# Modeling of Pyrite Oxidation and Sulfate Reduction in Former German Hard Coal Mines

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## Abstract

Former mine workings are inaccessible today, making site-specific mine water sampling impossible. Samples are taken at pumping stations, mixing waters from large areas. To identify processes influencing mine water chemistry pyrite oxidation and sulfate reduction were modelled using PHREEQC, trying to reproduce the mine water chemistry of a former mine. The first step of modelling included pyrite oxidation with subsequent weathering of dolomite and calcite. In a second step sulfate reduction was modelled using acetate as substrate. The modelled values correspond roughly to measured values and show that further development is necessary and many processes are yet to be integrated.

**Keywords:** Sulfate reduction, pyrite oxidation, hydrogeochemical modelling, sulfur cycle, mine water rebound

## Introduction

With the closure of the last coal mine in the Ruhr region in 2018, maintaining drainage and ventilation systems was no longer necessary for coal mining operations. However, since more than 5 million people now live in the Ruhr region, an uncontrolled mine water rise is not possible. In order to minimize the risk to the environment, the mining operator RAG AG remains obligated to pump out mine water. At the same time, these long-term tasks must be carried out as efficiently as possible. To this end, the mine water is raised to safe levels in a controlled manner (RAG 2024). Locations of the pumping stations in the Ruhr region are shown in Figure 1.

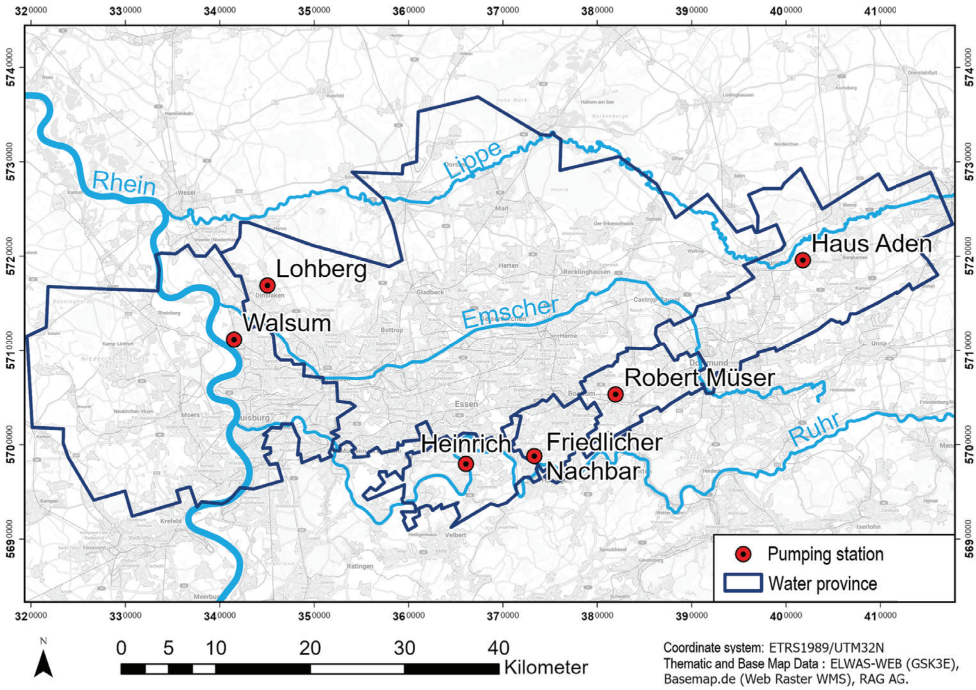
### *Mine water chemistry*

The coal-bearing strata of the Carboniferous emerge at the surface near the Ruhr River and dip to the north. The thickness of the overlying strata increases to around 1,000 metres near the River Lippe (Wedewardt 1995). Consequently, the mine water in the southern part of the mining area originates from meteoric water and has a lower degree of mineralisation, whereas in the north the mine water is fed by deep groundwater and has a higher degree of mineralisation. In addition to the inflowing waters, the mine water chemistry is also controlled by various hydrogeochemical processes. As a result of dewatering and ventilation of the mine workings, pyrite, contained in the coal seams and surrounding rock layers, comes into contact with oxygen and is oxidised, as shown in Equation [1]:

$$[1] \quad FeS_2 + 3{,}5\, O_2 + H_2O \rightarrow Fe^{2+} + 2\, SO_4^{2-} + 2\, H^+$$

The oxidation products form secondary minerals that are water-soluble. When these secondary minerals dissolve as a result of inflows or a rise in the mine water level, sulfate and iron enter the mine water. Ferrous iron is generally less mobile in this process, as it is oxidized by oxygen to form ferric iron and iron hydroxides; see Equation [2]. Both the oxidation of sulfide and the oxidation of ferrous iron release protons. In the Ruhr region weathering of carbonate minerals buffers the pH to circum-neutral levels.

$$[2] \quad 2\, Fe^{2+} + 0{,}5\, O_2 + 5\, H_2O \rightarrow 2\, Fe(OH)_3 + 4\, H^+$$



Coordinate system: ETRS1989/UTM32N
Thematic and Base Map Data : ELWAS-WEB (GSK3E), Basemap.de (Web Raster WMS), RAG AG.

***Figure 1** Water management provinces and pumping stations between the rivers Ruhr, Rhein and Lippe in the Ruhr area, Germany. Pumping stations Lohberg and Haus Aden are currently under construction. Map provided by Dr. Benjamin Haske, 2025.*

In anoxic parts of the mine water body the sulfate is reduced by sulfate reducing bacteria (SRB). Equation [3] shows sulfate reduction using acetate as substrate. In circumneutral mine waters hydrogen sulfide is deprotonated and sulfide (HS-) is predominant.

[3] $$SO_4^{2-} + CH_2COO^- + H^+ \rightarrow 2\,HCO_3^- + H_2S$$

If ferrous iron is present, it can react with the sulfide to form iron sulfides, as described in Equation [4].

[4] $$Fe^{2+} + HS^- \rightarrow FeS + H^+$$

The change of the sulfate concentration can be described by a Michaelis-Menten kinetic, as shown in Equation [5].

[5] $$\frac{d[SO_4^{2-}]}{dt} = R_{Michaelis-Menten} = -v_{max} \times \frac{[S]}{K_M + [S]}$$

Where [S] is the substrate concentration, *t* is the time, $v_{(max)}$ is the maximum growth rate, $K_M$ is the half-saturation constant for acetate or sulfate as substrate (Ingvorsen, Zehnder, Jørgensen 1984).

## Methods

### *Conceptual model*

To model the geochemical processes of pyrite oxidation and sulfate reduction, a conceptual model was developed. Critical parameters for the assessment of the geochemical reactions are:

- Porosity and grain density of the surrounding rock
- Content of pyrite in coal seams and surrounding rock
- Content of carbonate minerals in the surrounding rock
- Fraction of $Fe^{2+}$ which is oxidized to $Fe^{3+}$ and immobilized as $Fe(OH)_3$
- Rates, half saturation constants and substrates for the sulfate reduction by SRB
- Transport of formed sulfate in the mine water
- Pyrite grain size and micro texture

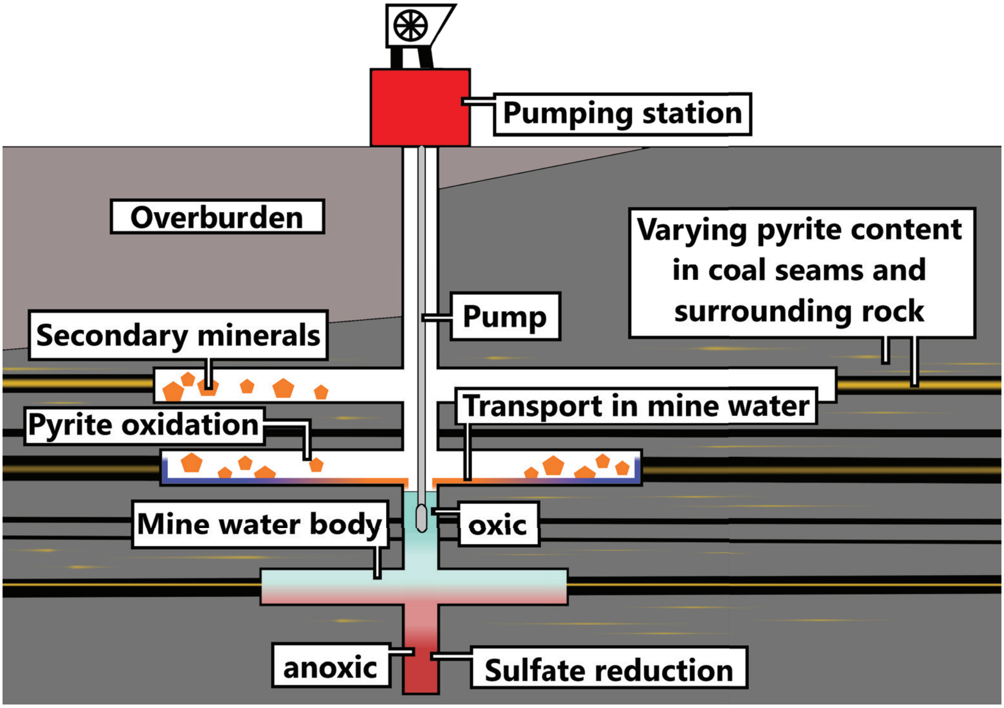


***Figure 2*** *Schematic drawing of the relevant geochemical processes at the water management sites.*

Since the mines are closed and no longer accessible, it proves difficult or impossible to measure these parameters in the field. Consequently, comparable values from the literature were used. At certain stages of the model development assumptions were made that are not supported by data from the literature or measurements. The geological parameters of the Ruhr Carboniferous rocks are listed in Table 1. Transport in the mine water was neglected in the calculations and it was assumed, that the mine water chemistry, that resulted from pyrite oxidation, was the initial water for the modeling of sulfate reduction. No estimations for the reactive surface of pyrite were made.

### *Numerical model*

For numerical modeling of the mine water chemistry, the mine site RM was selected, where sulfate reduction occurs and SRB were detected using a BART-Test from Hach. Average values from this site, obtained in a monitoring campaign with two-month intervals, were used as the target function and were tried to reproduce during numerical modeling (see Table 3). PHREEQC Interactive (version 3.8.6-17100, USGS) was used for geochemical modeling. The sulfate reduction was modeled according to equation [5] with the parameters listed in Table 2.

A representative volume was defined assuming a porosity of 10%. A high value was chosen, as the surrounding rocks were impacted by mining activities and are likely to have an increased porosity. A grain density of 2.67 kg/L was assumed. Since pyrite content varies over a wide range, a conservative approach was taken, using a fraction of 0.1% pyrite for the calculation, corresponding to 222.5 mmol of pyrite. For calcite a value of 0.1% calcite was used, and dolomite was assumed to be 0.1% of the solid phase, corresponding to 266.8 mmol of calcite, and 144.7 mmol of dolomite per representative volume. The assumption of the dolomite fraction is not supported by measured data. The values from Table 3 were used to calculate the saturation index (SI) for $CO_2$ using PHREEQC, resulting in an

*Table 1 Geological Parameters.*

| Parameter | Value/Range | Mean value | Source |
|---|---|---|---|
| Porosity | 0.3-15.6 % | 5.5 % | (Greve et. al. 2024b) |
| Grain density | 2.6 – 2.9 g/cm3 | | (Bär et. al 2020, Greve et. al. 2024a) |
| Pyrite content | 0.0 – 6.0 % | 0.2 % | (Greve et. al. 2024a) |
| Calcite content | 0.0 – 1.0 % | 0.1 % | (Greve et. al. 2024a) |

*Table 2 Kinetic Parameters.*

| Parameter | Value | Source |
|---|---|---|
| $v_{(max,Acetate)}$ | $5.3 \times 10^{-5}$ [mmol × $L^{-1}$ × $min^{-1}$ × g dry weight-1] | (Ingvorsen, Zehnder, Jørgensen, 1984) |
| $K_{(M,Acetate)}$ | $7.7 \times 10^{-5}$ [mmol × $L^{-1}$] | (Ingvorsen, Zehnder, Jørgensen, 1984) |

*Table 3 Mine water chemistry of RM as target function.*

| Site [mg/L] | pH | Na | Ca | Mg | $SO_4^{2-}$ | Fe(+II) | Cl | $HCO_3$– |
|---|---|---|---|---|---|---|---|---|
| RM | 7.5 | 1139.8 | 127.0 | 45.7 | 87.3 | 0.2 | 1703.3 | 979.1 |
| **Site [mmol/L]** | **pH** | **Na** | **Ca** | **Mg** | **$SO_4^{2-}$** | **Fe(+II)** | **Cl** | **$HCO_3^-$** |
| RM | 7.5 | 49.58 | 3.17 | 1.88 | 0.91 | 0.0036 | 48.04 | 16.05 |

SI of -1.63, assuming ideal gas behaviour. This SI was used as a proxy for $\log(pCO_2)$ and used for subsequent calculations. All calculations were initiated with neutral water at 22 °C. Additionally, it was assumed that 90% and 95% of the $Fe^{2+}$ produced during pyrite oxidation react with $O_2$. Since $Ca^{2+}$ does not react in sulfate reduction, the calculated values corresponding to the $Ca^{2+}$-concentration that best matched the target value of 3.17 mmol/L were selected as the basis for the subsequent sulfate reduction modelling. The sulfate reduction was carried out using the data from Table 4 as the initial solution in PHREEQC and the kinetic constants in Table 2. The calculations were carried out with and without the formation of FeS according to Equation [4]. The substrate concentration was varied between 2.0, 2.5, 3.0. 3.5 and 4.0 mmol/L acetate as substrate, respectively. Values for pH, Ca, Mg, S(+VI), Fe(+II), C(+IV) were obtained by running the simulation for 100 minutes. The results are shown in Table 5.

## Results

Substrate concentrations of 2 mmol/L acetate did not reduce the S(+VI) concentration below 1.5 mmol/L and were neglected. Substrate concentrations of 3.0 mmol/L acetate and above depleted all S(+VI) and were also neglected. Calculated concentrations of the C(+IV) species were 10.77 and 10.73 mmol for $C(+IV)_{90\%Ox}$ and $C(+IV)_{95\%Ox}$, respectively. Concentrations of Mg and Ca species were unchanged from the input data in Table 4, as they do not participate as reactants in the sulfate reduction reaction. A substrate concentration of 2.5 mmol/L acetate resulted in S(+VI) concentrations of 1.01 and 1.00 mmol/L, respectively. The target $HCO_3^-$ concentration was higher than the calculated concentrations of C(+IV) species after the sulfate reduction. Additional formation of $HCO_3^-$ during sulfate reduction contributes to elevated concentrations of $HCO_3^-$, but does not reach levels of the target function with 16.05 mmol/L. Calculated concentrations of Fe(+II) species were good approximations of

*Table 4* *Calculated weathering processes pyrite oxidation and carbonate weathering for the location RM with 90% and 95% of $Fe^{2+}$ reacting with $O_2$*

| 90%Ox [mmol/L] | pH | Ca | Mg | S(+VI) | Fe(+II) | C(+IV) |
|---|---|---|---|---|---|---|
| $RM_{Wea,90\%Ox}$ | 7.05 | 3.21 | 2.63 | 3.56 | 0.18 | 5.77 |
| **95%Ox [mmol/L]** | **pH** | **Ca** | **Mg** | **S(+VI)** | **Fe(+II)** | **C(+IV)** |
| $RM_{Wea,95\%Ox}$ | 7.05 | 3.25 | 2.66 | 3.56 | 0.09 | 5.73 |

*Table 5* *Calculated sulfate reduction with 2.5 mmol/L acetate*

| [mmol/L] | pH | Ca | Mg | S(+VI) | Fe(+II) | C(+IV) |
|---|---|---|---|---|---|---|
| 90% Ox FeS | 7.58 | 3.21 | 2.63 | 1.01 | 0.0051 | 10.77 |
| 90% Ox No FeS | 7.67 | 3.21 | 2.63 | 1.01 | 0.18 | 10.77 |
| **[mmol/L]** | **pH** | **Ca** | **Mg** | **S(+VI)** | **Fe(+II)** | **C(+IV)** |
| 95% Ox FeS | 7.67 | 3.25 | 2.66 | 1.00 | 0.0046 | 10.73 |
| 95% Ox No FeS | 7.71 | 3.25 | 2.66 | 1.00 | 0.09 | 10.73 |

the target value of 0.0036 mmol/L if sulfate reduction was modelled with formation of FeS. With no formation of FeS calculated concentrations of Fe(+II) species remained unchanged at 0.18 and 0.09 mmol/L.

## Conclusions

Initial model development shows that the basic geochemical reactions, especially the sulfur cycling processes taking place in the mine workings, can be reproduced. Low iron concentrations can be attributed to the formation of iron sulfide. High $HCO_3^-$ concentrations in the target function of RM could be partly reproduced by weathering reactions and sulfate reduction, but the model needs further development with regards to mineralization the inflowing water.

However, the results show that this first version of the model still relies on too many assumptions. In further steps of model development, it will be important to include:

- Transport processes from sites of pyrite oxidation into the water body
  As the water chemistry from the weathering was directly used for the simulation of sulfate reduction, the reaction of ferric iron with oxygen during transport was approximated by a fraction of 90% and 95% reacting with oxygen.
- Better characterization of the SRB and their abundance
  The use of BART test proves the presence of SRB in the mine water, but is not species-specific. Here Desulfobacter postgatei was chosen as a model compound on the basis of available results. A general microbial analysis of the bacterial species in the mine water and their abundance is necessary, in order to better estimate the reduced amount of sulfate. It will also allow for a
- Incorporation of pyrite grain size and reactive surface
  The geological parameters, which were obtained from studies within the Ruhr region, were not measured in the Robert Mueser water province. It remains unclear how representative the figures are of the situation at the Robert Mueser mine.
- Mine Geometry and rising mine water levels
  The final aim is also to take the geometry of the mine into account so that rising mine water levels can be represented in the model. However, as the calculated values in this article show, there are still many stages of model development between that final step and the current model.

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