

Pyrite Weathering in Coal Mine Tailings

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Abstract The formation of acid mine drainage is the main environmental impact of the deposition of waste rock of both lignite and hard coal mines. Based on the concept of diffusive oxygen recharge equations are presented which allow an estimate of the change of the pyrite release, the location of the depyritization depth, and seepage water concentrations as a function of time from deposition. These equations are especially useful when evaluating the short and long term effects of such deposits and for estimating the expected demand of buffer material. According to the calculations, critical parameters are time of near surface exposure, the volume fraction filled with air and the diffusion coefficient - both correlated with the permeability coefficient - and the pyrite content of the material. Minimizing these three factors will minimize the formation of acid mine drainage. In subaquatic environments especially waste rock from hard coal mining might be suitable for the use as structural material and - due to its high compactability - as base sealing for landfills.

Keywords acid mine drainage, pyrite weathering, mine tailings, buffering, estimation, measures.

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 - 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 and dissolved iron into the seepage water. 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 of 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.

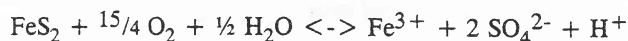
In our hydrogeochemistry group at the University of Bremen one of the major topics is the investigation of the formation of acid mine drainage associated with lignite and hard coal mining. Geochemical and transport-reaction modeling is supported by laboratory experiments with original and artificial overburden materials resulting in important material parameters such as specific surface dependent reaction rates. During a more recent study some simple mathematic formulations to estimate pyrite weathering rates, resulting seepage water concentrations and the temporal and spatial concentration distribution in the seepage water of unsaturated permeable rocks have been found. These

estimates are based on the concept of oxygen availability controlled by diffusion through the air-filled pore space of the unsaturated overburden material.

2 PYRITE WEATHERING

2.1 Chemical Reactions

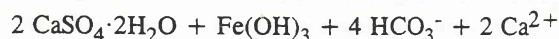
Pyrite oxidation requires oxygen, yet, the actual oxidation takes place via ferric iron. The oxidation of ferrous iron with oxygen is microbiologically mediated by thiobacilli that are capable of reproduction even under the extremely acidic conditions induced by pyrite weathering. Actually, the pH-optimum of e.g. *thiobacillus ferrooxidans* is in the range of pH 2-3. The overall reaction may be written as



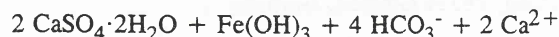
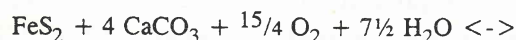
Thus weathering of one mole pyrite requires $15/4$ moles of oxygen and results in the release of one mole of ferric iron, two moles of sulfate, and one mole of H^+ .

The main buffering reactions are carbonate and silicate buffering and sorption on 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 $\text{mg}\cdot\text{liter}^{-1}$ 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 released over a greater period.

Carbonate buffering binds H^+ ions and leads to the precipitation of sulfate (as gypsum) and ferric iron (as iron hydroxide).



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.

2.2 Limitation of Pyrite weathering

2.2.1 Reaction kinetics

As a first possibility for the limitation of pyrite weathering one may concern weathering rates. Under laboratory conditions pyrite weathering rates have been found to be in the range of $5 \cdot 10^{-10}$ to $5 \cdot 10^{-9} \text{ mol} \cdot \text{m}^{-2} \cdot \text{sec}^{-1}$ (Kölling, (1)). In other experiments with unsaturated columns (10 wt.% pyrite) incubated with Thiobacilli slightly lower weathering rates with an optimum at pH 2-3 have been found (1).

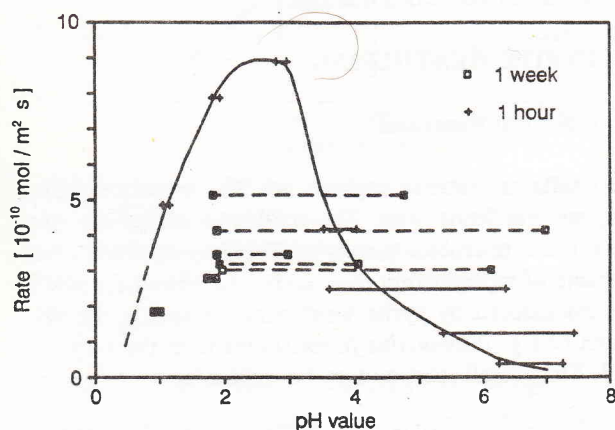


Figure 1: pH dependence of pyrite weathering rates in unsaturated columns incubated with Thiobacilli. Horizontal lines show rates for the span between column input and output pH. Irrigation to exchange column seepage water weekly (squares) and hourly (crosses). From Kölling (1).

Example calculation

Assuming one cubic meter of waste rock containing 0.65 wt.% pyrite at a dry density of $1855 \text{ kg} \cdot \text{m}^{-3}$ this sample volume contains 12 kg or 100 moles of pyrite. With an average pyrite grain size of $50 \mu\text{m}$ and some grain roughness we may calculate a specific surface of $0.05 \text{ m}^2 \cdot \text{g}^{-1}$ and thus 600 m^2 of pyrite surface contained in the cubic meter considered. At a uniform rate of $1 \cdot 10^{-9} \text{ mol} \cdot \text{m}^{-2} \cdot \text{sec}^{-1}$ this means that $6 \cdot 10^{-7} \text{ mol} \cdot \text{sec}^{-1}$ pyrite are weathered or that it takes approximately 5 years until the sample volume is pyrite free.

Relating the amount of 100 moles of pyrite which may be released from this sample volume within 5 years to an annual infiltration of $200 \text{ liter} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$ - typical for a German humid climate - this results in a seepage water pH of pH 1.00 and a sulfate concentration of $19200 \text{ mg} \cdot \text{liter}^{-1}$.

While these estimates seem to be quite reasonable, the same calculation for a pyrite content of 2 wt.% and a lower infiltration of $100 \text{ liter} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$ with otherwise unchanged boundary conditions yields pH 0.18 and a sulfate content of $128000 \text{ mg} \cdot \text{liter}^{-1}$.

It is evident, that apart from dissolution rates there must be a control which prevents the water from becoming too acid or too loaded. This control is already contained in figure 1 since it shows decreasing weathering rates with decreasing pH below the pH-optimum. Thus, the metabolism of thiobacilli creating the acid conditions does slow down at very low pH such that there is a lower pH-limit.

This means that especially at low infiltration rates where transport of weathering products is slow there is a self regulation of pyrite weathering rates.

2.2.2 Diffusive oxygen recharge

Considering reaction kinetics limited only by the specific grain surface as above means considering a uniform weathering rate throughout our sample volume. However, since large amounts of oxygen are needed for pyrite weathering, oxygen recharge within the sediment body and therefore the depth below surface of the reaction front is critically important.

The oxygen diffusion within the ground air may be described by Fick's first law

$$(1) \quad F_{\text{O}_2} = n_L \cdot D \cdot \Delta c \cdot \Delta x^{-1}$$

and since $15/4$ moles of O_2 are needed to dissolve one mole of pyrite we do have an expression for the pyrite "flux"

$$(2) \quad F_{\text{Py}} = 4/15 \cdot n_L \cdot D \cdot \Delta c \cdot \Delta x^{-1}$$

with n_L - gas phase fraction of volume, D - diffusion coefficient of oxygen in ground air, $\Delta c \cdot \Delta x^{-1}$ - oxygen concentration gradient in ground air, and Δx - diffusion distance. Assuming that pyrite weathering occurs as a reaction front at which all oxygen is being consumed Δc becomes $8.7 \text{ mol} \cdot \text{m}^{-3}$ (ambient oxygen concentration) and Δx becomes the surface distance of the reaction front or depyritization depth x_{depy} .

The location of the reaction front and thus Δx depends upon the pyrite content of the material m_{py} and the amount of pyrite that has already been dissolved at a given time thus the integral of F_{Py} over time.

$$(3) \quad x_{\text{depy}} = \Delta x = \int F_{\text{py}} dt \cdot m_{\text{py}}^{-1}$$

Rearranging 2 and 3 we get

$$(4) \quad F_{\text{py}} \cdot \int F_{\text{py}} dt = {}^{4/15} \cdot n_L \cdot D \cdot \Delta c \cdot m_{\text{py}}$$

to simplify the formulation we introduce a pyrite weathering constant PW defined as

$$(5) \quad \text{PW}^2 = {}^{4/15} \cdot n_L \cdot D \cdot \Delta c \cdot m_{\text{py}}$$

and get a simple solution to 4 which is

$$(6) \quad F_{\text{py}} = 2^{-1/2} \cdot \text{PW} \cdot t^{-1/2}$$

$$(7) \quad \int F_{\text{py}} dt = 2^{1/2} \cdot \text{PW} \cdot t^{1/2}$$

$$(8) \quad x_{\text{depy}} = 2^{1/2} \cdot \text{PW} \cdot m_{\text{py}}^{-1} \cdot t^{1/2}$$

F_{py} gives us the time dependant release of pyrite weathering products at the actual reaction front for an unsaturated waste rock initially having one uniform pyrite content m_{py} . The decrease of the pyrite release with $t^{-1/2}$ stems from the fact that the upper layers become pyrite-free and the diffusion distance for oxygen recharge increases. The time dependant location of the reaction front which equals the depyritization depth x_{depy} may be calculated by (8).

The concentration of weathering products in seepage water at the reaction front may be calculated by relating the release to the infiltration I

$$(10) \quad c = F_{\text{py}} \cdot I^{-1}$$

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

The concentration depth distribution at any given time is found by taking into consideration transport at the seepage water velocity v_{sw} from the reaction front to the given depth. The concentration at any x at a specific time $c(x, t)$ may be calculated if the time t_n at which a water element currently at x passed the reaction front is replaced in (10).

for $t = t_n$

$$(11) \quad x_{\text{depy}} = x$$

with

$$(12) \quad x = v_{\text{sw}} \cdot (t - t_0)$$

and thus combining (11), (12), and (8) we get

$$(13) \quad v_{\text{sw}} \cdot (t_n - t_0) = 2^{1/2} \cdot \text{PW} \cdot m_{\text{py}}^{-1} \cdot t_n^{1/2}$$

to simplify calculations we introduce another constant B defined as

$$(14) \quad B = 2^{1/2} \cdot \text{PW} \cdot m_{\text{py}}^{-1} \cdot v_{\text{sw}}^{-1}$$

and can rewrite (13) as

$$(15) \quad t_n^{1/2} = B + (B^2 + t - x \cdot v_{\text{sw}}^{-1})^{1/2} \\ = B + (B^2 + t - x \cdot v_{\text{sw}}^{-1})^{1/2}$$

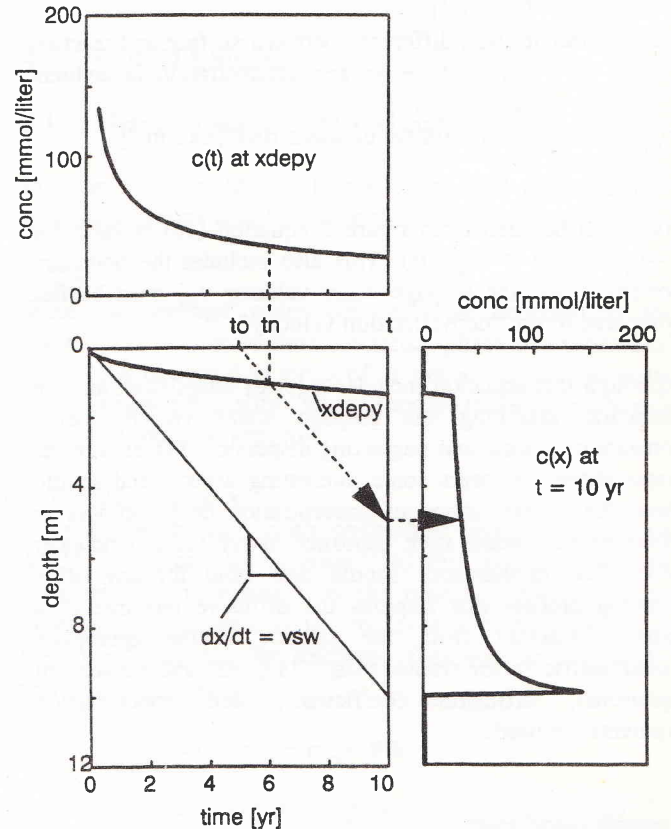


Figure 2: Change of concentration of pyrite weathering products with time (above, equation (10)) due to the depyritization controlled by diffusive oxygen recharge (left, equation (8)). Transporting the concentration peak at the reaction front located at x_{depy} at seepage water velocity (v_{sw}) yields the concentration depth distribution at any given time (right) as given by equation (16).

Replacing t_n from equation (15) for t in (10) yields a final equation for $c(x, t)$ and thus a possibility to estimate the concentration depth distribution in seepage water at any time t from deposition from

$$(16) \quad c(x, t) = 2^{-1/2} \cdot \text{PW} \cdot I^{-1} \cdot (B + (B^2 + t - x \cdot v_{\text{sw}}^{-1})^{1/2})^{-1}$$

$$\text{PW} = ({}^{4/15} \cdot n_L \cdot D \cdot \Delta c \cdot m_{\text{py}})^{1/2}$$

$$B = 2^{-1/2} \cdot \text{PW} \cdot m_{\text{py}}^{-1} \cdot v_{\text{sw}}^{-1}$$

$$\text{for } x = v_{\text{sw}} \cdot t > x > x_{\text{depy}}(t)$$

$c(x, t)$ - concentration of pyrite weathering products in seepage water at depth x from surface t years after deposition of waste rock [$\text{mol} \cdot \text{m}^{-3}$]

I	-	Infiltration [$\text{m}^3 \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$]
t	-	time [yr]
v_{sw}	-	seepage water velocity [$\text{m} \cdot \text{yr}^{-1}$]
x_{depy}	-	depyritization depth [m]
n_L	-	fraction of waste rock volume filled with ground air [$\text{m}^3 \cdot \text{m}^{-3}$]
D	-	diffusion coefficient of oxygen in ground air [$\text{m}^2 \cdot \text{yr}^{-1}$]
Δc	-	concentration difference between surface and reaction zone - here oxygen concentration in ambient air [$\text{mol} \cdot \text{m}^{-3}$]
m_{py}	-	pyrite content of waste rock [$\text{mol} \cdot \text{m}^{-3}$]

As it can be seen from figure 2 equation (16) is valid for $x = v_{\text{sw}} \cdot t > x > x_{\text{depy}}(t)$. This also includes the boundary condition that the seepage water velocity v_{sw} must be fast compared to the "depyritization velocity".

Although this equation includes a lot of simplifications - in particular assuming the seepage water velocity being constant over time and neglecting dispersion/diffusion in the water phase - it bears some interesting aspects and should show the general shape of concentration depth profiles in pyrite-bearing waste rock deposited above the groundwater table. The mathematics should also hold for any other leaching process that requires the diffusive recharge of a gaseous reactant from the surface if the appropriate stoichiometric factor (rather than $4/15$ in (2) and subsequent equations), diffusion coefficients, and concentration gradients are used.

Example calculations

Using the same values as above

$$\begin{aligned} I &= 0.2 \text{ m} \cdot \text{yr}^{-1} \\ v_{\text{sw}} &= 1 \text{ m} \cdot \text{yr}^{-1} \\ m_{\text{py}} &= 100 \text{ mol} \cdot \text{m}^{-3} \\ \Delta c &= 8.7 \text{ mol} \cdot \text{m}^{-3} \end{aligned}$$

and some good estimates for material parameters

$$\begin{aligned} D &= 2.5 \cdot 10^{-6} \text{ m}^2 \cdot \text{s}^{-1} = 77 \text{ m}^2 \cdot \text{yr}^{-1} \\ n_L &= 0.05 \end{aligned}$$

we get a value for the "pyrite weathering constant" PW

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

With these values we can estimate the flux of pyrite weathering products from $F_{\text{py}} = 21 \cdot t^{1/2}$. After 100 years from deposition the flux will be $2.1 \text{ mol} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$. Relating this to the infiltration we get a concentration of dissolved pyrite of $10.5 \text{ mmol} \cdot \text{liter}^{-1}$ which corresponds to $590 \text{ mg} \cdot \text{liter}^{-1}$ Fe, $2000 \text{ mg} \cdot \text{liter}^{-1}$ SO_4 and a pH of 1.98. The total area based output may be estimated from (7) as $424 \text{ mol} \cdot \text{m}^{-2}$ after 100 years. According to the stoichiometry of the weathering reaction this corresponds

to 24 kg dissolved iron and 81 kg of dissolved sulfate per square meter. At the pyrite content assumed here after hundred years the reaction front will be located 4.24 m below the surface.

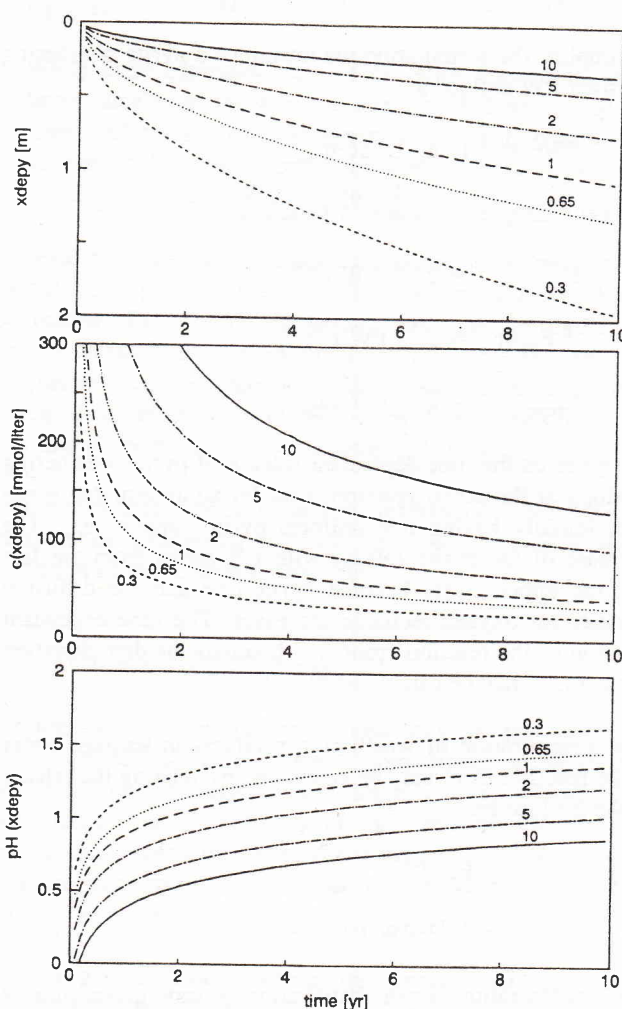


Figure 3: Depyritization depth (above) concentration at the reaction front (middle) and pH values (below) over time for waste rock material with a pyrite content of 0.3, 0.65, 1, 2, 5, and 10 wt.%. Other material constants as described in text.

Using equation (8) we find that after five years the reaction front is at 0.94 m thus pretty similar to the first example with $c = 47 \text{ mmol} \cdot \text{liter}^{-1}$ and pH 1.32. Yet, with the higher pyrite content of 2 wt.% or $300 \text{ mol} \cdot \text{m}^{-3}$ PW becomes $51 \text{ mol} \cdot \text{m}^{-2} \cdot \text{yr}^{-1/2}$ and after five years the reaction front will be only at 0.54 m below the surface at a concentration of $166 \text{ mmol} \cdot \text{liter}^{-1}$ corresponding with $9300 \text{ mg} \cdot \text{liter}^{-1}$ iron, $32000 \text{ mg} \cdot \text{liter}^{-1}$ sulfate, and pH 0.78.

While the single grain dissolution rates depend on specific surfaces of pyrite grains the overall effect is independent from the total amount of pyrite which is very unsatisfactory. Using oxygen diffusion as a limitation the reaction rates are

strictly depending on the pyrite content of the material, yet independent from dissolution rates at the individual grains. While this seems to be a serious source of error this is compensated by the fact that in material with low dissolution rates (low pyrite content and/or low specific surface) oxygen is being consumed more slowly such that the reaction front becomes a wider reaction zone and the overall effect on the output seepage water will be comparable with material with much higher reactivity

3 BUFFERING AMD OUTPUT

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

$$m_{cc} = 4 \cdot 424 = 1696 \text{ mol} \cdot \text{m}^{-2}$$

or with the molar weight of calcite ($0.1 \text{ kg} \cdot \text{mol}^{-1}$) to 170 kg Calcite per square meter. This quantity corresponds to the pyrite contained within a layer of 4.24 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 $x_{cc} = 50 \text{ m}$ where this buffering should occur this corresponds to a limestone content of

$$m_{cc} \% = m_{cc} \cdot 100 / (x_{cc} \cdot \rho_{dry})$$

$$m_{cc} \% = 170 \cdot 100 / (50 \cdot 1855) = 0.18 \text{ wt. \%}$$

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 term processes after the original groundwater level is reached additional buffer material might be needed

3.1 Location of buffer material

The location of the buffer material is critically important since it has to be situated in a way that the highly mineralized waters have to move through a buffer zone containing limestone. Since in waste rock of an open-cast lignite mine 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 $>0.25 \text{ wt \%}$ as calculated above.

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

4 CONCLUSIONS

4.1 Measures against AMD formation

In order to minimize the formation of acid mine drainage some conclusions may be drawn directly from equation (16).

1. Time

Since the seepage water concentration depends on the inverse square root of time the initial phase of exposure of waste rock is critical in terms of its impact on seepage water and groundwater quality. Thus exposure times of pyrite-rich material have to be kept low.

2. Diffusion distance

Covering waste rock with pyrite-free layers slows down AMD formation. In equation (16) this situation may be calculated by increasing t by the time t_{cov} that would be necessary to produce a pyrite-free layer with the thickness of the cover layer x_{cov} by leaching. This may be derived by rearranging equation (8)

$$t_{cov} = 0.5 \cdot x_{cov}^2 \cdot m_{py}^2 \cdot PW^{-2}$$

$$(17) \quad c(x, t) = 2^{-1/2} \cdot PW \cdot I^{-1} \cdot (B + (B^2 + t + t_{cov} \cdot x \cdot v_{sw}^{-1})^{1/2})^{-1}$$

t_{cov} - time necessary to produce pyrite free layer of x_{cov} thickness
 x_{cov} - thickness of pyrite-free cover layer

3. Permeability

The deposition of material with low permeability on top of pyrite-bearing waste rock means decreased seepage water velocities and infiltration at a lower diffusion coefficient and ground air volume fraction. In this case it is much more convenient to look at the flux of pyrite weathering products F_{py} as described in equation (6) thus the area based output rather than concentrations which may become very high when the infiltration is low.

4.2 Long term effects

In large open-cast lignite mines as we have them in Germany where the groundwater table is lowered for several tens of meters for some 50 years of mine operation time an AMD peak of highly mineralized seepage water is situated in the unsaturated zone and will mix into the rising groundwater after the mine is abandoned.

If the depth of the final groundwater level in a former lignite pit is greater than the thickness of the pyrite-free zone that

has already formed up to the time when stable hydraulic conditions are met after closing down the mine there will be a long term effect since AMD formation will go on until the material becomes water saturated.

4.3 Perspective

Since pyrite weathering slows down rapidly when the material is water saturated, in Germany it is thought about using waste rock from hard coal mining preferably in subaquatic environments i.e. as structural material for water engineering and even as base sealing for landfills (Wiggering, (2)).

This is especially interesting since due to the wide range and unconformity of grain sizes in such waste rock it may be compacted to permeability coefficients of k_f 10^{-8} m·sec⁻¹ to 10^{-9} m·sec⁻¹.

In our working group the effectivity of oxidants other than oxygen that might be active under water-saturated conditions and the adsorption capacities of waste-rock material from two typical hard-coal mining locations in Germany are currently being investigated in saturated-column experiments. In order to check the suitability as base sealing material for landfills the diffusion of different pollutants through the fine grained fraction is being investigated in diffusion cell experiments, where a polluted water is separated from a blank groundwater by a 5 mm wide sample and the concentration increase on the blank side is being monitored.

5 REFERENCES

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