

Investigations on microbial reduction processes in a flooded underground mine

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Abstract This paper deals with the investigation of hydro-(bio-)geochemical processes in a flooded uranium underground mine in Germany. Processes were investigated by means of an extended sampling campaign. Focus was on the detection of microbial reduction processes. Achieved data was compared to the long-term monitoring data of the last decade(s).

Key words mine closure, flood water, uranium, microbial reduction, environmental parameters

Introduction

Wismut GmbH as the legal successor of the former mining company SDAG Wismut has been remediating its legacies in Central Germany since the closure of the former uranium mines by the end of 1990. The Wismut project is one of the most important environmental tasks in the German federal states of Saxony and Thuringia. One key aspect of the remediation activities is dedicated to the closure of several underground mines including mine flooding. At most of the mine sites, flooding is nowadays far progressed or already finished. Mine flooding in general causes an extensive change of hydrogeochemical conditions inside underground mines. In the beginning, soluble components are mobilized from altered and oxidized rock bodies. Later, mine water composition changes due to elution/dilution, mineral reactions and redox-sensitive, microbially catalyzed processes. Therefore, water quality and load predictions are essential for environmental impact assessment and mitigation planning, especially for mine water treatment.

Due to the existing environmental monitoring program of Wismut, a detailed description of mine water qualities and evolutions is available for a great amount of monitoring points over the last 25 years. At one particular Wismut mine site, where flooding was conducted between 1998 and 2007, predictions based on pre-flooding data show a clear deviation for some contaminants compared to the long-term monitoring data. For example, uranium concentrations and concentrations of bicarbonate (HCO_3^-) are characterized by stagnation or even increase instead of decrease over the last years. Aim of the study was to describe possible processes inside the flooded underground mine that allow an interpretation of the monitoring data. Therefore, required parameters for the detection of those processes during the mine water sampling and analysis are discussed.

Subject of Investigation

According to Younger et al. (2002), contaminant concentrations in a mine water pool should decrease over time after flooding is completed, mainly due to elution/dilution processes. At the investigated mine site, most of the parameters (including iron and other metals) fol-

low this very general predictive trend, and a sufficient fit between predicted and measured monitoring data can be stated. However, two important parameters show a clear deviation between predicted and measured values: uranium and bicarbonate (HCO_3^-). Both concentrations are characterized by a stagnation or even increase instead of a decrease over the last years, approximately since the end of the flooding process (G.E.O.S. 2014).

There are different approaches for explaining these phenomena. Two potential explanations will be described by means of the following hypotheses:

- The surrounding rock body contains primary carbonates, such as dolomite ($\text{CaMg}[\text{CO}_3]_2$), calcite (CaCO_3), and siderite (FeCO_3). During mine flooding, carbonates are dissolved and HCO_3^- is increasing. In addition, iron and uranium are released during the dissolution process. There is also buffering due to the formation of secondary carbonates.
- There are microbial reduction processes of organic matter, which cause iron reduction. (Primary) Iron hydroxide phases are dissolved, so that elements that are bound to these phases are also released. Bicarbonate (HCO_3^-) or rather carbon dioxide (CO_2) is a product of the microbial reduction of organic matter.

For the investigation of the two hypotheses, previous monitoring data was evaluated. It became obvious that for a clear distinction between carbonate dissolution and microbial processes, the existing data from routine monitoring was not sufficient, e.g. there was no information about reduced species (ferrous iron, sulphide) in solution. Additional parameters needed to be determined during an extended sampling campaign.

Methods

An extended sampling campaign was carried out in order to realize additional measurements compared to the regular sampling of the long-term monitoring program. The additional data was needed to provide further information e.g. about redox processes. As a first step, several existing sampling points (cased boreholes) were chosen to describe different areas of the flooded mine. The additional sampling was then carried out in parallel to a regular sampling, so that it was possible to compare the obtained data. The main aspects of the sampling were the following:

- Determination of reduced species, which is necessary to characterize reduction processes inside the flooded mine. Therefore, Fe (II) and Fe-total, as well as sulfide and sulfate were analyzed by means of photometric measurements.
- Investigation of the formation of gas phases, such as H_2S , CH_4 and CO_2 , which are indicators of reduction processes. On the one hand, they were measured qualitatively by means of an on-site method, where mine water could degas in a closed bucket (filled with N_2) and the developing gas phase was characterized (Fig. 1). On the other hand, samples were collected in closed exetainers for the quantitative measurement of dissolved gas phases in an external laboratory (gas chromatography).

- Influence of hydrostatic pressure, as the sampling depths at the selected monitoring points were between 103 and 345 meters below surface. Hence, the hydrostatic pressure of the sampled mine waters is between 10 and 35 bars. To determine the influence of the pressure on the water samples, a constant-pressure sampling was carried out using a vacuum sampler of 5 liters volume (VS, Figs. 2, 3) in addition to the regular pump sample (PS). Differences in the contents of gas phases, e.g. CO₂ and therefore DIC (dissolved inorganic carbon, e.g. HCO₃⁻ and CO₂), were expected, as the mine water is able to degas to a certain extent during the regular pump sampling.



Fig. 1 On-site Measurement of gas phases



Fig. 2 Vacuum Sampler



Fig. 3 Outlet valve of the VS

- Evaluation of the standard procedure for the analysis of DIC (dissolved inorganic carbon, HCO₃⁻) during a regular sampling in context to the degassing effects. Comparative analyses were carried out by on-site titration and by taking samples for TC/TIC/TOC (total carbon, total inorganic/organic carbon) analyses in the laboratory.
- Distinction between DIC resulting from reduction processes or from carbonate buffering/dissolution, which was investigated using the ¹³C signature of the stable carbon isotopes.
- Evaluation of the saturation states of different relevant mineral phases, which was done by hydrogeochemical modeling with PhreeqC (Parkhurst & Appelo 1999). The results of the chemical analyses of the extended sampling campaign serve as input data.

Results and Discussion

Reduced Species

In general, the reduction status of a water sample is described by the redox potential. Furthermore, the relation between Fe (II) and Fe-total and the presence of dissolved sulfide are indicators for reduction processes. Tab. 1 summarizes results for the standard pump sampling (PS) and the vacuum sampling (VS), respectively.

Concerning the redox potential, values between 100 and 200 mV characterize a semi-reduced environment. For all of the samples, Fe (II) and Fe-total are approximately the same concentration, indicating that all of the iron in solution is reduced. That means, the mine waters are characterized by iron reduction in a post-oxic environment. The next reaction in the ideal redox sequence is sulfate reduction to sulfide (Appelo & Postma 2005). Sulfide

has been detected in some of the samples, but only in very small concentrations. Sulfide in a solution often precipitates with dissolved metal ions, e.g. iron, lead, zinc. Sulfate concentrations are on a high level, so it is assumed that on the one hand, sulfate reduction is still in an early state and on the other hand, there is a sulfate source available (e.g. primary/secondary mineralization of gypsum).

Table 1 Measurement results of pH, redox potential, Fe (II), Fe-total, sulfide and sulfate concentrations at different sampling points

	pH value [-]	Redox potential [mV]	Fe (II) [mg/L]	Fe-total [mg/L]	Sulfide [µg/L]	Sulfate [mg/L]
e-1301 PS	6,9	133	102	102	9	860
e-1301 VS	6,8	117	98	94	57	810
e-1306 PS	6,7	165	146	146	5	2300
e-1306 VS	6,5	186	144	152	44	2430
e-1307 PS	7,4	47	22	21	<3	1980
e-1307 VS	7,4	145	15	10	<3	1890
e-1328 PS	6,6	139	108	108	<3	1190
e-1328 VS	6,8	178	12	13	42	630

The presence of mentioned reduced species is an indication for microbial reduction of organic compounds. Those are supposedly old wooden mine supports, which suffer from rotting inside the flooded mine.

Dissolved Gas Phases

By means of the on-site degassing test, H₂S and high CO₂ concentrations have been detected in the gas content of the bucket. In addition, oxygen concentrations were very low. Because of the large volume (~7 liters) of water needed, the measurement was only possible during pump sampling. Nevertheless, typical anoxic conditions were shown qualitatively by the results of the test. In order to describe steady state conditions between the mine water and the gas phase, the authors work on an optimized on-site method, where mine water is flowing steadily through the bucket without getting into contact with air.

GC analyses of the samples provided no analytical results for H₂S concentrations, as the detection limits for H₂S were higher than the expectable contents. However, methane and high CO₂ concentrations have been detected by GC analyses, which account for the post-oxic environment inside the mine waters. Low but considerable O₂ and N₂ concentrations show an influence of air, which is caused by minor irregularities during sampling and measurement.

Pump Sample vs. Vacuum Sample

Results in Tab. 1 show that there is no significant improvement using a vacuum sampler (VS) instead of a pump sampling (PS). Comparing PS and VS samples of the same measurement point, good correlations of most of the results can be observed, except for e-1328, where PS and VS supposedly supplied different mine waters with a different character.

By means of a manometer (Fig. 3) at the outlet valve, the pressure inside the VS was measured. Metered pressure was always a little lower than the theoretically expected value based on the water column. We assume that during the operation, complete sealing of the VS could not be ensured, so that there was still pressure loss and degassing to a certain extent. In contrast, PS allows reasonable results concerning the redox conditions of the mine waters. An exception is the measurement of sulfide, which is more accurate with VS samples.

DIC Analyses

One supplementary result was achieved due to the analyses of DIC during the sampling campaign. During the regular monitoring procedure, HCO_3^- concentrations are determined by titration within the laboratory. On-site titration of acidity/alkalinity and laboratory analyses of TIC revealed significantly higher concentrations of HCO_3^- compared to the lab titration results. This effect is probably caused by degassing of CO_2 between sampling and lab analysis.

Systematic underestimation of HCO_3^- concentrations may apply to most of the monitoring data of the past. Degassing potentials depend e.g. on the sampling depth and on the pH value of the respective mine water. HCO_3^- concentrations have a great influence on the hydrogeochemical evaluation of the datasets, e.g. concerning the buffering behavior of (primary/secondary) carbonates. In the future, either titration of acidity/alkalinity should be conducted on-site, or degassing of the samples should be prevented more efficiently. In general, TC/TIC/TOC analysis in the laboratory from airtight sealed samples is preferred as a method. On-site titration is justified in order to obtain immediate information on the characteristics of the respective mine water sample.

Stable Isotopes

Stable isotope analyses were assigned to determine different sources of DIC. In order to distinguish between microbial reduction and solid carbonate dissolution/buffering as the source for carbon, ^{13}C stable isotope analyses of TIC were carried out at Helmholtz-Centre for Environmental Research – UFZ (Department Catchment Hydrology, Halle/Saale, Dr. Kay Knöller). Results are shown in Tab. 2.

Usually, isotopic signatures of about 0 ‰_{VPDB} characterize marine limestones as TIC source, whereas freshwater carbonate buffering results in values between -14 and 0 ‰_{VPDB}. Degradation of older organic matter (wood, coal) as TIC source is characterized by rather light isotopic signatures between -30 and -20 ‰_{VPDB}. (Clark & Fritz 1997)

Table 2 Results of ^{13}C measurements of TIC in solution (UFZ Halle)

	$^{13}\text{C} - \text{TIC}$ [‰ _{VPDB}]
e-1301 PS	-14,1
e-1301 VS	-13,3
e-1306 PS	-13,8
e-1306 VS	-13,6
e-1307 PS	-16,4
e-1307 VS	-15,4
e-1328 PS	-14,2
e-1328 VS	-11,6

The results of the ^{13}C stable isotope analysis (Tab. 2) show a small range between -17 ‰ and 11 ‰_{VPDB} for the different samples.

Based on that, there is not only an influence of the dissolution of carbonates (marine limestones), but also a shifting to more negative values, supposedly due to microbial reduction (of organic matter). However, this conclusion is not considered without any doubt taking into account the presence of fresh water carbonates, which could interact with the mine water (dumped material etc.). In summary, there is no clear argument for or against microbial reaction processes.

Hydrogeochemical Modeling

By means of hydrogeochemical modeling with PhreeqC (Parkhurst & Appelo 1999), selected mineral phases were evaluated concerning their saturation conditions. Mineral phases that are relevant for the equilibrium of the mine water were in the focus of the investigations, such as carbonates (calcite, dolomite, siderite, etc.), iron and aluminium hydroxides, metal sulfides (FeS, PbS, ZnS, etc.) and sulfates (gypsum, jarosite, jurbanite, etc.). In the following, results for carbonate and sulfide phases will be presented.

As shown in Fig. 4, calcite and dolomite are in equilibrium or slightly oversaturated for most of the mine waters, whereas siderite shows a considerable oversaturation (SI = 1-2). However, precipitation of siderite is probably inhibited by kinetics or hydraulic conditions. It is obvious that the solution equilibria of carbonates are of great importance for the quality of mine waters.

Fig. 5 shows saturation indices of selected metal sulfides. Under the given conditions, non-crystalline iron sulfides like mackinawite and amorphous iron sulfide do not tend to oversaturate due to the present sulfide concentrations. In contrast, other metal sulfides like

lead sulfide and zinc sulfide are characterized by oversaturation. Amorphous sulfide phases like ZnS(a) will precipitate potentially in the presence of sulfide, whereas the precipitation of crystalline sulfide phases like galena and sphalerite is kinetically inhibited.

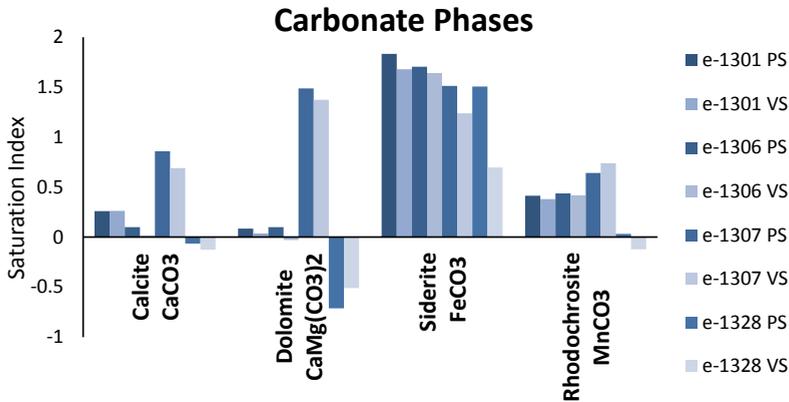


Fig. 4 Saturation indices of selected carbonates

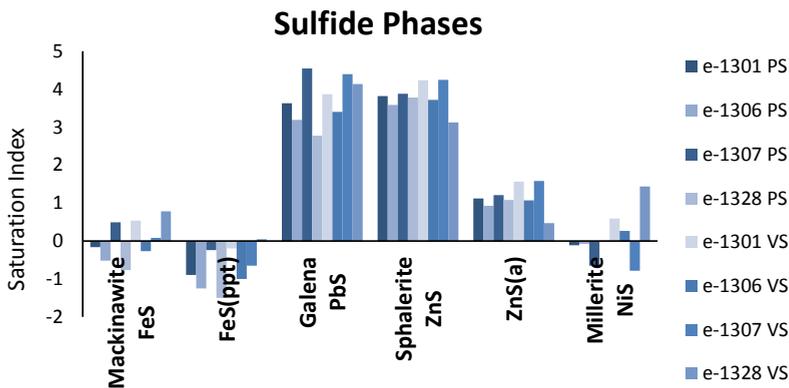


Fig. 5 Saturation indices of selected metal sulfides

Based on that, it is assumed that high metal contents inside the mine waters are the reason for low sulfide contents. Generated sulfide will soon precipitate with metal ions like zinc or lead.

Modeling with PhreeqC was done considering additional data from the extended sampling campaign, such as sulfide concentrations and improved bicarbonate concentrations. Therefore, a comparison with modeling results based on the long-term monitoring data showed a clear deviation concerning the described mineral phases. Due to the lower alkalinity, carbonate phases showed lower saturation indices. Furthermore, due to the missing sulfide values, PhreeqC was not able to evaluate sulfide phases. This is another reason to have a closer look on former monitoring data.

Conclusions

The study leads to different conclusions. On the one hand, hydrogeochemical processes inside the flooded mine were investigated by means of an extended sampling approach, so that additional parameters, such as reduced species, could be evaluated. On the other hand, extended data sets were compared to long-term monitoring data and some new aspects could be revealed.

Additional investigations during the extended sampling improved the understanding of key processes within the flooded mine. It is advised to include some of the methods used also during the regular monitoring procedure.

The investigations as a whole revealed that inside the flooded uranium mine there is not only one dominating process determining the long-term evolution of the mine water quality. The combination of microbial reduction, carbonate dissolution and buffering by hydroxides, carbonates and gypsum leads to a very complex situation. Thus, prediction of the behavior and development of the mine water quality needs sophisticated models that involve many process and reaction parameters.

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