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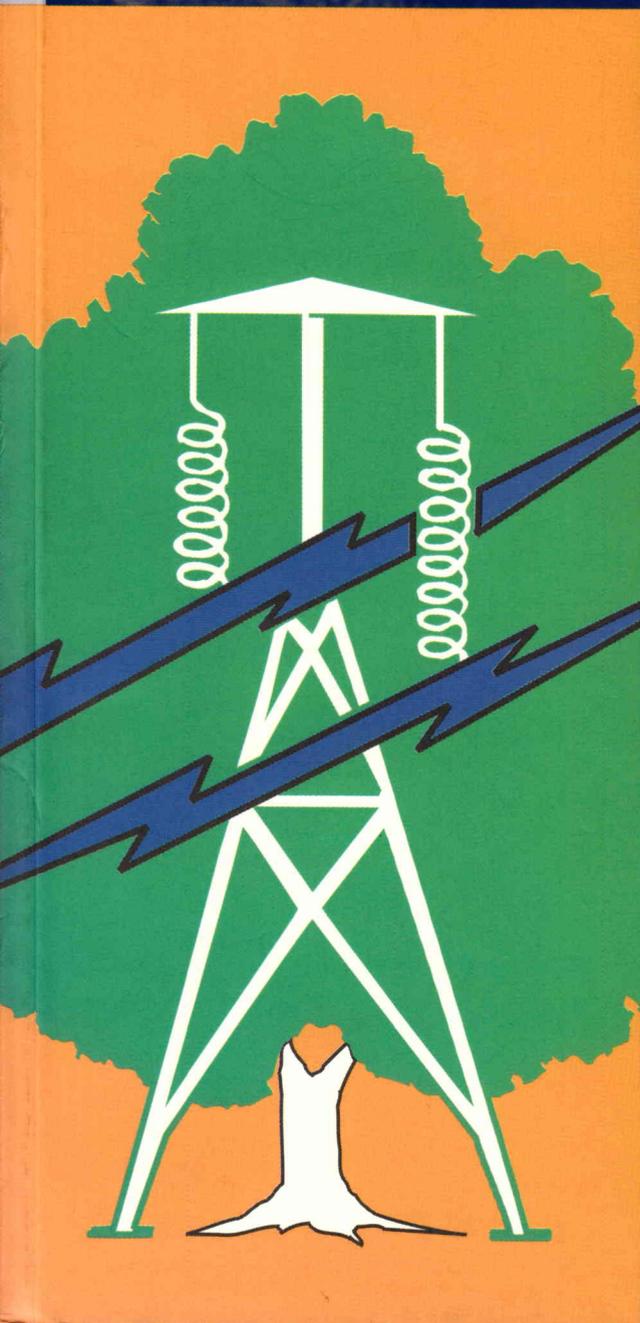
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## **12. IMPACT OF LIGNITE SLAG HEAPS ON GROUNDWATER QUALITY**

### **12.1 Introduction**

From a hydrogeochemical point of view the main impact induced by open-cast lignite mining is the formation of acid mine drainage (AMD). Overburden sediments of lignite deposits contain - like lignite itself - significant amounts of iron sulfides (Pyrite -  $\text{FeS}_2$ ) which are affected by microbially mediated weathering when brought into contact with atmospheric oxygen. Sulfide mineral oxidation results in the release of large amounts of sulfuric acid into the seepage water which is known as "acid mine drainage". Seepage waters within the dumped overburden of lignite mines have been reported to have pH-values as low as pH 1 and sulfate contents of several tens grams per liter. Subsequent reactions along the flow path are mineral dissolution and cation exchange (both may cause heavy metal release) and buffering (most effectively by carbonates) resulting in reprecipitation of cations. The seepage water AMD signal is transferred to the underlying groundwater according to the hydraulic conditions and may affect the quality of groundwater resources.

### **12.2 Mining Process**

Open-cast lignite mining is carried out by uncovering lignite in a sector shaped pit and transporting overburden material from the mining side of the sector to the dumping side where lignite has already been excavated.

This way the location of the pit is moving radially. The advantages of this system are

- the open part of the mine is relatively "small"
- the distribution station for lignite and overburden material may remain stationary in the center of the mining area

The excavation and dumping takes place at different levels which are determined by the size of the excavators and by stability factors. Situated on these levels are conveyor belt systems that allow transport of overburden material to the dumping side of the sector and transport of lignite to the distribution station for further transport to the power plant by either conveyor belt or train.

The operation time for Garzweiler II is prospected for approximately 50 years. After the mine is cleared there will be a residual lake with a size that corresponds to the amount of lignite excavated.

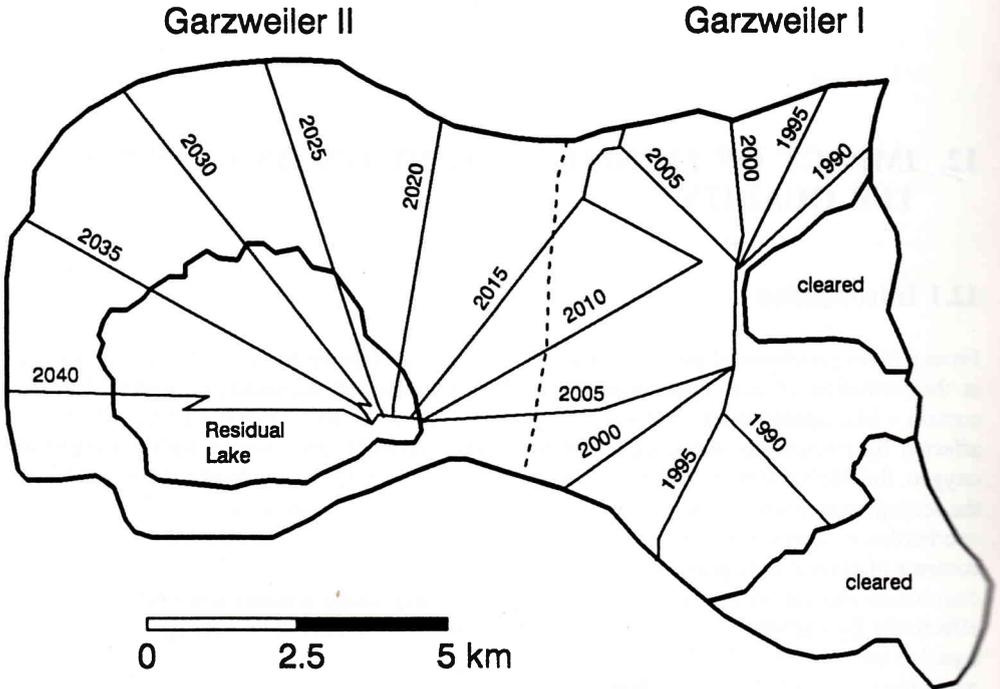


Figure 12.1 Progress of the active mining sector with time for Garzweiler I/II after (Obermann, 1991)

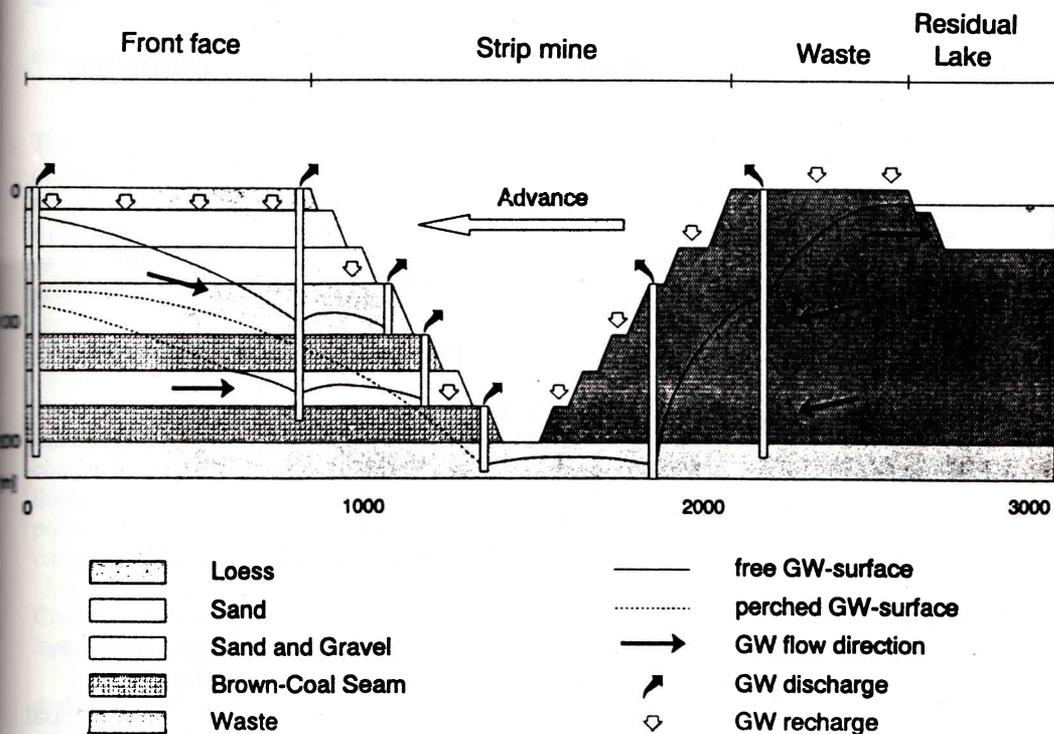
### 12.3 Acid Mine Drainage Formation

Pyrite is stable within a water saturated sediment while it becomes oxidized when **greater** amounts of oxygen are available which is true for water unsaturated sediments near **surface**. Therefore, in a natural groundwater situation the unsaturated zone above the groundwater **table** has become pyrite free while in regions that have been steadily water saturated the pyrite is stable i.e. naturally occurring pyrite will not dissolve due to very small oxygen recharge **within** the groundwater.

Figure 12.3 shows the pyrite content in two profiles from the mining area of Garzweiler II. In these sediments, the upper 25 to 35 meters are pyrite-free due to long termed **oxic** conditions.

In order to perform "dry" open-cast lignite mining the groundwater table has to be lowered (compare Figure 12.2). This causes an initial aeration of the sediments which allows an initial small peak of pyrite weathering products to occur in the seepage water. However, as the initial small amount of oxygen contained in the air that replaces groundwater is used up pyrite weathering becomes minimal again. This results from the fact that the upper part of the sediment column is pyrite free already and serves as an oxygen diffusion barrier (see below).

However, during the mining process pyrite bearing material becomes exposed on both the



**Figure 12.2** Schematic profile across the active mining sector with location of the lowered groundwater table(s) and residual lake, after (Obermann, 1991)

excavation and dumping sides of the pit. Figure 12.4 shows the slag heap regions where pyrite weathering mainly occurs. Also, up to now there has been no pyrite content control for the dumping position of overburden materials but the dumping position is selected mainly due to stability demands. This way pyrite rich material may be surficially exposed not only on the slopes of the active mine area but also on the final surface which will be approximately in the former natural position prior to opening the mine.

Since only recently measures to minimize AMD formation are taken into account both the case of unassorted dumping of waste rock - which has been true for most lignite mines up to now - and the case of controlled dumping with pyrite rich sediments dumped in the lower parts of the slag heap will be discussed.

### 12.3.1 Pyrite Weathering - Chemical Reactions

Pyrite oxidation requires oxygen, yet, the actual oxidation takes place via ferric iron. Since large amounts of ferrous iron are released by the weathering process there has to be a reoxidation of ferrous to ferric iron in order to maintain the process. The oxidation of ferrous iron with oxygen is microbiologically mediated by thiobacilli that are capable of reproduction even under the extremely acidic conditions induced by pyrite weathering. Actually, the pH-

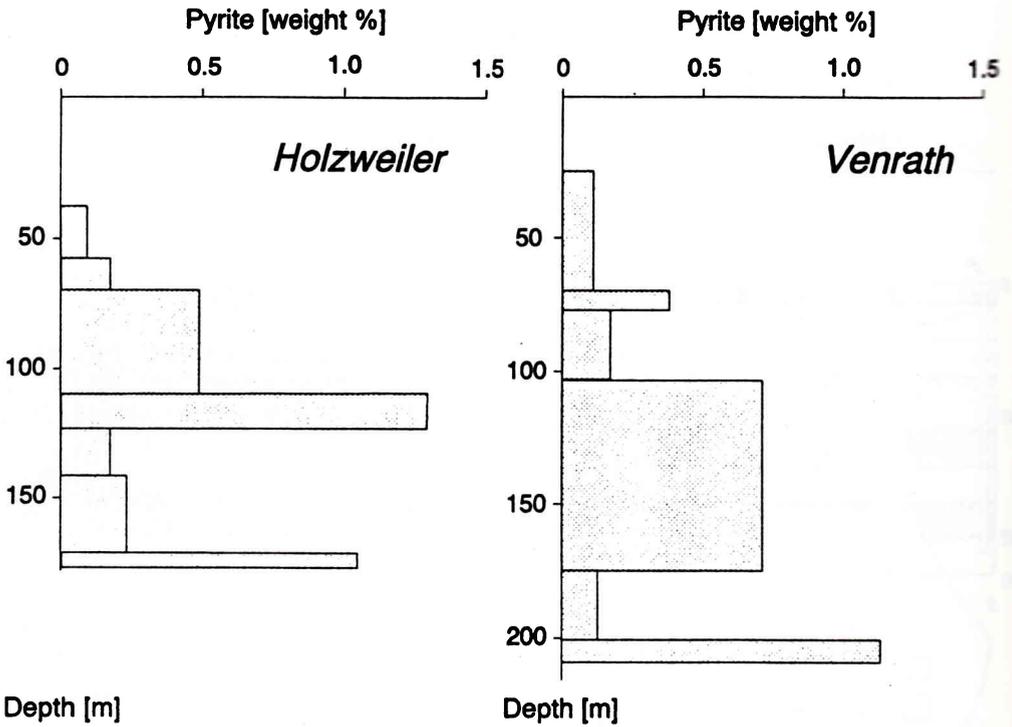


Figure 12.3 Natural pyrite content across depth profiles from two locations within the mining area of Garzweiler II, data from (Obermann et. al, 1991)

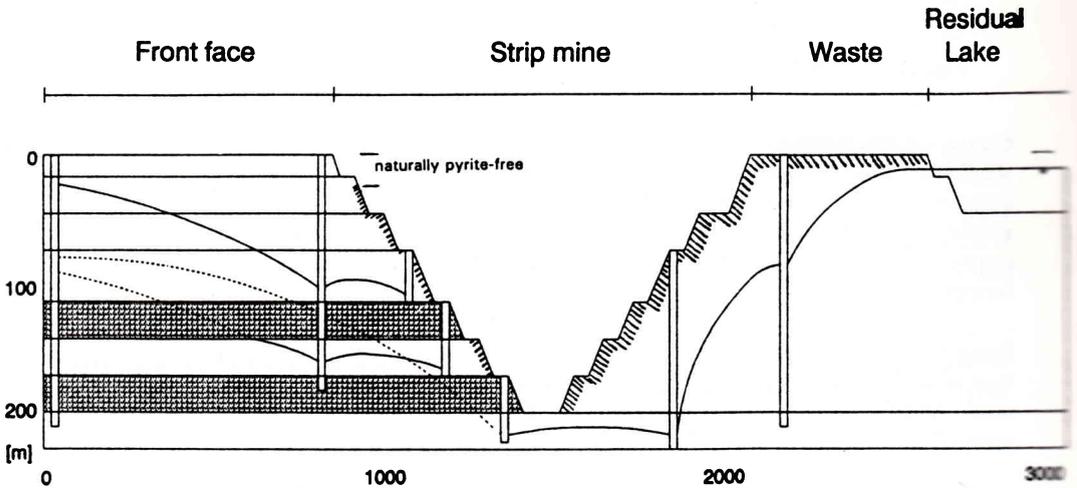


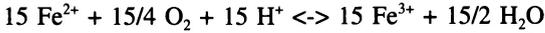
Figure 12.4 Main pyrite weathering regions within the excavation and dumping side of the active mining sector, after (Obermann, 1991)

optimum of e.g. *thiobacillus ferrooxidans* is in the range of pH 2-3.

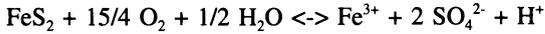
pyrite oxidation:



ferrous iron reoxidation:



overall reaction



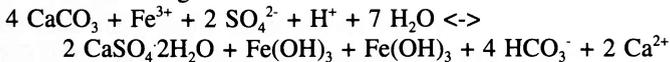
Thus weathering of one mole pyrite requires 15/4 moles of oxygen and results in the release of one mole of ferric iron, two moles of sulfate, and one mole of  $\text{H}^+$ . Converting this with the molar weights of  $\text{O}_2$  (32 g/mol), pyrite (120 g/mol), iron (56 g/mol), sulfate (96 g/mol), and hydrogen (1 g/mol) this means that weathering 120 grams of pyrite consumes 120 grams of oxygen (the quantity contained in 431 liters of air) and releases 56 grams ferric iron, 192 grams of sulfate and one mol or one gram of hydrogen ions (acid).

### 12.3.2 Buffering and Secondary Reactions

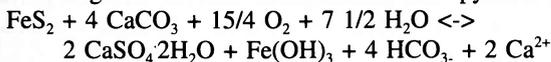
The main buffering reactions are carbonate and silicate buffering and sorption by clay minerals. Carbonate buffering neutralizes pH-values and results in iron and heavy metal concentrations near background level while sulfate concentrations are limited only to some thousand mg/l by the formation of gypsum. Clay mineral sorption has the effect of storing pollutants which may be washed off the mineral surfaces later thus resulting in decreased concentrations spread out over greater emission times.

Carbonate buffering bind  $\text{H}^+$  ions and causes the precipitation of sulfate (as gypsum and ferric iron (as iron hydroxide).

carbonate buffering:



Combining this with the overall reaction for pyrite weathering we get



thus four moles or 400 grams of limestone are needed to neutralize the AMD produced by one mol or 120 grams of pyrite.

In environments with low calcite content other important secondary reactions at high sulfate and iron contents of seepage waters influenced by AMD are jarosite (iron sulfate) and siderite (iron carbonate) formation. Obermann et al. (1991) found that seepage water concentrations observed within dumped waste rock may be explained by a simultaneous equilibrium of gypsum, Ca-siderite, jarosite, and iron hydroxide with an equilibrium pH of pH 4.4.

### 12.4 Limitations of Pyrite Weathering Rates

Pyrite weathering is limited by three factors which are of different importance. These are limitations of weathering rates by

- specific pyrite grain surface
- oxygen availability
- maximum seepage water concentrations/pH-dependence

Buffering reactions do not seem to significantly limit pyrite weathering rates itself, yet, the pyrite weathering products are fixed such that depyritization proceeds but seepage water concentrations are limited. This effect seems to be caused by acidic micro-environments around single pyrite grains opposed by an overall environment that is buffered by buffer mineral dissolution and precipitation of secondary minerals.

This means that we will have to differentiate between the amount of pyrite dissolved by weathering processes resulting in an initial "production concentration" and the effluent concentration that is controlled by buffering processes.

#### 12.4.1 Limitation by Available Surface

The dissolution rate at the surface of the pyrite grain is linearly dependent on the quantity of grain surface available. This causes a grain size effect since the specific surface  $A$  decreases with the reciprocal grain diameter  $d$

$$A [\text{m}^2_{\text{surf}}/\text{m}^3] = 6/d \quad (d \text{ in m})$$

A rough value for pyrite weathering rates at optimum pH-values is  $5 \cdot 10^{-9} \text{ mol} \cdot \text{m}^{-2}_{\text{surf}} \cdot \text{sec}^{-1}$  (Kölling, 1990) where  $\text{m}^2_{\text{surf}}$  stands for the amount of grain surface available.

However, when looking at a sediment column this rate control at the single grain does not necessarily limit an overall weathering rate since oxygen that is not consumed due to this first limitation may penetrate deeper into the sediment body. Therefore, comparing two sediments one with high pyrite surface (high pyrite content / fine grained pyrite) and one with low pyrite surface, in the low pyrite material the reaction zone thickness will increase the same while the rates per volume unit are significantly smaller.

#### 12.4.2 Limitation by Oxygen Availability

The second limitation is the availability of oxygen. From the chemical chapter we see that oxygen is critically important to let the weathering process persist. Oxygen recharge  $F_{\text{O}_2}$  inside a sediment mainly occurs via molecular diffusion in the gas phase which may be described by Fick's first law from the fraction of volume filled with ground air  $n_L$ , a diffusion coefficient within the sediment  $D$  and an oxygen concentration gradient  $dc/dx$  across a distance  $dx$

$$F_{\text{O}_2} = n_L \cdot D \cdot dc/dx$$

while the pyrite weathering rates are dependent from oxygen availabilities with the stoichiometric factor of the chemical reaction 15/4

$$F_{\text{Pyrite}} = F_{\text{O}_2} \cdot 4/15$$

Taking the fraction of volume filled with ground air  $n_L$  and the diffusion coefficient  $D$  as material constants and assuming a pyrite reaction front consuming all oxygen available at a certain depth  $x$  such that the oxygen concentration difference  $dc$  remains constant (atmospheric concentration at the surface minus zero at the pyrite weathering front) pyrite weathering rates become dependent from  $1/x$ .

Using this effect (diffusive control of oxygen recharge) is another way of limiting emissions from pyrite oxidation (Kölling & Schulz, 1993) since putting pyrite free cover layers on top of the overburden material serves as a diffusion barrier for oxygen. The cover layer thickness necessary may range from 10 meters for a highly permeable sand to below 1 meter for silt or clay materials with low permeability. However, since lignite mining is a dynamic process and the main weathering occurs as freshly dumped material is exposed to the atmosphere it is impossible to keep material with high pyrite content covered. The only practicable way of utilizing this effect is to dump high pyrite overburden material in the lower parts of the slag heap and keep exposure times as low as possible.

#### **12.4.3 Limitation by Maximum Seepage Water Concentration / pH Control**

At seepage water pH-values below pH 2 pyrite weathering rates significantly decrease (Kölling, 1990). Also there is a pH-dependent limitation of the solubility of sulfate and iron in water. Therefore, at very high mineralization and low pH-values of seepage waters pyrite weathering is inhibited along the further pathway down the profile, although there might be sufficient oxygen and reactive pyrite grain surface available. Otherwise at very low surface distances ( $dx$  in Fick's first law) the reaction rates and therefore the seepage water concentrations would become unlimitedly high, theoretically yielding pH-values below zero. We will use pH 1 (equal to a  $H^+$  concentration of 100 mmol/l) as a maximum concentration limit.

### **12.5 The Impact Pathway**

The amount of acid mine drainage that may form within dumped overburden sediments during and after the lignite mining process depends on

- pyrite content
- oxygen availability
- time
- (specific surface area of pyrite / grain size)
- (temperature)

where especially the oxygen availability is critically important and depends on

- gas permeability of overlying material
- surface distance of overburden (still) containing pyrite

**Therefore, worst case conditions are met when highly permeable sediments with a high content of fine grained pyrite are surficially exposed for long time periods.**

Actions accompanied with open-cast lignite mining that favor AMD formation are

- lowering of groundwater table (initial aeration of sediments)
- aeration of overburden during excavation, transport and dumping
- increase of exposed surface area by stair shape of the active mine area
- aeration of overburden by advective ground air flow induced by wind pressure on tilted surfaces

Measures minimizing AMD formation in open-cast lignite mines have only been taken into account in the last years:

- minimization of oxygen diffusion by either thin (< 1 m) cover layers of low permeability (compaction) or thick (> 10 m) cover layers of pyrite-free overburden material
- optimization of excavation layer planning to minimize exposure time and area and maximize surface distance of pyrite-rich layers
- increasing acid buffer capacity of overburden material by adding crushed limestone before dumping.

The overall effect is an AMD peak within the seepage water which moves downwards at seepage water velocity (approximately 1 m/yr for sandy aquifer). The increase of acid, iron, and sulfate contents in the seepage water is due to mainly near surface pyrite oxidation processes, while the decrease results from a lack of ground air oxygen recharge (decreases with squared surface distance) as upper layers become depyritized.

This AMD peak will then either mix into the groundwater or - if the mine is cleared before the peak reaches the lowered groundwater table - will be taken up by the groundwater as the water table rises after shutting down the mine. Figure 12.5 shows a generalized scheme of the impact pathway for acid mine drainage formation inside lignite mine slag heaps.

### 12.5.1 Emission Startpoint

In contrast to e.g. atmospheric emissions that may be quantified directly by measurement at the exhaust there are five major differences when identifying and quantifying emissions to seepage and groundwater caused by acid mine drainage formation.

- The emission source is a two dimensional reaction front rather than a point source.
- Since the location of the slag heap surface changes during operation of the mine it is impossible to precisely describe physical startpoints.
- The location of the reaction front is moving downwards from the (temporal position of the) slag heap surface with time.
- The quantity of emissions changes with time depending on the surface distance of the reaction front.
- As long as pyrite-bearing regions inside the slag heaps are not saturated with groundwater the emissions may persist possibly decades or centuries after closing down a mine.

### 12.5.2 Physical Endpoint

Acid mine drainage formed in the upper part of a lignite mine slag heap moves downward

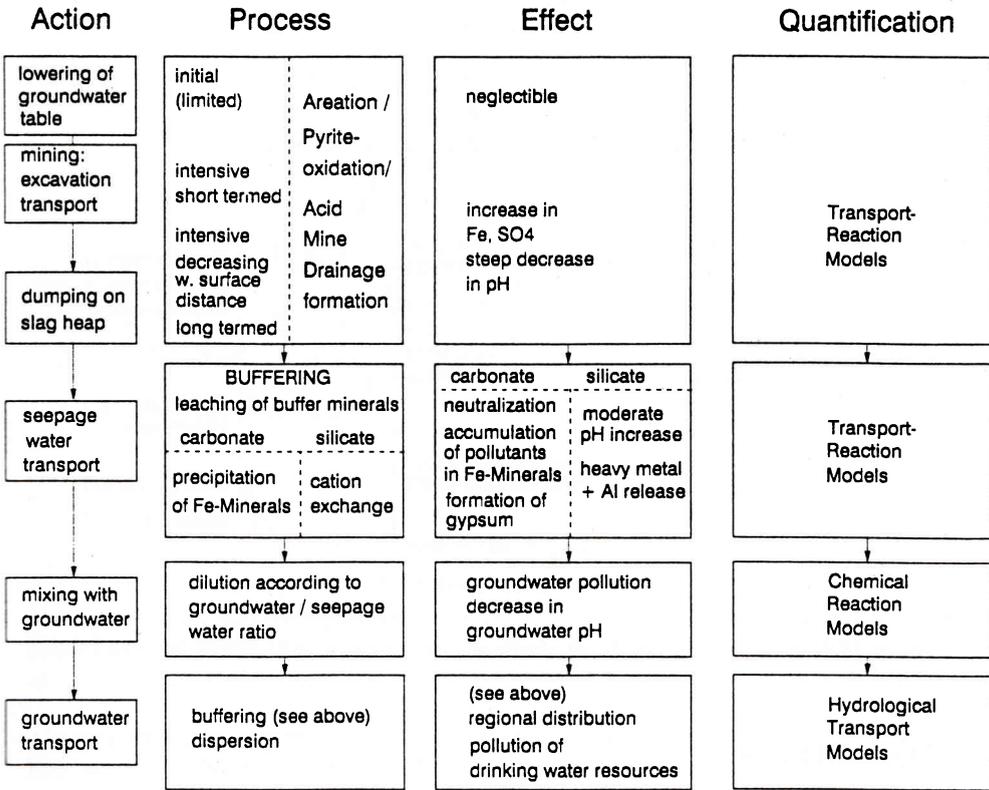


Figure 12.5 Impact pathway for acid mine drainage formation inside lignite mine slag heaps

with the seepage water flow, may be altered (buffered) along its pathway through the water-unsaturated zone and then enters the groundwater. Depending upon the ratios of seepage water to groundwater and on the subsequent pathway (or use) of the groundwater there may be different impacts that may be divided into three groups

- During operation of the mine there might be an impact on water extracted from drainage wells
- The impact on rising groundwater after turning off the drainage wells depends on the quantity of mobile pollutants stored inside the water-unsaturated zone at that time.
- Long termed impact on surface-near groundwater at an equilibrium level of the groundwater table.

For the second (and third) group it is more convenient to mathematically describe the overall sum of released pollutants underneath the total mine area and then apply different hydraulic models for the temporal and spatial distributions of the total impact.

### Slag heap model elements

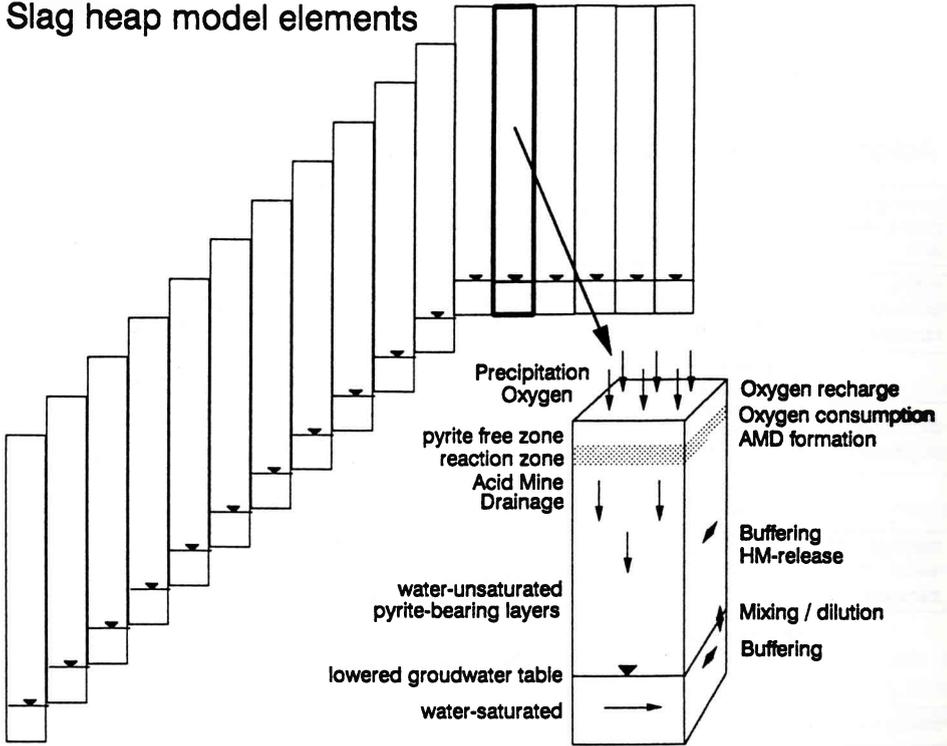


Figure 12.6 Scheme of possible locations of the model element inside the slag heap body

## 12.6 Quantification

If we want to quantify the effect of the pyrite weathering processes, we need to simplify the complex spatial distribution of reaction zones with time. We will look at a sediment column inside the slag heap with an initially lowered groundwater table, which is allowed to rise after a certain time. The mathematic formulations to describe seepage water concentrations, area based release, and the time dependence of the depyritization depth are given below. We will choose a sediment column situated just outside the active mine area, where the groundwater level lowering is active but oxygen diffusion from the slag heap slopes is neglectible (Figure 12.6). Such a situation should be long termed representative for wide regions of the slag heap body.

### 12.6.1 Boundary Conditions

In order to approximate total impact, we have to describe boundary conditions for all relevant parameters. For the planning of Garzweiler II several values that may be used are available.

At Garzweiler II, lowering of the groundwater table will be kept up for approximately 50 years and there will be another 50 years until the original groundwater level is reached. In the mining area the groundwater table is lowered 80 to 120 m below the natural levels. We will choose a surface distance of the groundwater table during operation of the mine as 110 m (90 m below a natural level of 20 m below surface; compare Figure 12.8).

With an infiltration  $I$  in the mine area of 250 mm/yr and a volume fraction occupied by seepage water  $n_{sw} = 0.25$  the seepage water velocity  $v_{sw}$  may be estimated as 1 m/yr. With a pyrite content of  $m_{py}\% = 0.65$  wt.% a dry density of overburden material of  $\rho_{dry} = 1855$  kg m<sup>-3</sup> and a molar weight of pyrite  $MW_{py} = 120$  g/mol we get a molar pyrite content of

$$m_{py} = m_{py}\% \cdot 10^{-2} \cdot \rho_{dry} \cdot 10^3 / MW_{py} = 100 \text{ mol m}^{-3}$$

Using some good estimates for material parameters ( $n_L = 0.05$ ,  $D = 3.5 \cdot 10^{-6}$  m<sup>2</sup> s<sup>-1</sup> = 77 m<sup>2</sup> yr<sup>-1</sup>,  $dc_{O_2} = 8.7$  mol m<sup>-3</sup>) we get a value for the "pyrite weathering constant"  $PW$  that may be defined as

$$PW = (4/15 \cdot 2^{-1/2} \cdot n_L \cdot D \cdot dc_{O_2} \cdot m_{py})^{1/2}$$

$$PW = 30 \text{ mol m}^{-2} \text{ yr}^{1/2}$$

### 12.6.2 Mathematic Formulations

Using the estimates above the seepage water concentration at the reaction front may be estimated from

$$c = PW/I \cdot t^{-1/2}$$

$$c [\text{mol/m}^3] = 120 \cdot t^{1/2} \text{ (t in years)}$$

so after 100 years the unbuffered concentration at the reaction front will be 12 mmol dissolved pyrite per liter resulting in a seepage water sulfate concentration of approximately 2300 mg/l at pH 1.92.

The total emissions may be calculated by integrating the concentration profile and multiplying this by the area based seepage water quantity. Doing this we may calculate total emissions over time and find a potential total area based release. Within the water unsaturated zone of a slag heap the total release may be estimated by

$$R_{tot} = 2 \cdot PW \cdot t^{1/2}$$

$$R_{tot} [\text{mol/m}^2] = 60 \cdot t^{1/2} \text{ (t in years)}$$

such that after hundred years the total release should sum up to 600 mol m<sup>-2</sup> pyrite weathering products that are taken up by the rising groundwater level.

Taking into account the limitation of pyrite weathering at very low pH (Figure 12.7) we may estimate the duration of this limitation  $t_{lim}$  with  $c_{max} = 100$  mmol/l (i.e. pH 1)

$$t_{lim} = 2 \cdot PW^2 / (c_{max}^2 \cdot I^2)$$

$$t_{lim} = 2.9 \text{ years}$$

This way the total release over 100 years reduces for these material constants slightly to 596 mol/m<sup>2</sup> from

$$R_{tot} = 2 \cdot PW \cdot (t - 0.5 \cdot t_{lim})^{1/2}$$

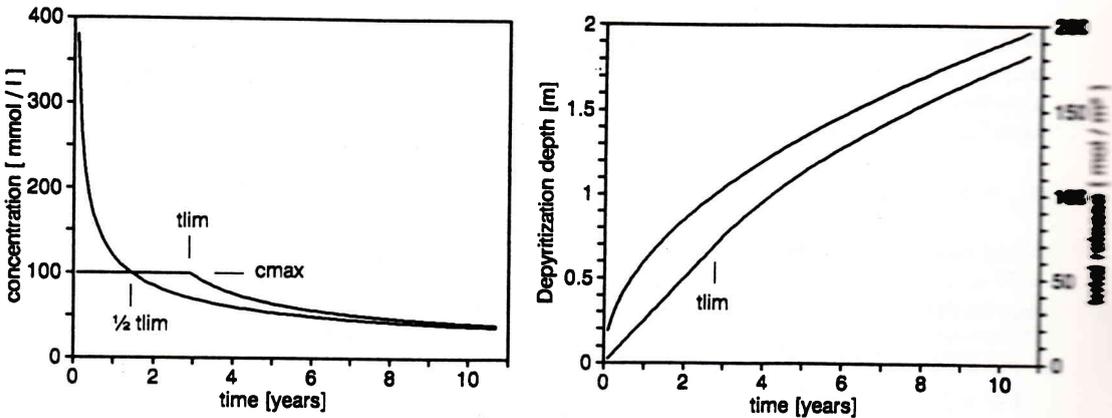


Figure 12.7 Effect of limited maximum concentration on concentration, depyritization depth and total release over the first ten years after dumping

The depyritization depth dependence from time is in the range of

$$x_{\text{depy}} = 2 \cdot PW / m_{\text{py}} \cdot t^{1/2} = R_{\text{tot}} / m_{\text{py}}$$

$$x_{\text{depy}} \text{ [m]} = 0.6 \cdot t^{1/2} \text{ (t in years)}$$

meaning that after 100 years the upper six meters of the slag heap material will be pyrite-free (or 12 m in 400 years). Therefore, only if the surface distance of the final groundwater level is less than six meters, the process of pyrite weathering will stop.

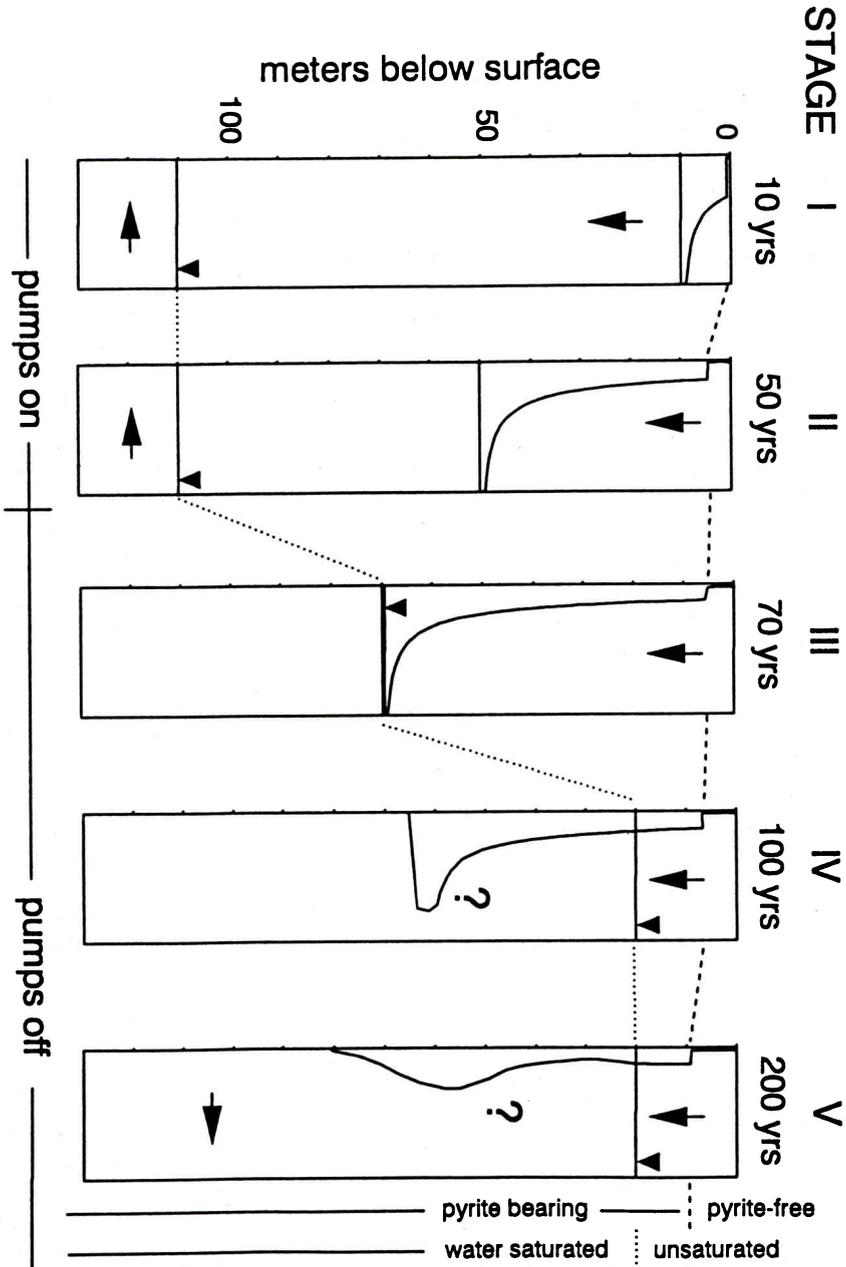
Taking into account the release reduced by the limitation of a maximum concentration (Figure 12.7) the depyritization depth after 100 years becomes smaller

$$X_{\text{depy}} = R_{\text{tot}} / m_{\text{py}} = 5.96 \text{ m}$$

Figure 12.8 schematically shows the temporal change of the seepage and groundwater concentration profiles within the dumped overburden material of a lignite mine. The values shown are based on estimates for material constants as described above with the mathematic formulations to describe the concentration curve shape. With these estimates the width of the columns corresponds to a concentration of 100 mmol/l.

In general we see a sharp concentration peak moving downwards at seepage water velocity in stages I to III. The depth where the first concentration increase occurs (1 to 9 meters) shows the location of the actual reaction front. The location of the concentration peak is moving downwards until it reaches the groundwater table (stage III). After the drainage pumps are turned off the peak will move upwards due to the fraction of groundwater rather than seepage water responsible for the water table rise (stage IV). Note that in this stage where the water table has reached the natural equilibrium level only one third of the water unsaturated zone is pyrite free.

Subsequently the peak now situated inside the groundwater will become dispersed and diluted by free groundwater mainly moving horizontally (stage V). At the values chosen it will take



**Figure 12.8** (next page) Movement of the AMD concentration peak with time after deposition. Only above the broken line waste rock has become pyrite free. After stage II the pumps are turned off so that the water table (dotted line) which has been artificially lowered returns to its equilibrium position (stages IV and V). The column width corresponds to 100 mmol/l.

approximately 1100 years until all of the upper 20 meters of the profile have become pyrite free. During this time there will be a slowly decreasing release of pyrite weathering products at seepage water concentrations in the range of 10 mmol/l which still corresponds to 2000 mg/l of sulfate and pH 2.

In stages I to IV of Figure 12.7 the total release of pyrite weathering products corresponds to the area underneath the concentration curve. Carbonate buffering will dramatically decrease the concentrations of iron and heavy metals and neutralizes pH values while the sulfate concentrations will remain elevated with the peak being attenuated by precipitation of gypsum.

### 12.6.3 Impact on Drainage Water

Since seepage water velocities are slow (rough value  $1 \text{ m}\cdot\text{yr}^{-1}$ ) compared to the groundwater table lowering (in the order of 100 m) during the operation of a mine there is a significant time lag before seepage water affected by pyrite weathering will first reach the groundwater table. Until this happens seepage water with background concentration will mix into the groundwater and the duration of this is therefore regarded as  $t_{BG}$ . The time lag  $t_{BG}$  may be roughly estimated by multiplying the seepage water velocity  $v_{sw}$  by the vertical surface distance of the groundwater table  $X_{GW}$

$$t_{BG} = v_{sw} \cdot X_{GW}$$

the seepage water velocity  $v_{sw}$  is more may be calculated from the infiltration  $I$  (rough value  $0.25 \text{ m}\cdot\text{yr}^{-1}$ ) divided by the fraction of the total slag heap volume occupied by seepage water  $n_{sw}$  (rough value 0.25)

$$v_{sw} = I n_{sw}$$
$$t_{BG} = I n_{sw} \cdot X_{GW}$$

With the estimates given above this means that for sandy material the time lag in years roughly equals the surface distance of the groundwater table in meters i.e. given a groundwater table lowered down to 110 m below surface it will take 110 years until a seepage water volume unit will reach the groundwater table. During this time lag - in a simple model - only normally mineralized waters will mix into the groundwater. Actually variable seepage water compositions with a mineralization significant above background concentrations may occur earlier (after some decades), since the mining process is dynamic and slag heaps are built up layered from ground to top with different exposure times and surface to groundwater table distances of every new slag heap surface.

Since groundwater table lowering is kept up only for approximately 50 years this means that the acid mine drainage peak will not have reached the groundwater table when the last drainage well pumps are turned off. Therefore, an impact on water extracted from drainage wells is low and may only be seen in situations where short seepage water pathways are given.

### 12.6.4 Impact on Rising Groundwater Body

Relating the total release over 100 years ( $596 \text{ mol}\cdot\text{m}^{-2}$ ) until the original groundwater level

is reached to the amount of water contained in the formerly water-unsaturated zone of the thickness  $x_{low}$  we may calculate an average concentration within this region with the total pore volume  $n_p = n_{sw} + n_L$  (in our case 0.3) from

$$c = R_{tot}/(x_{low} \cdot (n_{sw} + n_L))$$

so for  $x_{low} = 90$  m we get  $c = 20$  mmol/l which corresponds to an average pH 1.68 and average sulfate and iron contents of approximately 3950 mg/l and 1150 mg/l respectively.

### 12.6.5 Long Termed Impact on Surface-Near Groundwater

Up to now we considered the phase before the original groundwater level is reached. We have seen that within the assumed 100 years of this phase approximately six meters of overburden material have become pyrite-free. If the surface distance of the final groundwater level greater than the thickness of the pyrite-free zone, this means that the processes forming AMD will go on thus resulting in a further dissolution of pyrite assumed that the upper layers of the slag heap have not been selectively built up from material poor in pyrite. Linking this to the calculations this means that part of the tailing of the AMD peak is still situated in the seepage water above the final groundwater level. Using the same formulas and material constants from above this means, that after 100 years the seepage water concentrations are still in the range of

$$c \text{ [mmol/l]} = 120 \cdot t^{-1/2} = 12 \text{ mmol/l}$$

The time needed until all of the assumed 20 m of water unsaturated zone has become pyrite free ( $x_{depy} = 20$  m) may be calculated from

$$t_{depy} = x_{depy}^2 \cdot 0.6^2 = 1100 \text{ years}$$

for the depyritization of 20 m. During this time the total release may be calculated from the total release in 1100 years minus the release from the first 100 years which is now situated in the slag heap groundwater body

$$R_{tot}(100 < t < 1100) = 2 \cdot PW \cdot (100^{1/2} - 1100^{1/2})$$

which results in approximately 1400 moles of pyrite weathering products per square meter of slag heap surface area that will be released within 1000 years after the original groundwater level has been reached. Relating this to the infiltration during this time ( $0.25 \text{ m} \cdot \text{yr}^{-1}$ ) we get an average seepage water concentration of 5.6 mmol/l which means pH 2.25, and approximate sulfate an iron concentrations of 1000 mg/l and 300 mg/l respectively.

Since the reaction front moves downward from the surface slowly emissions will persist until the slag heap is pyrite-free down to the final groundwater table.

### 12.7 Buffering Total Release

If measures to buffer AMD products are already included in the process one may calculate

the amount of buffer material (limestone) necessary to match the release calculated above. From the chemical reactions chapter we see that the fourfold molar amount of limestone  $m_{cc}$  is needed which results in our case for the first hundred years to

$$m_{cc} = 4 \cdot 459 = 2384 \text{ mol/m}^2$$

or with the molar weight of calcite (0.1 kg/mol) to 238 kg Calcite per square meter slag heap area. This quantity corresponds to the pyrite contained within a layer of 5.96 m thickness which becomes pyrite free during the first hundred years after opening the mine. Relating this limestone quantity to a sediment column thickness of  $x_{cc} = 50$  m where this buffering should occur this corresponds to a limestone content of

$$\begin{aligned} m_{cc}\% &= m_{cc} \cdot 100 / (x_{cc} \cdot \rho_{\text{dry}}) \\ m_{cc}\% &= 238 \cdot 100 / (50 \cdot 1855) = 0.25 \text{ wt.}\% \end{aligned}$$

Adding limestone will neutralize the pH-values, reduce iron and heavy metal contents to natural levels but will not significantly reduce the sulfate content.

For the long termed processes after the original groundwater level is reached additional buffer material is needed

$$m_{cc} = 4 \cdot 1400 = 5600 \text{ mol}\cdot\text{m}^2$$

corresponding to 560 kg Calcite per square meter slag heap area resulting in a total for the two phases 0 to 100 years and 100 to 1100 years of approximately 800 kg/m<sup>2</sup> resulting in an average limestone content for the upper 50 m of the slag heap necessary to buffer the total release from unassorted material of 0.86 wt%.

Comparing this to adding buffer material sufficient to buffer the total pyrite content in the sediment column which is water unsaturated during mine operation (4000 kg/m<sup>2</sup>) which has been proposed before (Kölling, 1990) this quantity is smaller by a factor of 5.

Assuming an effective carbonate buffering, only the emission of waters with elevated sulfate concentrations has to be considered. For a sulfate concentration in equilibrium with gypsum of approximately 1000 mg/l at an infiltration of 250 l·m<sup>-2</sup> we get an average sulfate emission of 0.25 kg·m<sup>-2</sup>·yr<sup>-1</sup> which will be almost constant over long periods.

### 12.7.1 Location of Buffer Material

The location of the buffer material is critically important since it has to be situated such that the highly mineralized water have to move through a buffer zone containing limestone. Since the AMD peak first moves downwards with the seepage water and then moves upwards with the rising groundwater table it is hard to determine an optimum location of a buffer layer. In order to allow buffering of the seepage waters for the phase of lowered groundwater table (first 100 years) safer (but more cost intensive) to mix relatively small quantities of limestone into the upper 50 meters of the slag heap body to get the limestone content of >0.25 wt% as calculated above.

For buffering the long termed release in the subsequent 1000 years the buffer material has to be concentrated in the lower part of the unsaturated zone or just above the final groundwater level (around 20 m below surface in our example). Since carbonate buffering results in a fixation of most pollutants by precipitation (pollutant sink) it is critically important not to underestimate the limestone demand.

### 12.7.2 Effects of Measures Minimizing AMD Formation

Recently, in the planning for Garzweiler II it is also thought of covering open surfaces as fast as possible such that exposure times are only in the range of 0.5 years. With the material constants assumed above this is within  $t_{lim}$  such that the total release may be calculated from

$$R_{tot} = c_{max} \cdot I \cdot t$$

$$R_{tot} = 100 \cdot 0.25 \cdot 0.5$$

such that the total release is reduced to 12.5 mol/m<sup>2</sup> which is equal to a factor of almost 200 below the release from unassorted material being dumped uncovered. Yet, this factor holds only if we may assume that the cover is impermeable enough to minimize oxygen recharge. This quantity may be buffered by only 5 kg limestone per square meter of slag heap area which corresponds to a limestone content of 0.005 % if relating this to a sediment column of 50 m thickness.

From the equations above we may also calculate material parameters for a cover layer thick and impermeable enough to assure a certain maximum concentration  $c_{lim}$  or better maximum output  $c_{lim} \cdot I$  since in more impermeable cover layers  $I$  may become very small so that it is more convenient to consider a maximum output  $I \cdot c_{lim}$  [mol·m<sup>-2</sup>·yr<sup>-1</sup>] rather than a maximum concentration which is of only little importance.

$$c_{lim} = PW / (I \cdot t^{1/2} \cdot lim)$$

$$t_{lim} = PW^2 / (I^2 \cdot c_{lim}^2)$$

After the time  $t_{lim}$  the depyritization depth is sufficient to let the concentrations fall below  $c_{lim}$ . The thickness of the cover may then be calculated from

$$x_{cov} = 2 \cdot PW / (m_{py} \cdot t_{lim}^{1/2}) \text{ or}$$

$$x_{cov} = 2 \cdot PW^2 / (m_{py} \cdot I \cdot c_{lim})$$

replacing the full expression for  $PW$  we get

$$x_{cov} = 2 \cdot (4/15 \cdot 2^{-1/2} \cdot n_L \cdot dc_{O_2} \cdot D \cdot m_{py}) / (m_{py} \cdot I \cdot c_{lim}) \text{ or}$$

$$x_{cov} = 8 \cdot n_L \cdot dc_{O_2} \cdot D / (15 \cdot 2^{-1/2} \cdot I \cdot c_{lim})$$

$dc_{O_2}$  may be taken as constant (8.7 mol·m<sup>-3</sup>) such that from the expression

$$x_{cov} = 3.28 n_L \cdot D / (I \cdot c_{lim})$$

valid combinations of air filled volume fraction  $n_L$ , diffusion coefficient of oxygen in ground air  $D$ , infiltration  $I$ , and thickness of pyrite-free cover  $x_{cov}$  may be calculated for every maximum concentration given. Since the diffusion coefficient  $D$  is variable only in the range of  $1 \cdot 10^{-7}$  and  $5 \cdot 10^{-6} \text{ m}^2 \cdot \text{sec}^{-1}$  or 3 to 150  $\text{m}^2 \cdot \text{yr}^{-1}$  the main variable becomes  $n_L$ .

In our example the thickness of a pyrite-free cover layer of the same material constants as the waste rock which allows only background sulfate output of  $1 \text{ mol} \cdot \text{m}^{-3} \cdot 0.25 \text{ m} \cdot \text{yr}^{-1}$  is

$$x_{cov} = 3.28 \cdot 0.05 \cdot 110 / (0.25 \cdot 1) = 72 \text{ m}$$

Vice versa, with a 10 m pyrite-free cover the output concentration would result to

$$c = 3.28 \cdot 0.05 \cdot 110 / (0.25 \cdot 10) = 7.2 \text{ mol} \cdot \text{m}^{-3}$$

or the 7-fold background concentration. To get a background output ( $0.25 \text{ mol} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$ ) with a 1 meter thick cover layer more impermeable for both air and water we may write the condition

$$I \cdot c_{lim} = 3.28 n_L \cdot D / x_{cov}$$

$$0.25 = 3.28 n_L \cdot D / l$$

$$n_L \cdot D = 0.076$$

which is true for a material with  $D = 7.6 \text{ m}^2 \cdot \text{yr}^{-1}$  and  $n_L = 0.01$  or 1 % of the total volume occupied by ground air.

## 12.8 Estimates of the Total Impact

Taking the total mine area of Garzweiler II of approximately 50  $\text{km}^2$ , a total of 300 million tons of lignite which are to be extracted from the mine and a lignite demand of 1.177  $\text{t/MWh}_{el}$  we may calculate very rough (!!) estimates for the total impact.

For the case of unsorted and unbuffered dumping of overburden material we may estimate the total energy production based impact from the total pyrite weathering product release of approximately 2000  $\text{mol/m}^2$

$$\text{IMP} = 2000 \cdot 50 \cdot 10^6 \cdot 1.177 / (300 \cdot 10^6)$$

$$\text{IMP} = 2000 \cdot 0.196$$

$$\text{IMP} = 392 \text{ mol/MWh}_{el}$$

which corresponds to the weathering of 47 kg of pyrite (resulting in the release of 75 kg of sulfate and 22 kg of iron for every  $\text{MWh}_{el}$  produced when taking into account short and long termed effects).

Background concentrations for sulfate and iron are 100 mg/l and 1 mg/l respectively. In order to evaluate the total impact we have to calculate the background and relate this to the area and energy produced to get comparable results

$$BG \text{ [kg/m}^2\text{]} = c_{BG}[\text{mg/l}] \cdot 10^{-6} \cdot I[\text{l/m}^2 \cdot \text{yr}] \cdot t[\text{yr}]$$

$$BG_{SO_4} = 100 \cdot 10^{-6} \cdot 250 \cdot 1100 = 27.5 \text{ mol} \cdot \text{m}^{-2}$$

$$BGIMP_{SO_4} = 27.5 \cdot 0.196 \cdot$$

$$BGIMP_{SO_4} = 5.4 \text{ kg/MWh}_{el}$$

$$BGIMP_{Fe} = 0.054 \text{ kg/MWh}_{el}$$

Thus the net impact reduces to  $75 - 5.4 = 69.6 \text{ kg/MWh}_{el}$  or the 13-fold background for sulfate while there is little change for iron.

Taking into account only the release over the first 50 years when the power plant is operated we still get

$$R = 2 \cdot PW \cdot t^{1/2}$$

$$R = 2 \cdot 30 \cdot 50^{1/2} = 424 \text{ mol/m}^2$$

$$IMP = 424 \cdot 0.196$$

$$IMP = 83 \text{ mol/MWh}_{el}$$

which corresponds to the weathering of 10 kg of pyrite resulting in the release of 16 kg (net impact  $10.6 \text{ kg/MWh}_{el}$  = twofold background) of sulfate and 4.6 kg or iron for every  $\text{MWh}_{el}$  produced. Yet, this calculation is errateous since four fifths of the total release of pyrite weathering products are released after closing down the mine.

For the unbuffered systems also the release of heavy metals and aluminum ions are of significant importance. Yet, exact predictions of the total impact depends on local conditions. Obermann et al. (1991) found concentrations of 10-100 mg/l Al, 1-10 mg/l Co, and 1-5 mg/l Ni in acid mine drainage (pH4) from the locality Berrenrath. Relating the high values of these ranges to the total area over the total time and to the energy production we get

$$R \text{ [kg/m}^2\text{]} = c[\text{mg/l}] \cdot 10^{-6} \cdot I \text{ [l/m}^2 \cdot \text{yr}] \cdot t[\text{yr}]$$

$$R_{Al} = 100 \cdot 10^{-6} \cdot 250 \cdot 1100 = 27.5 \text{ kg/m}^2$$

$$IMP_{Al} = 27.5 \cdot 0.196 = 5.4 \text{ kg / MWh}_{el}$$

While large amounts of aluminum are fixed in the silicates and clay minerals of the waste rock material which may be seen as a non limited source for the release of aluminum, for heavy metals such as Co and Ni leaching processes have to be considered such that the total release over time becomes much smaller.

For a limestone buffered system, only the release of sulfate is important which results to

approximately  $1300 \text{ mol/m}^2$  for the total time of depyritization of 1100 years.

$$\text{IMP} = 1300 \cdot 0.196$$

$$\text{IMP} = 255 \text{ mol/MWh}_{\text{el}}$$

This corresponds to more than half the impact ( $49 \text{ kg/MWh}_{\text{el}}$ , net impact  $43.6 \text{ kg/MWh}_{\text{el}}$  = eightfold background) for sulfate compared to the unbuffered system.

The limestone demand for the buffered but uncovered system has been calculated to  $800 \text{ kg/m}^2$  above and converts to

$$\text{Demand}_{\text{cc}} = 800 \cdot 0.196 = 157 \text{ kg/MWh}_{\text{el}}$$

Calculating the impact for a slag heap where exposure times of pyrite-bearing waste rock is limited to 0.5 years we get a release of  $12.5 \text{ mol/m}^2$  and the total impact results to

$$\text{IMP} = 12.5 \cdot 0.196 = 2.45 \text{ mol/MWh}_{\text{el}}$$

which corresponds to the weathering of  $0.3 \text{ kg}$  of pyrite resulting in the release of  $0.47 \text{ kg}$  of sulfate and  $0.14 \text{ kg}$  of iron for every  $\text{MWh}_{\text{el}}$  produced. the sulfate impact in this case is well below the background while iron release corresponds to the threefold background. In a buffered system, iron emissions will be far below background as well.

The limestone demand for buffering the AMD release from the covered system has been calculated to  $5 \text{ kg/m}^2$  above and converts to

$$\text{Demand}_{\text{cc}} = 5 \cdot 0.196 = 1 \text{ kg/MWh}_{\text{el}}$$

## 12.9 Summary

The total effect of AMD formation inside slag heaps of lignite mines is large in the case of unassorted dumping of waste rock material. Waters affected by AMD formation will be found in the groundwater body inside the slag heap after it has reached its equilibrium position and in surface-near groundwater. Especially the long termed effect of persisting pyrite weathering above the equilibrium water table are of importance, since these emissions will affect the quality of surface-near groundwater resources for centuries and will require processing of these waters prior to use.

When sufficient buffer material is added especially in the upper parts of the slag heap body the effects of AMD formation are reduced to the emission of sulfate-rich waters while iron and heavy metal contents and pH values are held at natural levels.

Directing the dumping position of pyrite-rich overburden material to the lower parts of the slag heap and assuring short exposure times of such sediments will dramatically reduces the total impact and the buffer material (limestone) demand such that in some cases the natural calcite content of the material might be sufficient to neutralize waters affected by AMD

formation. Yet, the conditions to assure the effectivity of an oxygen diffusion barrier have to be fulfilled.

## **12.10 References**

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