were three important glacial periods: the Elster, Saale and Weichsel glacial period. Typical sediments of the Quaternary are glacial till, glacial-limnic fine-sands, silt and clay as well as glacial-fluvial melt water sand and gravel. In the interglacial periods fluvial sand and gravel as well as peats and muds were deposited. The sandy-gravelly sediments are main aquifers. The thickness of the quaternary sediments ranges between a few meters at tertiary plateaus and more than 100 meters in Pleistocene channels. Deep channels intersect the 2. LFH and form the mosaic texture of the lignite mining area.

In the Lusatian open cast mines the lignite seams are excavated by conveyor bridges. Mostly, they consist of two chain-and-bucket excavators and a conveyor bridge. The conveyor bridge transports the overburden to the dump. In the open cast mine the disposal of the overburden is carried out in the open pit as inner dump. Due to the conveyor bridge technology the dumps have a three layered structure (fig. 1). At the base a dump consisting of non-cohesive material is prepared (base dump). Hereon the railway track of the conveyor bridge is located. The thickness of the base dump is between 10 and 20 meter. Above the main dump with a thickness between 40 and 65 meter follows, consisting of tertiary and quaternary material excavated by the conveyor bridge. It is a typical mixed soil dump. At the top a stacker dump is deposited to form the post-mining topography. Normally it consists of quaternary material free of pyrite or tertiary material with low pyrite get in the pre-cut of the mine. The stacker dump is usually between 10 and 30 meter thick.

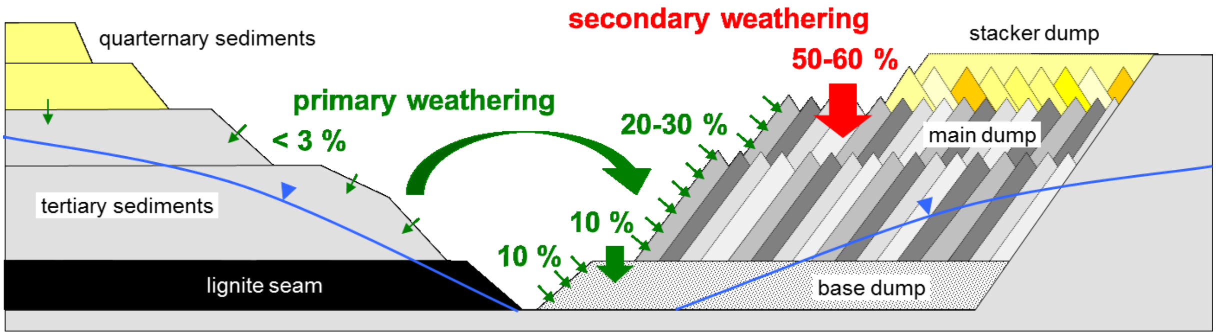

Figure 1 *Scheme of mining technology and dump structure in the Lusatian open cast mines and detailed information to rates of pyrite weathering*

Tertiary and quaternary overburden contains pyrite, which is mainly associated with organic and silty sediments. Low Pyrite is also contained in non-cohesive sediments. In contact with oxygen pyrite weathering occurs. This is the case during groundwater lowering as well as during exposure of the overburden in the open cast and in the dump. Depending on the geological and geochemical conditions groundwater chemistry is influenced by pyrite weathering e.g. by sulphate, metals and acidification.

Pyrite weathering can be distinguished into primary and secondary weathering. Primary weathering already begins during dewatering in the forefront of the mine. Furthermore primary weathering takes place at the temporary exposed work surfaces and slopes in mine and in dumps. At the dumps it ends by covering with new deposited overburden (fig. 1).

However, secondary weathering is more important. It takes place at long-term exposed surfaces at the top of the main dump and slopes. The depth as well as the rate of pyrite weathering is mainly determined by pyrite content and diffusion of oxygen. The latter one depends on time of exposure and on air permeability in the dump deposits. Secondary weathering normally ends by covering the main dump with a stacker dump, consisting of material free of pyrite or by groundwater rise. It is necessary to know specific rates of pyrite weathering to predict groundwater chemistry in dumps and to assess chemical balancing measures.

2 Methods

2.1 Geochemical investigations

Geochemical investigations in the forefront focus on the sediments above the lignite seam. Investigations in the dumps determine the geochemistry in the complete overburden of the open cast mine. Both investigations are realised by core drilling with liners DN80 to DN100. Liners studied geologically and geochemically. Laboratory investigations including determination of dry residue, loss on ignition as well as iron, carbon and sulphur content. Furthermore carbon and sulphur species are identified. Effective cation exchange capacity is determined at selected samples from the surrounding of the mines to estimate parameters for transport modelling. At samples from dump investigations the soluble substances are identified by water leaching tests. At the end of the year 2015 in total 35 drillings in the forefront and in the surrounding of Lusatian lignite mines as well as 25 drillings in dumps are geochemically investigated (fig. 2, tab. 1).

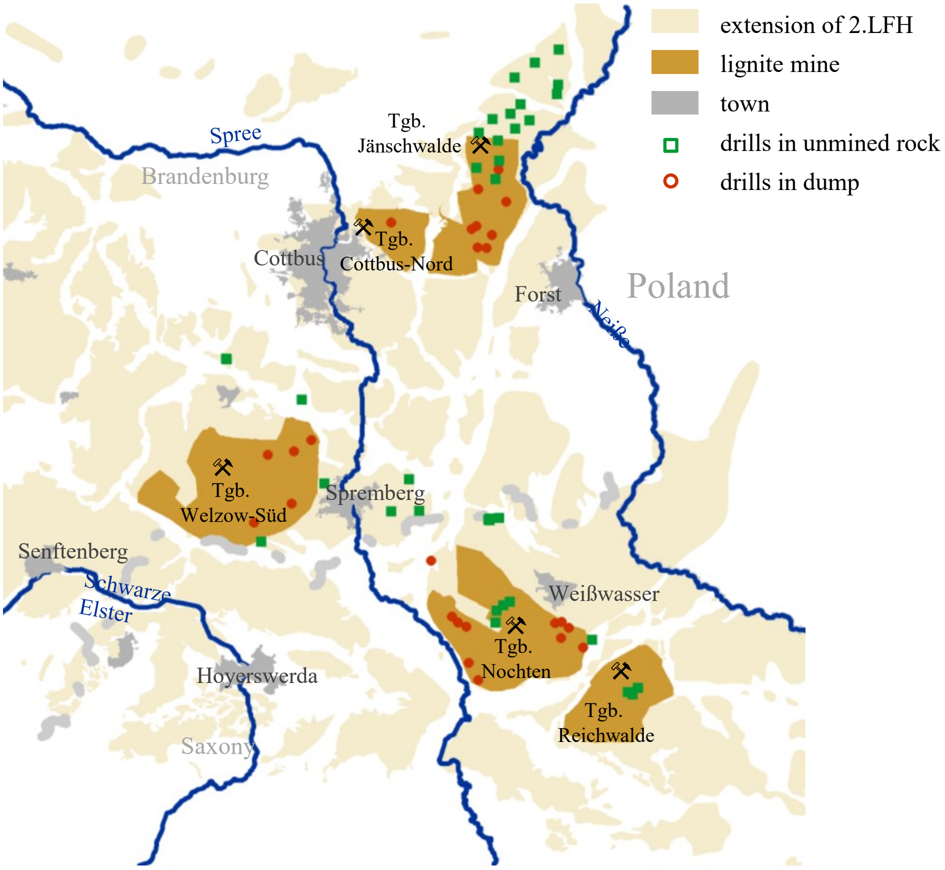

Figure 2 *Lusatian lignite open cast mines of the Vattenfall Europe Mining AG*

Table 1 *Number of geochemical investigations in Lusatian lignite mines*

Open cast mine	forefront and surrounding	Inner dump	Outer dump
Reichwalde	3	-	-
Nochten	12	10	1
Welzow-Süd	5	5	-
Cottbus-Nord	-	1	-
Jänschwalde	15	9	-

2.2 Acid-Base-Balancing

Balancing pyrite and calcite content may estimate the acidification potential as a worst case scenario, if the complete pyrite is weathered. At aerobic conditions 4 mole calcite per mole pyrite are necessary to buffer acids delivered by complete pyrite weathering at pH ≥ 7 (tab. 2). Anaerobic conditions requires half of calcite, however, ferrous iron remains in the groundwater. Discharge into surface water may oxidise ferrous iron and causes acidification of open pit lakes as well as sedimentation of iron ochre in water courses. The acid-base-balancing of the sediments is evaluated as follows (tab. 3).

Table 2 *Pyrite weathering and calcite buffering depending on oxygen conditions*

Pyrite weathering	Calcite buffering
anaerobic conditions	
$FeS_2 + \frac{7}{2}O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+$	$2H^+ + Fe^{2+} + 2CaCO_3 \rightarrow 2HCO_3^- + 2Ca^{2+} + Fe^{2+}$
Aerobic conditions	
$FeS_2 + \frac{7}{2}O_2 + \frac{1}{2}H_2O \rightarrow Fe^{3+} + 2SO_4^{2-} + H^+$	
$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+$	$4H^+ + 4CaCO_3 \rightarrow 4HCO_3^- + 4Ca^{2+}$

***Table 3** Classification of acid-base-balancing*

Molar ratio of calcite to pyrite	class
≥ 4	buffered
2 … 4	partially buffered
≤ 2	potentially acidic

2.3 Rates of pyrite weathering

The rate of pyrite weathering may be estimated on the basis of the ratio of sulphate-sulphur and the sum of inorganic sulphur:

$$r_{\frac{sulf}{sulf+dis}} = \frac{\sum_{i=1}^{n}\left(m(i)\cdot\rho_{tr}(i)\cdot\left(M_{sulf}(i)-\overline{M}_{sulf}^{0}\right)\right)}{\sum_{i=1}^{n}\left(m(i)\cdot\rho_{tr}(i)\cdot\left(M_{sulf}(i)-\overline{M}_{sulf}^{0}+M_{dis}(i)\right)\right)}$$

$r_{\frac{sulf}{sulf+dis}}$ .... Profile-averaged rate of pyrite weathering .... [%]
$m(i)$ .... Thickness of layer i .... [m]
M_{sulf} .... Content of sulphate sulphur in layer i.. [mass-%]
$\overline{M}_{sulf}^{0}$ .... Background of sulphate sulphur... [mass-%]
M_{dis} .... Content of disulphide sulphur in layer i .... [mass-%]
$\rho_{tr}(i)$.................... Dry bulk density of layer i...[g/m³]

The equation takes the background of sulphate sulphur ($\overline{M}_{sulf}^{0}$) into account, e.g. as gypsum or barite. In fact, investigations in the forefront show low content of sulphate sulphur in Pleistocene and Tertiary sediments. Normally dry bulk density is not determined. It is assumed that dry bulk density does not depend on sulphur content. Therefore dry bulk density may be cancelled in the equation. The thickness-averaged rate of pyrite weathering provides a sufficient estimation at the specific drilling location. Besides this, the rates of pyrite weathering for several layers may be falsified by mass transport (leaching). Normally in the upper part of the profile (releasing area) the rate is underestimated, whereas in the lower part of the profile (input area) the rate is overestimated.

2.4 Groundwater chemistry

Mineralisation and especially concentrations of sulphate are increased in groundwater of dump aquifers caused by pyrite weathering. Normally the groundwater is anaerobic, consists of varying portions of calcium, magnesium and ferrous iron and is slightly acidic. In case of a complete oxidation the acidity of the groundwater in the dumps is evaluated regarding to the effects on surface waters. This may be done by simple molar equivalent balancing of bicarbonate and iron concentrations:

$$Aci \approx K_{B8,2}^{ox} \approx [HCO_3^-] - 2\cdot[Fe^{2+}]$$

or by hydrogeochemical modelling. In the former case only acidity is determined, which correspond to $K_{B8,2}^{ox}$. In the second case pH-value (pH_{ox}) and further values of acidity e.g. $K_{B4.3}^{ox}$ and $K_{B8,2}^{ox}$, are represented.

3 Results

Results are presented for the lignite mines Nochten in the south and Jänschwalde in the north of the Lusatian lignite mining area.

3.1 Investigations in the forefront area and acid-base-balance of the sediments

Stratigraphic-geochemical profiles are constructed as a result of the investigations in the forefront (fig. 3 and fig. 4). On the basis of the results in different drillings a statistical data pool is generated for specific stratigraphic layers.

Generally the highest pyrite content is found in cohesive tertiary sediments (silt above and below the lignite seam). These sediments contain between 0.6 and 2.9 mass-% pyrite. Elevated pyrite content may also be found in transported tertiary material and in quaternary limnic sediments. For example limnic sediments deposited during the glacial period Elster in the open cast mine Jänschwalde contains between 0.6 and 2.3 mass-% pyrite.

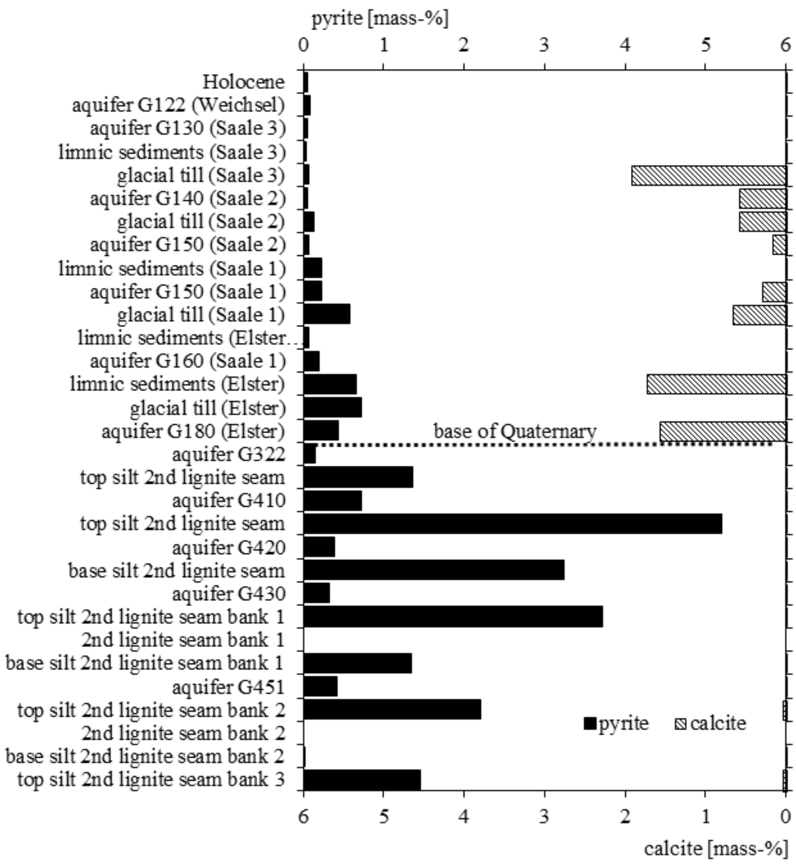

***Figure 3** Stratigraphic-geochemical profile in the forefront area of the lignite mine Jänschwalde*

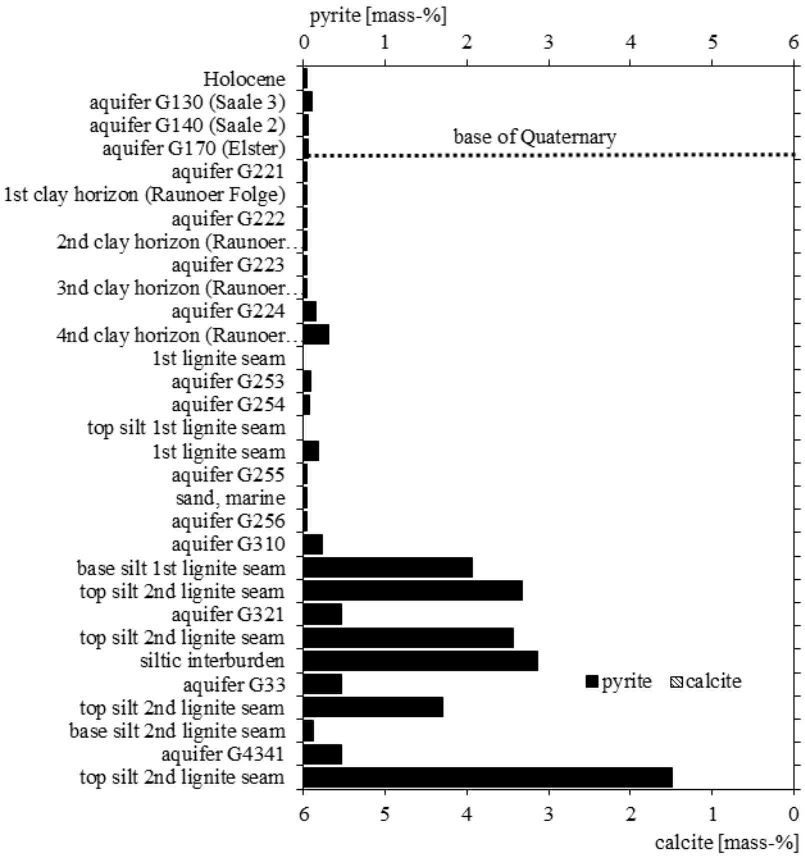

Figure 4 *Stratigraphic-geochemical profile in the forefront area of the lignite mine Nochten*

Appreciable contents of calcite can be found only in quaternary sediments. Glacial till and glacial-limnic sediments contain up to 5 mass-% calcite. These sediments are mainly common in the northern part of the Lusatian lignite mining area, for example open cast Jänschwalde (fig. 3, tab. 4). The calcite content in the open cast Nochten is very low caused by the thin quaternary overburden (fig. 4, tab. 5).

On average the overburden in the lignite mine Jänschwalde contains between 0.2 and 1.0 mass-% pyrite (fig. 3, tab. 4). Calcite typically is between 0.2 and 1.6 mass-%. In the lignite mine Nochten pyrite content is comparable to Jänschwalde. Due to the thin quaternary overburden calcite is often below the limit of determination (0.01 mass-%) and therefore negligible (fig. 4, tab. 5). Contents of disulphide sulphur, total sulphur, calcite, and iron as well as the distribution of each stratigraphic layer are stored in a digital stratigraphic model of the mine.

Table 4 *Averaged contents of sulphur, pyrite, and calcite and molar ratio of calcite to pyrite in the overburden of the lignite mine Jänschwalde*

location	drill hole	thick-ness	number of samples	sulphate as sulphur	disulphide as sulphur	pyrite FeS_2	calcite $CaCO_3$	molar ratio calcite to pyrite
		m	-	mass-%	mass-%	mass-%	mass-%	-
forefront Jänsch-walde	9323	77	35	<0,01	0,34	0,63	0,61	9,7
	10759	54	17	<0,01	0,51	0,96	0,27	2,8
	11651	100	68	<0,01	0,17	0,32	0,53	16,7
	11676	90	68	<0,01	0,24	0,45	0,39	8,8
	11703	77	86	<0,01	0,20	0,37	0,25	6,7
	12074	99	67	<0,01	0,14	0,27	0,31	11,5
	13211	103	74	<0,01	0,19	0,35	1,22	4,2
	14041	87	77	<0,01	0,46	0,86	1,58	2,2
	15217	104	92	0,02	0,12	0,23	0,75	4,0
forefront Jänsch-walde-Nord	14807	91	74	0,02	0,33	0,61	3,34	6,5
	14808	79	44	0,02	0,36	0,67	0,66	1,2
	14811	88	64	<0,01	0,29	0,54	1,55	3,5
	14813	75	53	<0,01	0,42	0,79	0,02	<0,1
	14814	65	46	<0,01	0,33	0,62	1,43	2,8

Table 5 *Averaged contents of sulphur, pyrite, and calcite and molar ratio of calcite to pyrite in the overburden of the lignite mine Nochten*

location	drill hole	thick-ness	number of samples	sulphate as sulphur	disulphide as sulphur	Pyrite FeS_2	calcite $CaCO_3$	molar ratio calcite to pyrite
		m	-	mass-%	mass-%	mass-%	mass-%	-
forefront Nochten	13165	93	100	<0,01	0,27	0,50	<0,01	<0,5
	13167	96	113	0,02	0,18	0,33	<0,01	<0,5
	13558	82	126	<0,01	0,33	0,62	<0,01	<0,5
	13561A	97	116	<0,01	0,25	0,47	<0,01	<0,5

The averaged acid-base-balancing is about 6 mole calcite per mole pyrite in lignite mine Jänschwalde (tab. 4). Mostly the overburden is well buffered. In contrast the molar ratio in overburden of the lignite mine Nochten is below 0.5 mole calcite per mole pyrite (tab. 5). Therefore the sediments are potentially acidic. Groundwater chemistry in the dump of the lignite mine Nochten verifies this.

Based on the molar ratio of calcite to pyrite the geochemical disposition of the overburden can be estimated. Mostly calcite is well available in the dumps. There is no calcite containing dump material which is acidic. Besides this rate of pyrite weathering largely depends on physical and geochemical soil properties as well as on exposure time. Therefore the evaluation of the geochemical disposition of dump material requires an estimation of the rate of pyrite weathering. These objectives are derived from the geochemical investigations in dumps.

3.2 Geochemical investigations in dumps and rate of pyrite weathering

In the Lusatian lignite mines the mean pyrite content is between 0.05 and 0.80 mass-% in dumps (tab. 6 to tab. 7). In the lignite mine Jänschwalde the mean calcite content is between 0.10 and 1.6 mass-% (tab. 6). Dumps in the lignite mine Nochten are nearly free of calcite (tab. 7).

Table 6 *Averaged contents of sulphur, pyrite, and calcite in the dump of lignite mine Jänschwalde*

location	drill hole	thick-ness	number of samples	sulphate sulphur	disulphide sulphur	pyrite FeS_2	calcite $CaCO_3$	profile-averaged rate of weathering
		m		mass-%	mass-%	mass-%	mass-%	-
inner dump	16412	73	24	0,03	0,40	0,75	0,65	6 %
	15483	80	63	0,03	0,16	0,30	0,38	16 %
	15484	66	37	0,04	0,38	0,71	0,13	8 %
	14430	50	18	0,02	0,22	0,40	0,31	6 %
	14431	57	17	0,01	0,17	0,32	0,94	6 %
	14432	68	16	0,06	0,11	0,20	0,14	35 %
	14433	61	39	0,04	0,17	0,32	0,29	20 %
	14434	51	28	0,03	0,30	0,55	1,62	7 %

Table 7 *Averaged contents of sulphur, pyrite, and calcite profile-averaged rates of pyrite weathering in outer and inner dumps of lignite mine Nochten*

location	drill hole	thick-ness	number of samples	sulphate sulphur	disulphide sulphur	pyrite FeS_2	calcite $CaCO_3$	profile-averaged rate of weathering
		m		mass-%	mass-%	mass-%	mass-%	-
outer dump	13587	26	14	0,10	0,26	0,48	0,02	28 %
inner dump	13638	70	21	0,02	0,09	0,17	0,02	18 %
	13352	130	81	0,01	0,03	0,06	0,01	18 %
	13353Z	97	68	0,01	0,08	0,15	0,03	12 %
	14541	94	55	0,02	0,14	0,27	0,03	9 %
	14542Z	100	51	0,02	0,18	0,33	0,02	8 %
	13420Z	91	38	0,03	0,21	0,39	0,03	12 %
	13422Z2	83	46	0,02	0,24	0,45	0,02	6 %

The effective rates of pyrite weathering, calculated by the ratio of sulphate sulphur and the sum of inorganic sulphur, is mainly between 6 % and 18 % in the lignite dumps (tab. 6 to tab. 7). The rates of pyrite weathering are comparable in the various open cast mines. Lower rates can be found at locations which are covered immediately. Higher rates can be found at locations which are uncovered over a long time.

The effective pyrite weathering rate is about 5 % in the zone of primary weathering. Often the zone of secondary pyrite weathering can be defined on the basis of contents of sulphate and disulphide sulphur as well as their ratio. In the zone of secondary weathering the rate exceeds 25 % and is therefore considerably higher than in the zone of primary weathering. The thickness of the zone of secondary weathering is between 5 and 40 meter. In the outer dump of the lignite mine Nochten rate of pyrite weathering is about 50 %. Recently the thickness of the secondary weathering zone is about 10 meter. Due to the missing cover of the outer dump and the location above the groundwater table the zone of secondary weathering extends over time. In contrast pyrite weathering stops in inner dumps by covering them with a stacker dump or by rising of the groundwater.

3.3 Groundwater chemistry

Hydrochemical analyses of the groundwater in dumps confirm geochemical estimations (tab. 8). The dump groundwater in the lignite mines Nochten and Jänschwalde have comparable sulphate concentrations and weathering rates but differ significantly in alkalinity, iron concentration and therefore in the acid-base-impact in case of oxidation. The groundwater in dumps remains buffered at oxidation in lignite mine Jänschwalde. In contrast the groundwater reacts acidic in the dump of the lignite mine Nochten due to the missing calcite content.

***Table 8** Range of hydrochemical parameters in groundwater in dumps of the lignite mines Nochten and Jänschwalde (mean values and standard deviation)*

parameter	unit	lignite mine Nochten	lignite mine Jänschwalde
number of wells	-	12	19
pH-value	-	5,3 ± 0,5	6,3 ± 0,6
electrical conductivity	µS/cm	2.300 ± 900	2.400 ± 1.000
DOC	mg/L	7 ± 5	9 ± 6
TIC	mg/L	80 ± 50	120 ± 60
alkalinity $K_{S4,3}$	mmol/L	1,3 ± 1,0	7,5 ± 5,2
acidity $K_{B8,2}$	mmol/L	11,7 ± 5,6	7,7 ± 6,0
calcium	mg/L	260 ± 120	430 ± 210
magnesium	mg/L	100 ± 50	90 ±70
sulphate	mg/L	1.500 ± 700	1.200 ± 800
ammonium-nitrogen	mg/L	2,2 ± 1,1	2,7 ± 1,9
iron	mg/L	260 ± 160	90 ± 130
manganese	mg/L	6 ± 5	3 ± 3
aluminium	mg/L	0,5 ± 0,4	1,6 ± 3,1
arsenic	mg/L	60 ± 50	30 ± 50
cobalt	mg/L	50 ± 60	40 ± 40
nickel	mg/L	80 ± 80	180 ± 170
zinc	mg/L	270 ± 330	220 ± 260
calculated values for the acid-base-impact in case of oxidation			
pH_{ox}	-	3,4 ± 0,5	6,2 ± 1,9
$K_{S4.3}^{ox}$	mmol/L	-	4,8 ± 7,2
$K_{B4.3}^{ox}$	mmol/L	4,9 ± 3,7	-

4 Conclusions

Based on the geochemical investigations of the overburden in open cast mines the geochemical disposition of future dumps may be estimated. Pyrite weathering in lignite dumps is not complete, thus a simple acid-base-balancing overestimates the effective acidification. Geochemical investigations of inner dumps estimate the rate of pyrite weathering more reasonable. Thus appropriate estimations of the acidification potential of dumps are possible.

Results of the geochemical investigations in the various open cast mines correspond to hydrochemical analysis of the groundwater in dumps. Thus, geochemical investigations are suitable for assessing chemical balancing measures.

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