Abstract
After flooding an underground mine, the quality of the discharging mine water usually improves. This effect is known as first flush, which has so far only been studied in the mine water at the point of discharge. Depth profile measurements at a former German uranium mine allowed to monitor and interpret the first flush over a 30 year period. In addition to the point of discharge, the first flush can be observed in the entire water body. It can therefore be assumed that the whole mine water body acts as a chemical reactor. Understanding the first flush details will help to improve predictions about water quality trend developments and helps in improving mine water treatment.

Keywords: first flush, mine water, flooding, mine water rebound, mine water management

Introduction
In many cases, discharging mine water must be treated after mines have been closed and flooded. It can be challenging to select and properly size an appropriate mine water treatment plant, because the mine water quality usually improves over time. First the water reaches maximum concentrations of the potential contaminants and then they gradually decrease – in the best case to natural background concentrations (Gzyl and Banks 2007; Wolkersdorfer 2021; Younger 2000). This effect is named first flush and has been, until now, only investigated with data from discharging mine water. Younger (1997) widely published about the first flush and described the typical curve as a rapid increase and the subsequent gradual, near exponential decrease of potential contaminants (Figure 3). Other possibilities to describe the curve have been published by Wolkersdorfer (2008) and Mack et al. (2010).

“Acid generating salt” (Bayless and Olyphant 1993) and therefore the leaching of secondary minerals cause an initial increase in concentrations over time. After this first contaminant increase, the vestigial acidity (Younger 1997) is flushed out and the first flush curve flattens. As a “rule of thumb”, four times the flooding period $t_r$ is the duration $t_f$ of the first flush (Eq. 1).

$$t_f = (3.95 \pm 1.2) \times t_r$$  \hspace{1cm} (1)

Although the first flush at the discharge point of a mine is a well-known phenomenon, it is still relatively unknown which hydrodynamic and chemical processes occur in the mine water body itself. By using different approaches to investigate the first flush in greater detail, the authors want to provide a better basis for the prediction of mine water quality during and after the flooding process as well as strategies for more effective mine water management.

Paul et al. (2011) described the development of the first flush with a perfectly mixed flow reactor (PMFR or MFR, more often referred to as complete mix flow reactor, CSTR, or completely mixed flow reactor, CMFR). Yet, as single CMFR would only account for the reaction and removal rate constant of one set of water reactants. Because the composition of mine water, and consequently the development of the first flush, results from a “potpourri of multiple reactions”, as described by Levenspiel (1999), Paul et al. (2011) was not able to fully describe...
the first flush scenario with one reactant or equation for all the mine water contaminants they investigated. Within a mine pool, a set of irreversible and reversible zero or higher order reactions, even fractions of reactions, takes place successive or in parallel. This requires more sophisticated assumptions than a single CMFR. A single conservative tracer substance follows the behavior of a CMFR. Further studies, with the Agricola Model Mine (AMM), shall reveal if it might be possible to describe first flush scenarios better compared to claiming the first flush are exponential decay.

Methods and data acquisition
Depth profile measurements from five flooded shafts of the former Schlema uranium mine, Saxony, Germany, were evaluated to understand the first flush within the mine water body. Depth profile measurements have been carried out once or twice a year by the remediation company Wismut GmbH since 1994. Therefore, a data set covering almost 30 years is available (Wismut GmbH 2022). Additional single measurement data before 1994 could be provided by the authors themselves. Electrical conductivity (EC) is a relevant parameter regarding the water quality, as higher electrical conductivities indicate a higher mineralisation and thus poorer mine water quality. For comparison, the EC values at the inflow of the water treatment plant were evaluated, and their temporal development corresponds with a characteristic first flush scenario.

An additional research method for investigating the first flush are analogue laboratory tests that were carried out at the Agricola Model Mine (AMM) at Tshwane University of Technology in Pretoria, South Africa. The AMM is a 6 × 4 m model mine consisting of insulated PVC tubes with four shafts, four levels and with a maximum volume of 153 L (Figure 1). It was the aim to verify, if the first flush can also be reproduced in the analogue model mine and thus whether more detailed experiments can be carried out. As density stratification normally occurs in flooded underground mines (Mugova and Wolkersdorfer 2022), a water body with higher density was prepared in the lower

Figure 1 Setup of the first flush experiment at the 6 × 4 m large Agricola Model Mine (AMM)
part of the AMM by adding bags filled with NaCl before flooding started. In the upper part of the model mine, the water was flushed out, due to a continuous flow. To simulate water inflow into the mine, tap water was continuously pumped into shaft #2 (15 mL/min) simulating ground water recharge and discharged at shaft #1. In order to examine the flushing effect, the tracer EosinY (EoY) was injected once after complete flooding of the AMM just below the inflow at section 2D and samples were taken daily at 11 sampling points in the upper area of the AMM and analysed fluorometrically (Cary Eclipse Flourescence Spectrophotometer; Agilent, Australia). Measuring with a constant fresh water supply lasted over a 2 month period.

**Results and Discussion**

For five different shafts in the Schlema-Alberoda district, first flush curves were analysed. Though all curves are similar, shaft 383 stands out, as data since October 1992 is available (mine flooding began in January 1991) (Figure 2, Figure 3). Initially, the EC increases from 4 mS/cm to 5.5 mS/cm, then it decreases exponentially since 1998/1999. Presently, the EC value is 1.6 mS/cm, and the improvement of water quality will be progressing only very slowly. A very similar curve can be seen in the EC values before the inflow into the mine water treatment plant. This indicates that the results of the measurements in the shafts are plausible. There is improvement in water quality and the first flush temporal development prevails in the mine pool as well. As the curves of the five shafts are very similar, a good hydraulic connection can be assumed between the shafts and the mine water discharge into the Schlema mine water treatment plant. This good hydraulic connection was already proven by a mine water tracer test in this mine (Wolkersdorfer 2001). As no stratification was detected due to the measurement depth not covering the entire vertical extend of the 1800 m deep mine, stratification cannot be discussed in connection with the Schlema mine’s first flush scenario.

Inflow of tap water and flushing the upper part of the AMM showed that nearly all the EoY tracer was flushed out after 11 days.
(Figure 4). Only in section 1C was a temporal delay, as there, analogous to a mine sump, less flow occurs. At the injection point (2D), the first measured tracer concentration, 15 min after injection, was 800 µg/L and 20 h after injection 196 µg/L. In comparison, the background tracer concentration in the discharge (section 1E) was 0.05 µg/L, 15 min after injection and reached 732 µg/L, 20 h after injection. After 5 days, almost no tracer could be found anymore at sampling point 2D. At section 1E, it took 11 days until almost no tracer could be found anymore, indicating that the tracer was flushed out quickly from the upper section of the AMM by advective transport. In the period from 2022-05-16 to 2022-07-20, for 70 days, 1500 L of water flowed through the upper part of the AMM. After 11 days the water in the upper part was exchanged about 4.6 times.

**Conclusions**

Mine water management and the design of mine water treatment plants requires to understand the hydraulic system in a flooded mine. Since the first flush is responsible for the change in water quality over time, the authors have gained new insights into this phenomenon through different approaches. First, the short-term deterioration and then exponential improvement of mine water quality does not only occur at the point of discharge. The same trend can also be observed within the complete mine water body. This is important regarding the duration of mine flooding and possible interventions in the mine water body. However, the faster the mine is flooded, the faster the first flush improves the water quality in the mine. Fluctuations in the water level must be avoided, as, for example, further disulfide weathering might take place, and the water quality can deteriorate again. Whether, for example, pumps for the geothermal use of mine water disturb the first flush and stratification in the mine water body will be verified by further experiments. Analogue modelling results show that it is possible to
use the AMM as a natural analogue to the flushing scenario in a flooded underground mine. In further studies, this fact will be used to understand mine flooding scenarios better. It will also allow to study mine water stratification and how density stratification can be generated artificially to improve the discharged mine water quality. Once stratification exists in a mine, the destruction of it, for example through pumping, must be avoided. Otherwise, the positive effect of improving the water quality through the first flush could be rendered obsolete.

Acknowledgements
The authors thank their respective research institutions for providing support in conducting this research. The German foundation “Forum Bergbau und Wasser” made travel funds available. The NRF SARChI chair for Mine Water Management, Department of Environmental, Water and Earth Sciences, Tshwane University of Technology under Grant № 86948 provided travel funds and financed the chair. We also thank Steffen Herrmann and Thomas Metschies (Wismut GmbH), David Banks, Thomas Walter and various colleagues for intensive discussions about the first flush, mine water stratification and continuous shaft measurements. Leshego Molaba conducted the experiments and measurements in the analogue Agricola Model Mine at Tshwane University of Technology (TUT).

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