Geochemical Modelling of Sulfur Cycling Processes During Mine Water Rebound in Former Hard Coal Mines of the Ruhr and Saar Regions, Germany

Simon E. Nikutta[1], Barbara M. A. Teichert[1], Henning Jasnowski-Peters[1], Harald Strauss[2], Sebastian Westermann[1]

[1]*Research Center of Post-Mining, Technische Hochschule Georg Agricola University, , 44787 Bochum, Germany, simon.nikutta@thga.de*

[2]*Universität Münster, Institut für Geologie und Paläontologie, 48149 Münster, Germany, hstrauss@uni-muenster.de, ORCID 0000-0003-2639-1225*

Abstract

A controlled mine water rebound is conducted in former hard coal mines of the Ruhr and Saar regions. To avoid risks for humans and the environment, the identification of old mine workings, which are prone to hydrogen sulfide (H_2S) formation is important. Thus, the sulfur content in coal is implemented in a geochemical model to assess future H_2S formation. Given the natural variability within a coal seam, mean sulfur contents for each mine water dewatering catchment area shall be used. For the southern Ruhr area, an influence of precipitation on the mine water geochemistry could be made visible.

Keywords: Geochemical modelling, sulfur cycling, pyrite oxidation, sulfate reduction, mine water rebound

Introduction

With the closure of the last active hard coal mines in 2018, the post-mining phase in the German hard coal mining areas began. Mine water management was no longer necessary to ensure mining operation, but to prevent an uncontrolled rise of mine water. Continuous maintenance of mine water management is therefore part of the perpetual tasks outlined in the legacy agreement between RAG AG (formerly Ruhrkohle AG) and the federal states of North Rhine-Westphalia and Saarland from 2007 (Balzer and Roth 2019; Jasnowski-Peters and Melchers 2022).

The RAG AG presented a concept for the long-term optimization of mine water management in order to achieve the perpetual tasks as sustainably and efficiently as possible. This concept establishes objectives aimed at protecting both human health and the environment from potential risks imposed by mine water, as well as a plan to allow for a controlled mine water rebound (RAG 2024). Rising mine water levels result in a series of beneficial effects for the whole mine water management. The depth from which mine water must be pumped is reduced, consequently decreasing the required energy and the respective costs (Balzer and Roth 2019). Furthermore, flooding of deeper mine workings can potentially limit the mobility of any remaining contaminants in those zones. Density differences between highly mineralized water from deeper parts of the mine and lower mineralized water from inflows closer to the surface cause the formation of density stratification (Kessler *et al.* 2020).

During the mine water rebound, previously dewatered areas of the mine workings come back into contact with the mine water body over time (Jasnowski-Peters and Melchers 2022). In these previously dewatered areas of the mine, weathering processes have led to the formation of easily soluble mineral phases like sulfates, hydroxides and carbonates which are consequently dissolved by the rising, often acidic, mine water (Wolkersdorfer and

Mugova 2023). The acidity results from pyrite oxidation. Hard coal usually has a total sulfur content ranging from 0.5 to 5 wt.-%, whereof pyrite sulfur is the major fraction (Chou 2012). As the dewatered mine workings are in contact with air, pyrite oxidation, which is described by equations [1] – [4], takes place (Evangelou and Zhang 1995).

[1] $2\ FeS_{2\ (s)} + 7\ O_{2\ (aq)} + 2\ H_2O \rightarrow 2\ Fe^{2+} + 4\ SO_4^{2-} + 4\ H^+$

[2] $2\ Fe^{2+} + ½\ O_2 + 2\ H^+ \rightarrow 2\ Fe^{3+}\ H_2O$

[3] $2\ Fe^{3+} + 6\ H_2O \leftrightarrow 2\ Fe(OH)_{3\ (s)} + 6\ H+$

[4] $14\ Fe^{3+} + FeS_2 + 8\ H_2O \rightarrow 15\ Fe^{2+} + 2\ SO_4^{2-} + 16\ H^+$

During abiotic pyrite oxidation, equation [2] is the rate limiting step. Fe^{3+} reacts with pyrite faster than it can be reproduced by reaction with O_2 (Evangelou and Zhang 1995). Additionally, oxidation can be catalysed by bacteria to a factor of $>10^6$ (Singer and Stumm 1970). With the rise of mine water levels and the ongoing depletion of oxygen in the (newly) flooded parts of the mine workings, pyrite oxidation will slow down (Wolkersdorfer and Mugova 2023). In anoxic regions of the mine workings, the sulfate resulting from pyrite oxidation, is released into the mine water (eq. [4]) and will be utilized as electron acceptor by sulfate-reducing bacteria (SRB). The sulfate reduction can either take place with an organic electron donor like lactate (eq. [5]) or an inorganic electron donor like elemental hydrogen (eq. [6]).

Chemo-organotrophic sulfate reduction with organic electron donor:

[5] $C_3H_5O_3^- + SO_4^{2-} + 3\ H+ \rightarrow C_2H_3O_2^- + HCO_3^- + HS^- + H_2O$

Sulfate reduction with inorganic electron donor:

[6] $SO_4^{2-} + 4\ H_2 + 2\ H^+ \rightarrow HS^- + 4 + H_2O$

In order to ensure groundwater quality, it is crucial to monitor the formation of hydrogen sulfide, which has strong adverse effects to (ground)-waterbodies. This is particularly important as the Haltern Formation aquifer in the region is used for drinking-water production (Drobniewski *et al.* 2018). In the context of the planned rise of mine water levels, it is important to predict whether and where sulfate reduction might occur as well as quantitatively estimating H_2S formation.

In order to achieve this, a hydrogeochemical model will be developed to account for the sulfur content of the coal seams, following an approach with two main objectives:

1. Determination of sulfur concentrations in the coal seams to identify areas within the mine workings that may be prone to increased pyrite oxidation and subsequent sulfate reduction during the rise of mine water.
2. Depth-dependent sampling of the mine shafts in order to enhance the understanding of the different geochemical zones in the mine workings and to investigate if density stratification has already developed.

Methods

Modelling

Sulfur concentrations were kindly provided by RAG AG and were partially derived from exploration drillings or from samples taken during mining operations. No discrimination between organic and inorganic sulfur species was possible, since the sulfur content was given in wt.-%. Hence, the values were interpreted as pyrite sulfur, as it is the major sulfur fraction in coal. Modelling the spatial distribution of sulfur contents was carried out using the Software ArcGIS Pro (version 3.3.2). Ordinary kriging was applied using a spherical function, where at least two and not more than ten neighbours were included. Initially, it was carried out for a larger area, using data available from exploration drillings and subsequently for a longwall mining operation in the same coal seam.

Seasonal influence of precipitation in the southern Ruhr area

In order to estimate the influence of precipitation on mine water geochemistry in two southern water provinces Friedlicher Nachbar (FN) and Robert Mueser (RM) in Bochum, precipitation data from the station of the German Weather Service (DWD) in Bochum was used to compare with the with the mine water geochemistry (Deutscher Wetterdienst 2025). From the daily precipitation the 6-weeks-sum was calculated, to allow for a better recognition of time periods with high precipitation.

Results and Conclusions

Modelling

For the input data, the sulfur content observed in the exploration drillings ranged from 0.61 to 1.93 wt.-% sulfur, with a mean value of 1.01±0.32 wt.-% sulfur. The sulfur content varies widely between the drillings without a discernible spatial trend. This led to a bullseye effect: In the centre of the modelled area, a pattern of concentric rings can be seen in Fig. 1. This can be attributed to one high sulfur concentration value with 1.86 wt.-%. The sample just south has almost half the sulfur content with 0.94 wt.-%. At the same time, the data density surrounding this point is low, which further enhances the bullseye effect.

To further revise the calculated sulfur content from the kriging interpolation, sulfur concentrations of samples of a longwall mining operation of the coal seam President 1 were investigated. The area of the operation is located in the west of the interpolated area, had an approximate extent of 2 km × 1 km and is depicted in Fig. 1 and 2. The measured sulfur values ranged from 0.57 to 1.73 wt.-%, with a mean value of 1.01±0.24 wt.-%. When compared to the sulfur map in Fig. 1, the modelled sulfur content in the mining field varied substantially, even when considering a smaller area. This leads to the conclusion, that the sulfur is unevenly distributed within the coal seam, resulting in highly variable sulfur contents even within relatively small areas. Highly variable sulfur contents within coal seams reflect the heterogeneity of fluvial and marine delta plains during coal formation and the varying intrusion of sea water (Casagrande 1987; Spears 2015; Dai *et al.* 2020). Consequently, ordinary Kriging interpolation is not the suitable method for this application. The same conclusion can be drawn when considering the Kriging interpolation carried out with the same parameters for the sulfur values in the longwall mining operation of coal seam President 1. Fig. 2 shows zig-zag patterns, which may be a result of high local variability in the observed data. A comparison of the mean sulfur contents in the exploration drillings and in the mining samples showed a very good agreement. In order to further substantiate this agreement, sulfur data for ten coal seams in the Ruhr area reported by Suess *et al.* (2007) were considered for comparison in Fig. 3. In general, a good agreement of the mean values was observed, certainly within the error margins.

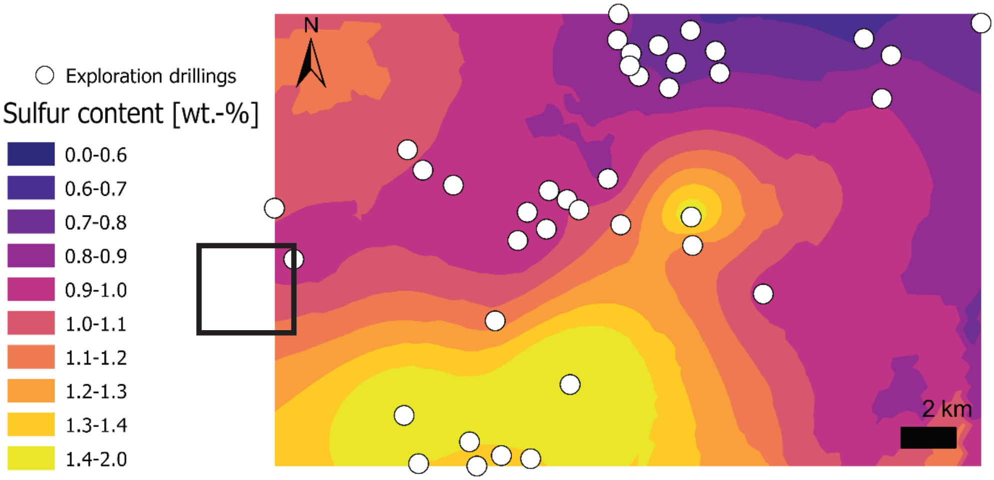

***Figure 1** Spatial distribution of the sulfur content in the coal seam President 1 resulting from Kriging interpolation of data from 45 exploration drillings in the western Ruhr area, depicted by the white circles. The black rectangle roughly represents the area of the longwall mining operation.*

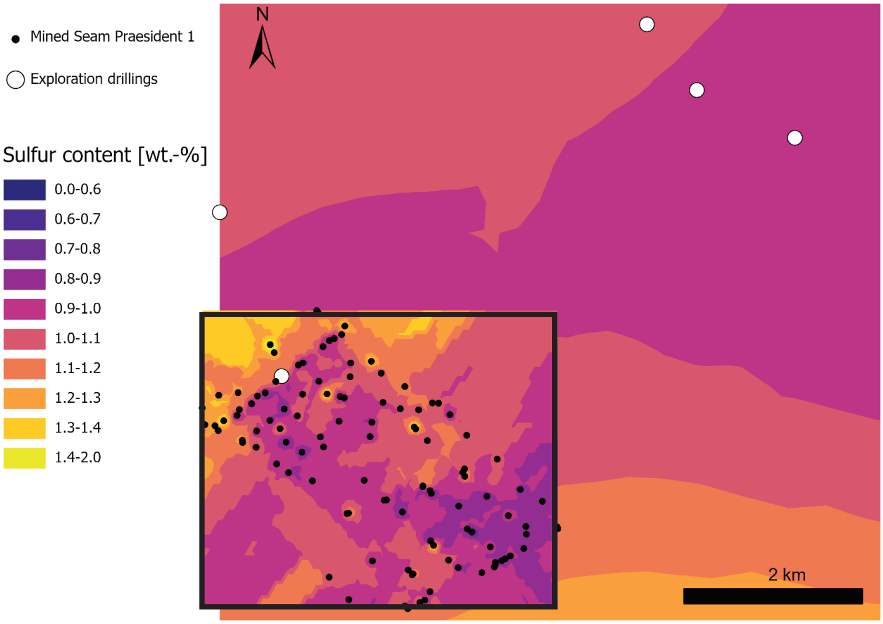

Figure 2 *Kriging interpolation for the spatial distribution of sulfur contents resulting from Kriging interpolation of observations for seam Praesident 1 from a longwall mining operation in the western Ruhr Area, depicted by the black circles.*

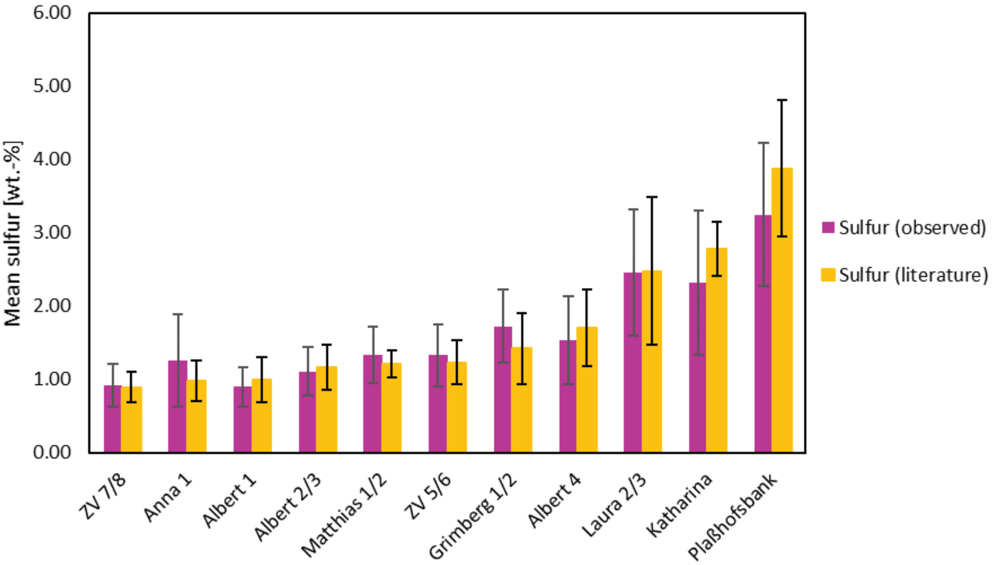

Figure 3 *Comparison of average sulfur contents observed in this study (orange) compared to average values reported by Suess et. al. (2007; purple) for several coal seams of the Ruhr Area. The error bars indicate the standard deviation.*

Consequently, for further modelling, mean sulfur contents will be used for each coal seam in each water management province, as the local variations of the sulfur content are too high to allow a more detailed geostatistical analysis.

Seasonal influence of precipitation in the southern Ruhr area

During the time period from November 2022 to December 2023 the sulfate concentrations ranged from 70 mg/L to 88 mg/L in RM and from 205 mg/L to 236 mg/L in FN, respectively.

The amount of precipitation was higher in the winter of 2023/2024, compared to the to the winter of 2022/2023. Additionally, the spring of 2024 had a high amount of precipitation, which was evenly distributed over a prolonged time period. This shows in the elevated baseline of the 6-weeks-sum of the precipitation, which was mostly higher than 100 mm from October 2023 to June 2024. The higher amounts of precipitation and its evenly distribution led to an increased ground water recharge and consequently to more water reaching the mine workings. This observation is consistent with the sulfate concentrations in the mine water, which showed rising values up to 210 mg/L in RM and 360 mg/L in FN, respectively. Iron-sulfide oxidation products from dewatered parts of the mine, which are in contact with air, were washed into the mine water body and led to a rise in concentrations. Sulfate concentrations seemed to start to decline again on the last available data point, however more samples will be necessary to confirm this trend.

Summary and outlook

Sulfur contents are highly variable even in close proximity within the same hard coal seam. This, in combination with a heterogenous data density, renders the interpolation of sulfur data inconclusive. However, the mean sulfur concentration for individual coal seams is somewhat consistent and within the same range as literature data (Suess *et al*. 2007). Therefore, the application of mean values will be more suitable for the development of a geochemical model.

An effect of precipitation on mine water geochemistry in the southern mine water provinces of the Ruhr region could be identified. After extended periods of precipitation the sulfate concentrations showed a rise, after a certain lag time. In order to gain further insight on the sources

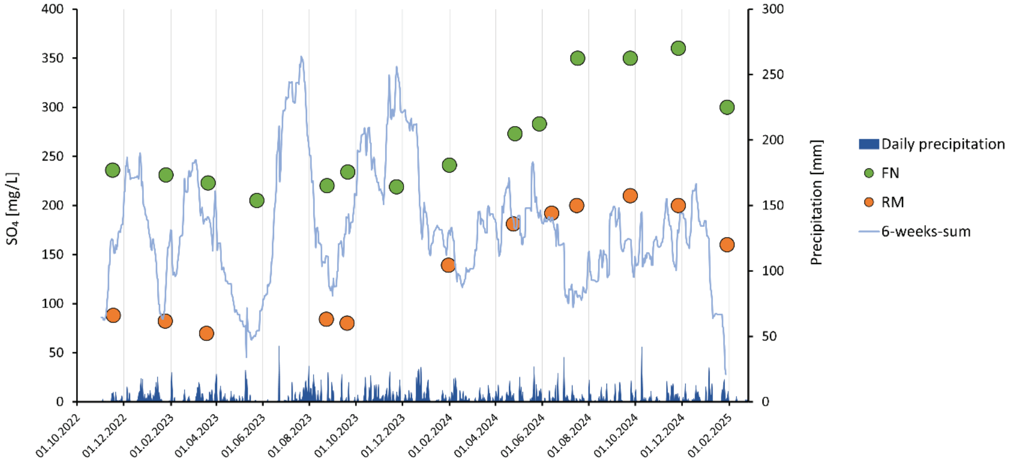

Figure 4 *Sulfate concentrations in mine waters of the water provinces RM, FN and daily precipitation, 6-weeks-sum of daily precipitation in mm over time.*

of the sulfate isotope measurements of the sulfate will be carried out.

Future work will comprise mine water sampling in shafts at discrete depths providing a better understanding of the sulfur turnover in different depths of the mine workings, if these measurements are possible and scientifically reasonable.

Acknowledgements

We sincerely thank RAG AG for providing the data used in this study, enabling valuable insights into mine water management processes and for providing financial support for this project.

References

Balzer I, Roth M (2019) Mine Water in the Ruhr Area-Opportunities for the Future. Mining Report 155

Casagrande DJ (1987) Sulphur in peat and coal. Geological Society, London, Special Publications 32:87–105

Chou C-L (2012) Sulfur in coals: A review of geochemistry and origins. International journal of coal geology 100:1–13

Dai S, Bechtel A, Eble CF, Flores RM, French D, Graham IT, Hood MM, Hower JC, Korasidis VA, Moore TA (2020) Recognition of peat depositional environments in coal: A review. International journal of coal geology 219:103383

Deutscher Wetterdienst (2025) Monatliche Niederschlagswerte. https://opendata.dwd.de/climate_environment/CDC/observations_germany/climate/monthly/more_precip/. Accessed 3 February 2025

Drobniewski M, Karus C, Löchte J (2018) Retreat to the future: shaping the post-mining era. Mine Water and the Environment 37:866–867

Evangelou VP, Zhang YL (1995) A review: pyrite oxidation mechanisms and acid mine drainage prevention. Critical Reviews in Environmental Science and Technology 25:141–199

Jasnowski-Peters HJ, Melchers C (2022) Mine Water Rebound in the Former Hard Coal Mining Area of the Ruhr District—Hydrogeochemical Monitoring for a Sustainable, Ecological and Economical Feasible Post-Mining Approach. Min. Rep. Glückauf 158:333–343

Kessler T, Mugova E, Jasnowski-Peters H, Rinder T, Stemke M, Wolkersdorfer C, Hilberg S, Melchers C, Struckmeier W, Wieber G (2020) Groundwater in former German coal mining areas—a scientific perspective on mine floodings. Grundwasser 25:259–272

RAG (2024) Konzept zur langfristigen Optimierung der Grubenwasserhaltung der RAG Aktiengesellschaft für Nordrhein-Westfalen. https://geodaten.rag.de/bid/tree/GenV/Grubenwasserkonzept%20NRW/Konzept%20%E2%80%93%20Grubenwasserhaltung%202024.pdf. Accessed 12 December 2024

Singer PC, Stumm W (1970) Acidic mine drainage: the rate-determining step. Science 167:1121–1123

Spears DA (2015) The geochemistry and mineralogy of high-S coals, with examples mainly from the East Pennines Coalfield in Yorkshire and Nottinghamshire, UK: an overview. Proceedings of the Yorkshire Geological Society 60:204–226

Suess MP, Drozdzewski G, Schaefer A (2007) Sedimentary environment dynamics and the formation of coal in the Pennsylvanian Variscan foreland in the Ruhr Basin (Germany, Western Europe). International journal of coal geology 69:267–287

Wolkersdorfer C, Mugova E (2023) Untersuchungen zum Verständnis von Grubenflutung und der Barrierewirkung von Dichteschichtung. 21. Albergbaukolloqium Essen:197–204