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TECHNICAL ARTICLE

Understanding the Mechanisms and Implications of the First Flush in Mine Pools: Insights from Field Studies in Europe's Deepest Metal Mine and Analogue Modelling

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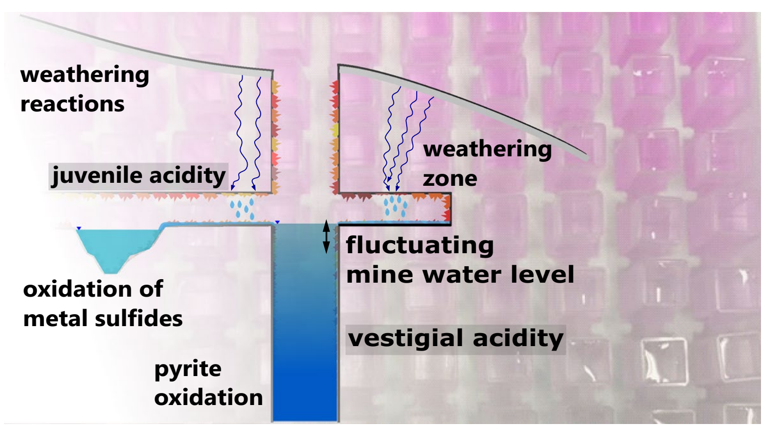
Abstract
The chemical composition of mine water discharged from flooded underground mines typically improves over time. This phenomenon is called first flush and can be described by a characteristic curve. Shortly after the mine water begins to discharge, water constituent concentrations rise and then fall in an almost exponential curve, improving water quality over time. In this study, the change in mine water quality was investigated throughout the mine water body. This mine water body commonly consists of different water bodies with individual densities, resulting in mine water stratification. Anthropogenic disturbance of the mine water body can disrupt this stratification and also the positive effect of the first flush. To better understand and predict the first flush, the first flush was simulated experimentally using an analogue model of a flooded underground mine, the Agricola Model Mine. The results were compared with field studies to help understanding and predicting the change in mine water quality. Overall, the results suggest that the first flush occurs throughout the mine water body, making it similar to a chemical reactor. This better understanding of the process can lead to more effective mine water management and design of mine water treatment facilities.

Graphical Abstract



Keywords Mining-influenced water · MIW · Mine flooding · Mine water rebound · Post-mining · Mine water management

Introduction

After mine closure, the aftereffects of mining operations are visible for decades, sometimes centuries (Sengupta 2021). This also applies to mining-influenced water (MIW) discharged into receiving water courses (Wolkersdorfer and

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Mugova 2022). Mine water quality usually improves over time, and the mine owner has to address these changes by adapting their mine water management (Merritt and Power 2022; Younger 1997). If this water exceeds discharge threshold values, suitable mine water treatment has to be in place, which often are active treatment plants (Wolkersdorfer 2022). These expensive systems can, however, be replaced by passive systems if the water quality improves over time and, ideally, mine water treatment is no longer necessary after a certain period. Yet, since passive systems usually require more space than active systems, this needs to be considered early enough during mine closure planning (Wood et al. 1999; Younger 1997).

For mine water management and water quality prediction, it is important to know and forecast temporal mine water changes. After a mine is decommissioned and the pumps are switched off, the infiltrating surface water and inflowing groundwater cause the water level in the mine void to rise. Because mining activities exposed the rock to oxygen, oxidation and weathering processes in the open mine voids were promoted, resulting in the formation of efflorescent salts. During the initial flooding process, the mine water dissolves these efflorescent salts and continues to mineralise until the water is discharged. This initially highly mineralised mine water is continuously flushed out of the mine by less mineralised infiltration and groundwater. Usually, discharged mine water reaches maximum concentrations of the potential contaminants, such as iron, sulfate and acidity, shortly after the mine is completely flooded, which then gradually decrease—in the best case to natural background concentrations (Gzyl and Banks 2007; Wolkersdorfer 2022; Younger 2000). These characteristics and explanations thereof have been published by Younger (1997), who commonly called that effect "first flush", although the term originally referred to soil leaching after a rainstorm following a dry period (Edwards 1973). It was—to our knowledge—first used in the mine water context by Aldous (1987), who characterised temporal concentration developments of mine water pollutants. Merritt and Power (2022) compare different empirical equations to describe the pollutant's decay, one of them being a "single-phase" model sensu Gzyl and Banks (2007). Perry and Rauch (2013) apply a "singe-phase" and a "two-phase" model to describe the concentration development from peak point till zero concentrations (Merritt and Power 2022). Mean decay constants were calculated by Mack et al. (2010) and Perry and Rauch (2013). Besides the exponential decay, Wolkersdorfer (2008) and Mack et al. (2010) introduced other potential equations for describing the course of the curves. In addition to empirical methods, numerical modelling of the longevity of mine water quality can be used. This was done for the Königstein uranium mine in Germany using reactive transport modelling, showing that even small variations in aquifer parameters can substantially alter the modelled metal mobility (Bain et al. 2001). Jakubick et al. (2002), for the same underground uranium mine, concluded that uncertainties in the results could have been caused by the model's boundary conditions. However, all of these authors concluded that although predictive modelling of mine water quality is only possible to a limited extent, it is nevertheless a useful tool for evaluating mine closure scenarios.

The initial increase in the time vs. concentration curve is caused by leaching of secondary minerals and efflorescent salts (Fig. 1). These form during or after (di)sulfide oxidation and weathering and are known as "acid generating salts" (Bayless and Olyphant 1993) or vestigial acidity (Younger 1997) due to their storage of acidity. Fluctuations in the mine beach within the underground mine pool can cause additional (di)sulfide weathering. This mine beach is defined as the zone of mine water fluctuation in a flooded underground mine pool (Aljoe and Hawkins 1993). Another pollution source is the proton acidity from disulfide oxidation in the unflooded mine workings caused by seepage water reacting with (di)sulfides or the dissolution of metal hydroxide and sulfate salts, named juvenile acidity (Perry 2009; Perry and Rauch 2013; Wolkersdorfer 2008; Younger 1997).

Various factors are responsible for the duration of the first flush. These include the acidity decrease, which is controlled by the influent fresh water and buffering. In addition, the dissolution of efflorescent salts, the weathering of (di)sulfides, the volume and hydraulic conductivity of the mine workings, hydraulic connections, and the groundwater recharge rate are decisive factors (Wolkersdorfer 2022; Younger et al. 2002). Immediately after the first mine water discharge, highly mineralised mine water, resulting from the dissolution of efflorescent salts, is flushed out for the first time.

In 1983, Glover considered using a rule of thumb to predict the longevity of iron concentrations in MIW. Based on Glover (1983), Younger (1997) summarised that "the iron concentration of uncontrolled mine water discharges falls by 50% in each subsequent period equal to that taken for the abandoned workings to fill with water after the pumps were withdrawn, i.e. an exponential decay" and determined an empirical equation for the duration of the first flush from investigating "80 individual discharges from abandoned coal workings" (Younger 2000). According to this investigation, the duration t_f of the first flush is approximately 3–5 times the flooding period t_r (Eq. 1), where the f-term is from Wolkersdorfer (2008):

$$t_f = f\left(aci_{rem}, r_w, V, K, R_{GW}\right) = (3.95 \pm 1.2) \cdot t_r \tag{1}$$

and t_f = duration of the first flush, aci_{rem} = acidity removal by buffering or dissolution, r_w = the weathering rate of

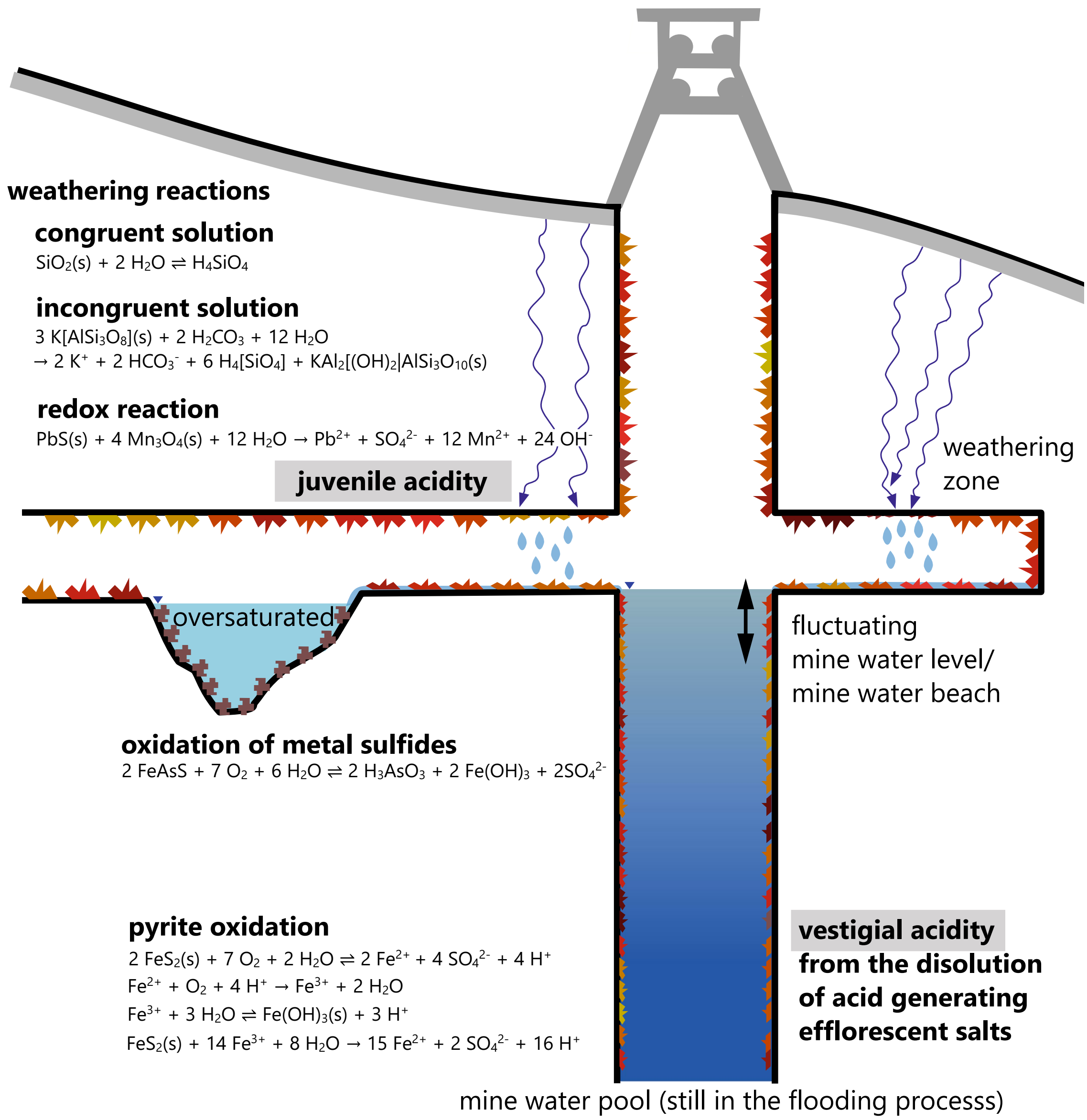

Fig. 1 Processes responsible for the formation of juvenile and vestigial acidity in a partly flooded underground mine

acid-containing efflorescent salts, V = the volume of mine voids (hydraulic connections), K = the conductivity of the mine workings, R_{GW} = the ground water recharge, and t_r = the rebound time. However, this equation is only a rough approximation, as the duration of the first flush can extend over years or decades, even with a relatively short flooding period. This is especially the case when juvenile acidity is formed by permanently infiltrating precipitation water (Gzyl and Banks 2007; Wolkersdorfer 2022) or strongly fluctuating water levels with an accordingly large mine beach. If the neutralisation capacity of the buffering minerals in the mine is not sufficient, additional concentration increases are possible, even after many years of relatively good water quality (Alpers et al. 2003; Nordstrom 2009; Younger 1997).

Rapantova et al. (2013), Gzyl and Banks (2007), and Merritt and Power (2022) have, to some extent, investigated the entire shaft water column to understand the first flush. Yet, other than these publications, this paper describes for the first-time detailed depth-dependent measurements of the water quality in shaft water columns and compares the results for several years to decades.

This study investigated the temporal water quality improvement within the shafts of a flooded underground mine over a 27-year period, interpreting these results in the view of the "first flush" sensu Aldous and Younger.

These measurements were supported by additional measurements from three other flooded mines. For supportive understanding these measurement's results, a large-scale laboratory experiment was set up, which for the first time should evaluate experimentally what causes the water quality improvement in a flooded mine on one side and the non-disturbance of stratification by ground water inflow on the other side.

Methods and Data Acquisition

Depth Profile Measurements

Description of Sampling Location

In the Schneeberg–Schlema–Alberoda area (Germany), the then SAG/SDAG Wismut mining company operated three large-scale uranium mines in the Schneeberg, Oberschlema, and Niederschlema–Alberoda deposits (Schuppan et al. 2008), which were the deepest European metal mines (about 2000 m deep). Two of these deposits, Oberschlema and Niederschlema–Alberoda, are hydraulically connected and together form the Schlema–Alberoda mine (Paul et al. 2013, 2016). Subsequent flooding of the Schlema–Alberoda uranium mine, which started in 1991, took about 10 years (≈ 90% of the mine void flooded), and was controlled by regulating the groundwater inflow into the voids. Thereafter, gradual residual flooding followed. In total, the mine pool of the Schlema–Alberoda mine has a volume of ≈ 35.5×10^6 m^3. Initially, mine water was pumped from greater depths, but starting in 2011, it was regularly pumped from close to the water level. Actively treated mine water has been discharged into the Zwickauer Mulde river since 1999 (Wismut GmbH 2022). The mine water from the Schneeberg mine district discharges via the historic Markus-Semmler adit, which has an elevation above the flooding level of the Schlema–Alberoda mine but is not hydraulically connected to the Schlema–Alberoda mine pool. At the adit's exit, the mine water discharges via a water conduit directly into the Schlemabach stream.

Currently, pumping keeps the mine water level at the Schlema–Alberoda mine ≈ 20 to 30 m below the potential point of discharge. This allows for ≈ 0.6 to 0.9×10^6 m^3 of storage space and serves as a buffer of several weeks for the operation of the water treatment plant, should pump maintenance or failures temporarily interrupt the pumping process (Wismut GmbH 2022, pers. Comm. Wismut GmbH).

Data from Depth Profile Measurements

Nearly three decades of depth profile measurements in various abandoned Schlema–Alberoda uranium mine shafts (Fig. 2) were evaluated regarding the first flush. Between 1994 and 2003, these depth-dependent measurements at shafts 208, 208 W, 371, 382, and 383 were carried out by an external company and from 2004 onwards by Wismut itself. Measurements were conducted with MMS-60 and LTS-42 probes and loggers (LogIn Bohrlochmeßgeräte GmbH, Gommern, Germany), and data from the periods 1994 to 2021 were available for this study. While the probes are lowered into the flooded shaft via a winch, various physicochemical parameters such as temperature and electrical conductivity (EC) are measured at regular time intervals. These depth profiles reflect the spatio-temporal parameter changes, with more recent measurements having been conducted at a higher spatial resolution. Since EC is directly proportional to the concentration of the total dissolved solids (TDS), it can be used to investigate the mineralisation of the mine pool. As the mine water is actively pumped in this mine, no noteworthy stratification could develop in the sampled part of the shaft, unlike in many other flooded shafts (this situation was different in deeper shafts of this mine during the flooding process, where density stratification was commonly observed). Therefore, the EC and temperature were taken from the top 10 m of the depth profile to construct the first flush curves and are therefore representative of the entire water column. In addition to the depth profile measurements, bulk water samples were available for shaft 371 between 1995 and 2021. During environmental monitoring, most water analysis were carried out in the accredited laboratories of Wismut GmbH (Seelingstädt, Aue and Königstein laboratories), though in the first years of Wismut GmbH remediation activities, external laboratories were commissioned to conduct sampling and chemical analyses (including the Grüna laboratory of DFA and later C&E Consulting & Engineering GmbH). Furthermore, data from a depth profile measurement in 1994 at shaft 371 was available (Wolkersdorfer 1996). Additional mine water parameters like EC, uranium, and sulfate concentrations were also evaluated for this study.

To gain a broader overview of the temporal change of mine water quality parameters within flooded mine pools, a selection of additional depth profile measurements were added to this study. These include measurements at Blindschacht I and II from the Pöhla–Tellerhäuser mine (Erzgebirge mountains, Germany) between 1994 and 2001 and at the Ü539 raise shaft and Flour shaft at the abandoned flourspar mine in Straßberg (Harz mountains, Germany) between 1992 and 2003; the first measurements there were taken during the flooding process. Supplementary depth profiles were investigated from the French Vouters 2 and

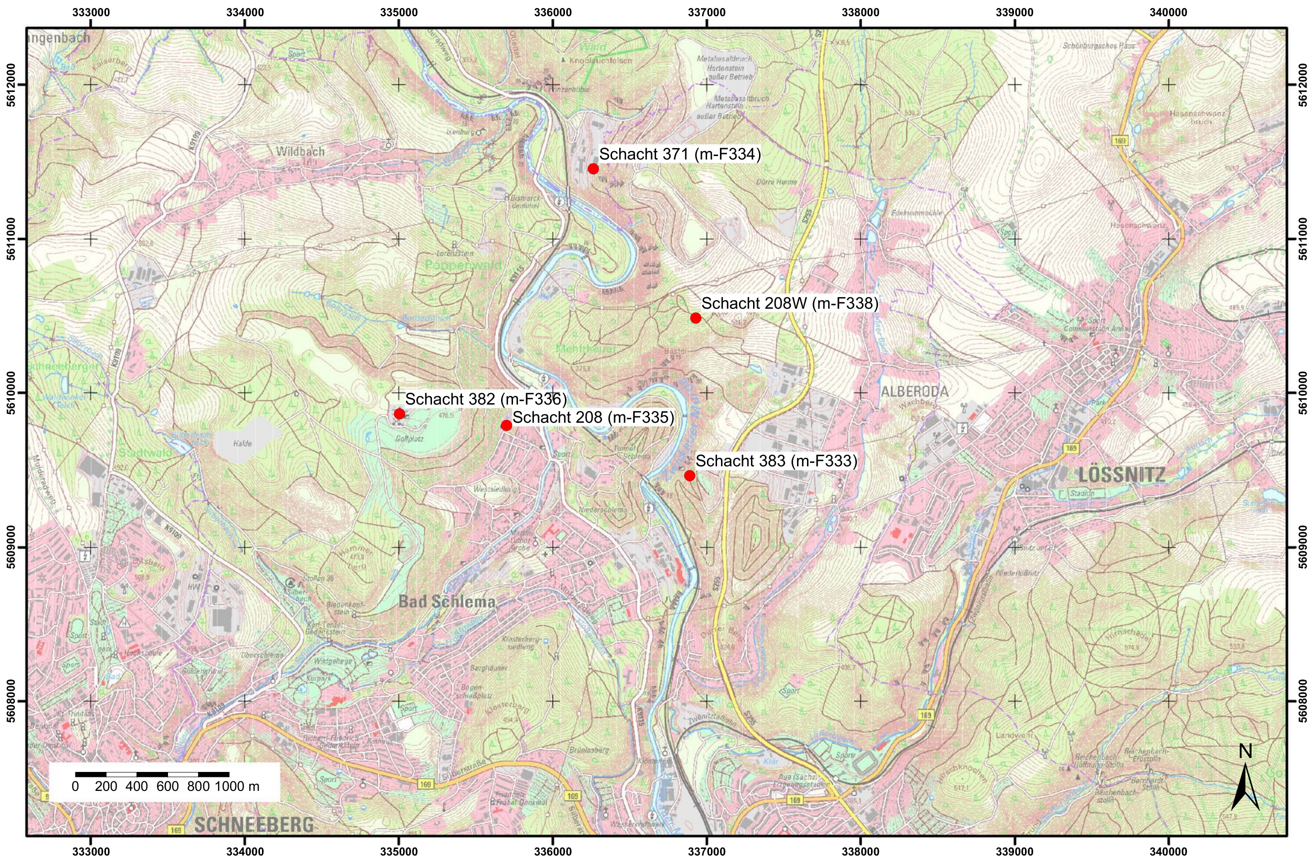

Fig. 2 Location of the five investigated Wismut shafts in the Schlema–Alberoda area, Germany, including sample location names. source: GeoSN, Wismut GmbH, geodetic datum ETRS89 UTM33, scale added

Simon 5 shafts (Lorraine basin, France, not discussed in detail here; Reichart 2015) and the British shaft S40—Horden South (the Horden mine, County Durham, UK, courtesy: the Coal Authority). For the selected examples, depth profile measurements were carried out over several years, thus allowing the compilation of first flush curves for these shafts. Using other examples, we aim to show that changes in mine water quality over time also occur in the entire water body at other mines, and that Schneeberg–Schlema–Alberoda is not an exceptional case.

First Flush Experiments with the Analogue Model Mine (AMM)

Description of the AMM

To support and understand the real-world results and how the pollutants decrease within the shaft, a first flush experiment was carried out aided by a 4 × 6 m analogue model mine (Agricola Model Mine: AMM). The hypothesis behind this analogue modelling was that the fluorescent dye "contaminated" AMM was a proxy for a flooded underground mine at the point of the initial discharge, with groundwater inflow from the surface and natural mine water stratification in deeper parts of the mine. As the model's Reynold's numbers (Re = 85–150) were similar to those of real mines (Re = 190–350), the authors of this study believe that the analogue model adequately represents a real mine. Density stratification, representative of flooded underground mines with inflow of deep formation water, was developed by filling the AMM with tap water containing 70 g/L NaCl at the bottom (WM water body: warm mineralised) and a water body of fresh tap water (CF water body: cold fresh) at the top, fitting the explanation on stratification given by Wolkersdorfer (2008) and Henkel and Melchers (2017). To investigate potential mixing of the CF and WM water body, two different fluorescent dyes were used as a proxy for a mine's mineralisation: sulforhodamine B (SRB) in the CF and sodium fluorescein (NaFl) in the WM water body. By flushing the CF water body with tap water from the top, simulating ground water inflow into a mine, the SRB dye concentration steadily decreased.

The analogue AMM consists of four shafts (shaft #1–#4) and four working levels, representing roadways, that can be isolated with valves (Fig. 3). They range from 65 to 305 cm in depth, and the whole model can hold a maximum of 153 L

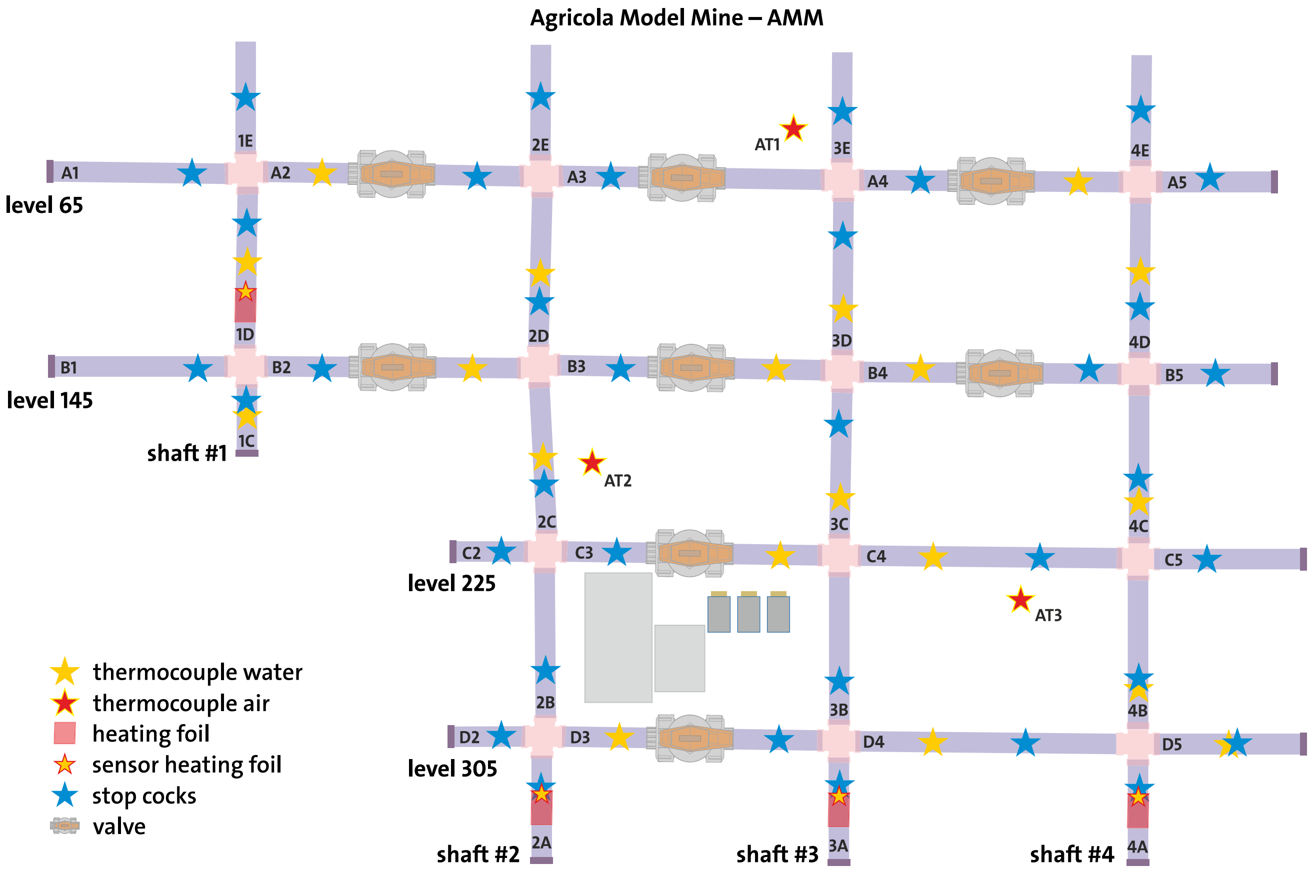

Fig. 3 Schematic representation of the Agricola Model Mine (AMM) at Tshwane University of Technology. Each section is numbered individually for identification purposes, and some can be separated from each other by valves (e.g. within sections A2 and A3)

of water. Its layout is based on the commonalities between dozens of worldwide mine flooding scenarios and conducting hundreds of in-situ measurements in a selection thereof.

All roadways and shafts were constructed with transparent 90 × 4.3 mm PVC tubes (inner diameter 81.4 mm, GF Piping Systems Africa, Cape Town) vertically mounted to a wall, which were insulated with foiled polystyrene sections (Insul-pro, South Africa) to retain heat. An artificial geothermal gradient can be achieved through eight temperature-controlled 12 V, 137 × 320 mm heating foils (Conrad Electronics, Germany; H-Tronig TSM 125 temperature controller, Germany). Thermocouples (Fig. 3) are inserted inside the tube at each section to record the fluid's temperature while flowing through the AMM, and three additional ones are installed outside to measure the ambient air temperature. Data was logged with three Huato S220-T8 data loggers (Shenzhen Huato System, China), equipped with a back-up power system. The AMM consists of top inlet pipes (Sects. 1E–4E) and bottom outlet pipes (Sects. 1C and 2A–4A) used to flood and release water from the model. Valves mounted on the AMM allow the shafts to be flooded individually as isolated shafts or simultaneously as an interconnected shaft system. A total of 36 sampling ports were installed for tracer injection or sampling.

Analogue First Flush Modelling in the AMM

To simulate the stratification that is observed in nearly all measured and undisturbed flooded underground mines, levels 225 to 305 were filled with 93 L of tap water using tubes lowered to the shafts' bottoms. Beneath this tap water, 60 L of water with concentrations of 70 g/L NaCl and 800 µg/L sodium fluorescein (uranine, NaFl) were simultaneously pumped into shafts #2, #3, and #4 at 0.33 L/min using a peristaltic pump (Heidolph, Germany). This NaCl concentration was chosen to avoid mixing with the fresh water based on preliminary small-scale column tests (50 cm high, 5 cm diameter) and the situation in selected real flooded underground mines (e.g. in Wolkersdorfer 2008). It represents mine water with an EC of ≈ 140 mS/cm and a density of 1.065 g/cm^3 and fresh water with a density of 0.998 g/cm^3 above it.

The freshwater CF water body extended from the top of the AMM down to level 225, with the mineralised WM water body below, from level 225 to the bottom of the AMM. The uniformity within each of these water bodies was proven by taking 36 water samples from the sampling ports and analysing the samples fluorometrically (Cary Eclipse Flourescence Spectrophotometer; Agilent, Australia) for uranine (excitation and emission wave lengths $\lambda_{ex} = 492$ and $\lambda_{em} = 515$ nm). To test the flushing of water from a flooded underground mine, the CF water body was injected with sulforhodamine B dye (SRB) with a concentration of 800 µg/L at sampling ports A2, A3, B4, and B5 ($\lambda_{ex} = 566$, $\lambda_{em} = 587$ nm).

Daily measurements were taken to monitor the processes transpiring in the AMM. On the 19th day of the experiment, after the SRB (as a proxy for contaminated mine water) equilibrated in the CF water body, the system was continuously flushed from Sect. 1E with tap water (used as a proxy for infiltration and groundwater) at a flow rate of 0.33 L/min and discharged at the outlet above sampling port 3E. Samples were collected every 10 min at the discharge outlet and every hour at the 35 sampling ports. These samples were subsequently analysed for both NaFl and SRB (supplementary Fig. S-1).

Results and Discussion

Results of Depth Profile Measurements

For the Schlema–Alberoda shafts, a characteristic first flush curve prevailed (Fig. 4). Flooding in this mine, with a volume of $\approx 36 \times 10^6$ m^3 (Wolkersdorfer 1996), started in January 1991. Since October 1992 (shaft 383) and November 1994 (shaft 371), the world's longest series of measurements in a flooded underground mine have been recorded. In the Schlema–Alberoda uranium mine, the 10 years of flooding was controlled by regulating the groundwater inflow into the mine void (≈ 90% of the mine void were flooded). Afterwards, gradual flooding of the remaining mine void took place. During that time, the EC increased from initially 4 mS/cm until it peaked at ≈ 5.5 mS/cm in April 1999; the highest EC (5.4 mS/cm) was recorded in shaft 208 in May 1999. All shafts showed a similar EC decrease: the curves initially drop steeply, and thereafter, the EC at each time step decreased slower, until it reached a value of 1.6 mS/cm 21 years later. In general, lower EC values predominated at the inlet to the water treatment plant, most likely due to dilution from mixing with the lower EC surface seepage water. Outliers in the water treatment plant curve are due to the recirculation mode of the Schlema–Alberoda water treatment plant, when discharge limits were not met and treated mine water was discharged back into the mine void. At shaft 371, the EC of the bulk samples and the depth profile measurements show a similar curve; however, the EC of the bulk samples was commonly (Fig. 5) up to 500 µS/cm less. A possible explanation might be precipitation between the sampling and measurement in the dedicated labs. Trying to identify other reasons for these differences were not successful (e.g. measurement of conductivity instead of EC, different cell constants, or temperature compensations). As the Schlema–Alberoda mining area is one of the largest uranium deposits in the world, the temporal decrease in uranium concentration in the mine water (before discharge to the water treatment plant) illustrates its environmental relevance (Fig. 6). As can be seen, a typical first flush curve with an exponential concentration decrease developed. Similar first flush trends apply to other mobilised ions (e.g. sulfate). Yet,

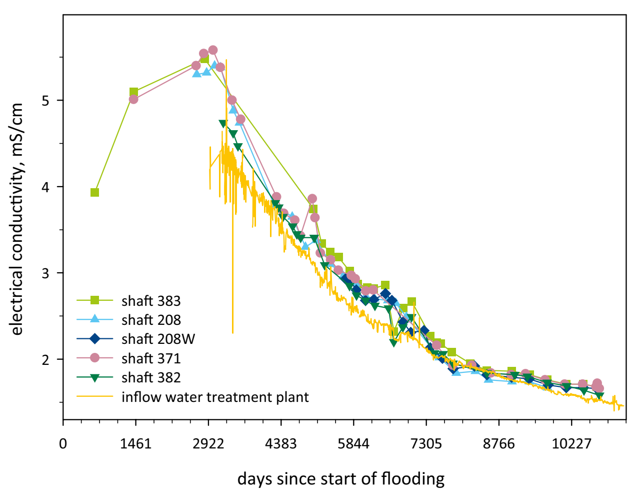

Fig. 4 First flush curves for several shafts in the Schlema–Alberoda mining area, Germany. Start of flooding in January 1991 (very high and low peaks at the inflow water treatment plant curve result from the recirculation of treated mine water back into the mine pool)

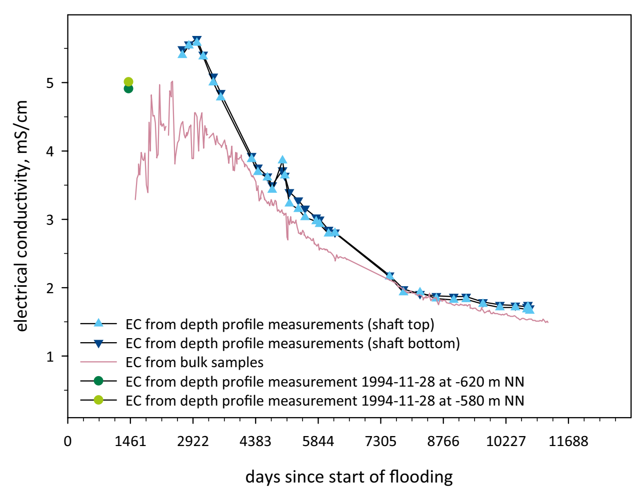

Fig. 5 First flush curves at different depths in shaft 371 of the Schlema–Alberoda mine and the discharged mine water. Start of flooding in January 1991

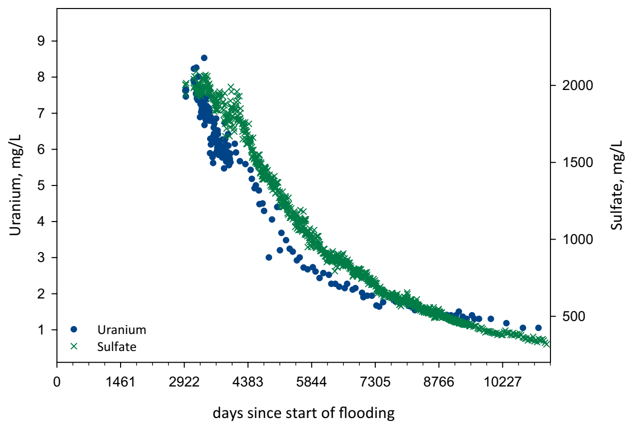

Fig. 6 First flush curve for uranium and sulfate concentrations at the inflow to the water treatment plant (m-F510) at the Schlema–Alberoda mine. Start of flooding in January 1991

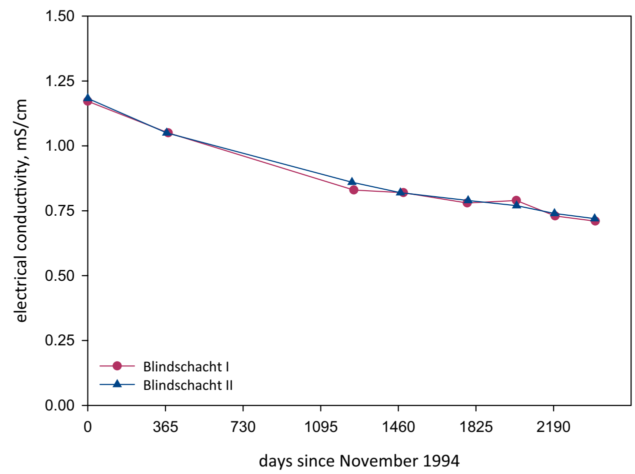

Fig. 7 First flush curves at the subvertical shafts Blindschacht I and II of the Pöhla–Tellerhäuser mines, Germany

concentrations of water constituents that take part in hydrochemical or exchange reactions in the already flooded mine pool show a different, even increasing behaviour. Examples of that are arsenic, iron, radium (^{226}Ra), and hydrogencarbonate, which are directly or indirectly important in water treatment.

In addition to the pumped mine water, the water in the Schlema–Alberoda mine pool itself also shows a characteristic first flush, indicating that the entire mine pool has experienced an improvement in water quality. Furthermore, the similarity in the time vs. EC curves for the pumped mine water and the mine pool display a hydraulically well-connected system with a fast mine water interchange. High flow dynamics between the shafts were confirmed by similar chemical water compositions in distant shafts and tracer tests carried out during mine flooding with flow velocities of up to 25 m/min (average 3 m/min) between shafts 371 and the sub-vertical shafts 296IIb as well as 366b (Wolkersdorfer et al. 1997).

To evaluate if the observations at the flooded Schlema–Alberoda mine also evolve elswhere, the authors obtained in-situ measurements from additional flooded mines. Because these measurements are rarely conducted on a spatio-temporal basis, only limited data was available. An exponential EC decline similar to the Schlema–Alberoda one was observed in the 800 m apart Blindschacht I and II subvertical shafts of the abandoned Pöhla–Tellerhäuser uranium mine (Fig. 7). Hydraulic connections between the two shafts exist at four galleries (level +120 m, +180 m, +240 m and +300 m). This might explain why the two curves of the subvertical shafts are similar, decreasing from 1.2 to 0.7 mS/cm, indicating good hydraulic interaction of the mine water in these shafts, very likely via the +240 m level. However, measurements exist only for a few years, as the mine workings were seperated from adjacent mine workings by a concrete dam and subsequent flooding, making measurements in the Tellerhäuser deposit no longer possible.

Influence of Density Stratification on the First Flush

When a mine is flooded, density stratification develops in nearly all cases, and it is known that stratification can develop even during mine flooding. As less mineralised infiltration water fills the mine voids, generally from above, highly mineralised flooding water rises, causing different water bodies to overlie each other. Therefore, density stratification in flooded underground mines can prevent the exchange of mine water from deeper parts of the mine with its shallower parts (Mugova and Wolkersdorfer 2022). It was therefore crucial to also investigate the first flush in stratified underground mines to identify how stratification affects the course of the first flush described in the previous section.

As can be shown, the first flush likewise develops in stratified mine water as exemplified by the Straßberg/Harz mine in Germany. This abandoned fluorspar mine was thoroughly investigated to prevent contamination of receiving water courses and a Natura 2000 area once the mine water discharges (Kindermann and Klemm 1996; Rüterkamp et al. 2004; Rüterkamp and Meßer 2000; Winkler 2001; Wolkersdorfer and Baierer 2013; Wolkersdorfer and Hasche 2004). During mine flooding, stratification became evident in the Flour and Ü539 shafts (Figs. 8, 9), which are 350 m and 150 m deep, respectively. Initially, there was an EC increase while the mine was in the flooding process, starting at 1.9–2.8 mS/cm, rising to 2.2–3.3 mS/cm, and then a steady decrease to 0.7 mS/cm. Though the curve progressions are similar, the EC values at different depths of one shaft differ considerably. This might be because the two shafts are 3200 m apart and the lowest section of Ü539 is connected to

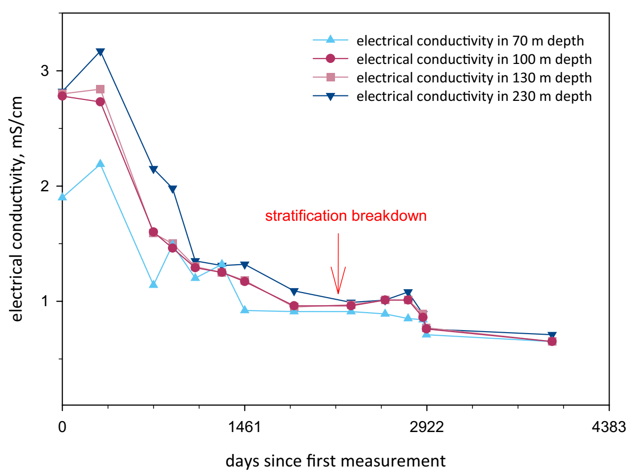

Fig. 8 First flush curves for the German Flour shaft, Straßberg/Harz with a stratified water body, first measured in July 1992 (modified after Rüterkamp and Meßer 2000; Rüterkamp et al. 2004)

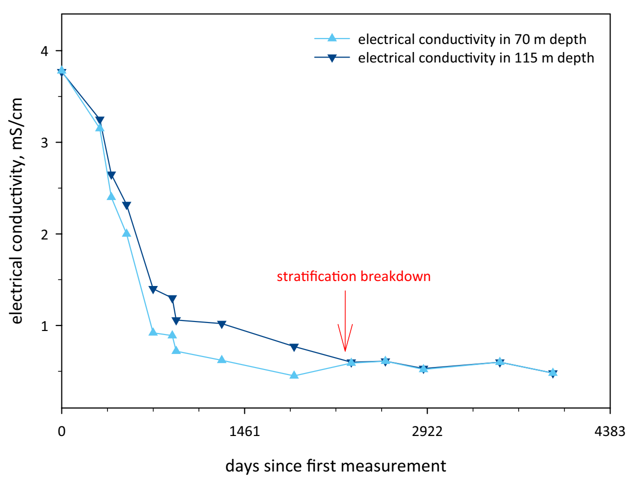

Fig. 9 First flush curves for shaft Ü539, Straßberg/Harz, Germany with a stratified water body, first measured in July 1992 (modified after Kahmann and Heinrich 1998)

the Flour shaft at a depth of 150 m. At greater depths, the EC is generally greater than in the upper part of the mine water body, indicating stratification. These data show that the first flush, despite the presence of stratification, takes place throughout the whole mine pool at different orders of magnitude. After the stratification breaks down, the EC decreases further within the entire mine pool, as can be seen by the near identical EC values at the end of the curves for both shafts. Similar observations were also described by Merritt (2021), who divides the first flush curves into two depth range categories: "shallow model" and "deep model", while pointing out that there are different peak concentrations and decay rates. Merritt (2021) further observed that the mine water quality improves more slowly in the shallower part of the mine compared to the deeper part. However, on the basis of the Straßberg data, his statement that "while the water quality in the shallow model is of better quality, the first flush is slower", cannot be generally confirmed.

Nevertheless, there are cases where the collapse of the stratification negatively affected the first flush. This can be seen from the French Vouters and Simon 5 shafts as well as the English Horden mine (Fig. 10) examples. In all three cases, pumping activities in the shafts resulted in a breakdown of the stratification and consequently, a deterioration of the mine water quality, an effect also described by Frost (1979) and Nuttall et al. (2002). According to Farr et al. (2021), the EC at the Horden S40 shaft changed from 1.2 mS/cm in the pre-pumping conditions of October 2003 to 18.1 mS/cm during pumping in July 2010. The pump is located 100 m below ground and the flow rate changed from 40 L/s (2004) to 120 L/s (2008) and back to 40 L/s (after 2008). A typical first flush curve progression at the three mines could not be observed during the measurement period, because poorer quality mine water from deeper parts of the mine pool mixed with better quality mine water closer to the surface.

Based on the studied examples, it seems as the first flush in flooded underground mines transpired independently in each of the individual mine water bodies. Stratification by itself is therefore only partly responsible for mine water quality improvement over time. However, the breakdown of stratification, for example through pumping, might prevent or delay the positive effects of the first flush on the mine water quality. The location of the point of discharge or that of the geothermal pumps is important for both the first flush development and density stratification. If they are in the upper CF (cold fresh) water body above the uppermost intermediate layer and the mine beach is too extensive (several metres or decametres), the water quality can again deteriorate because pyrite oxidation is reactivated above the fluctuating mine water level, causing the stratification to remain stable. However, if water is pumped from the WM (warm mineralised) deeper water body below the intermediate layer that often develops between water bodies with different densities, there is a high risk of stratification breakdown, causing the water quality in the entire mine pool to deteriorate (Mugova and Wolkersdorfer 2022), and resulting in the discharge of low-quality MIW.

Results and Discussion from the Analogue Model Mine

As described in the introduction, an analogue mine model was set up to understand the transpiring processes of the time–concentration development in a real stratified and flooded underground mine. Therefore, the AMM was filled with tap water (0.998 g/cm^3) at the upper levels (CF water body), while the bottom section contained mineralised water (1.065 g/cm^3, WM water body). During the experiment, the ambient room temperature averaged 17.5 °C (14.4–22.8 °C, $\sigma = 6.6\%$) and the water temperature within the insulated PVC pipes was 14.8 °C (4.6–28.5 °C, $\sigma = 8.9\%$). On average, that results in a Reynolds number of Re = 85. On the 19th day of the experiment, after the flushing experiment started, the SRB dye in the CF water body was evenly distributed (Fig. 11), with a concentration averaging 367 µg/L in all sections except 2C, which had a concentration of 19 µg/L. The 19 days were very likely not long enough for all the SRB to be distributed evenly by convection and diffusion. The SRB remained undetected in the WM water body, with an average background concentration of 0.15 µg/L. This confirms that two individual, stratified water bodies existed at the beginning of the flooding test (Fig. 11).

Flushing of the AMM with tap water at a rate of 0.33 L/min commenced 19 days after the SRB injection. After 281 min, the tracer distribution has changed considerably compared to the initial situation (supplementary Fig. S-2). The tracer was flushed out in all shafts except in Sect. 4C, between levels 225 and 65 and Sects. 1E and 1D between the collar of the shaft and level 145. It was still visible at the top of all the shafts, though fading off slightly at level 65. The CF water body had an average concentration of 181 µg/L, indicating a drop in concentration, while the

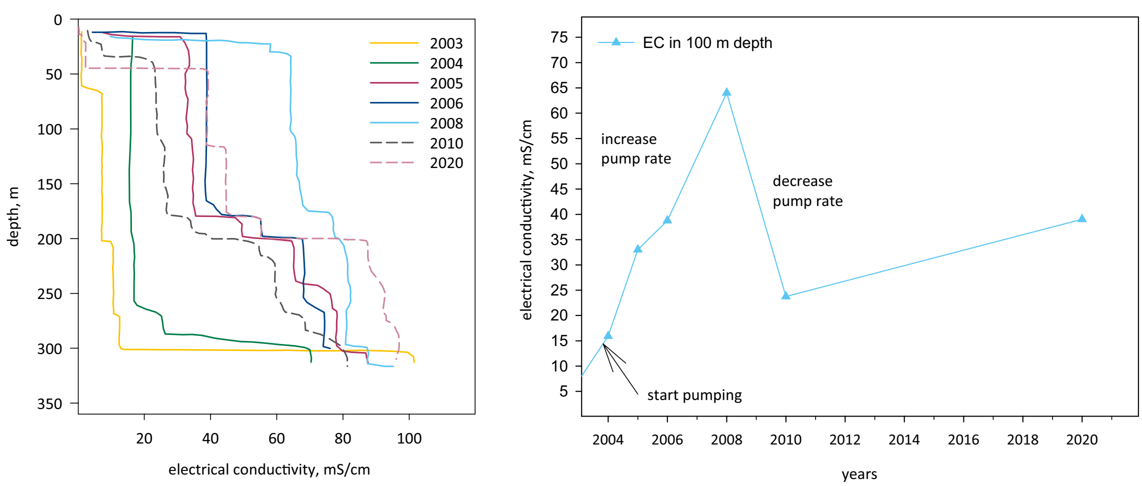

Fig. 10 Depth profiles (left) and electrical conductivity at a depth of 100 m between 2003 and 2020 at the S40 South Shaft, Horden Mine, UK (modified after Farr et al. 2021; Watson 2011; Wyatt et al. 2021)

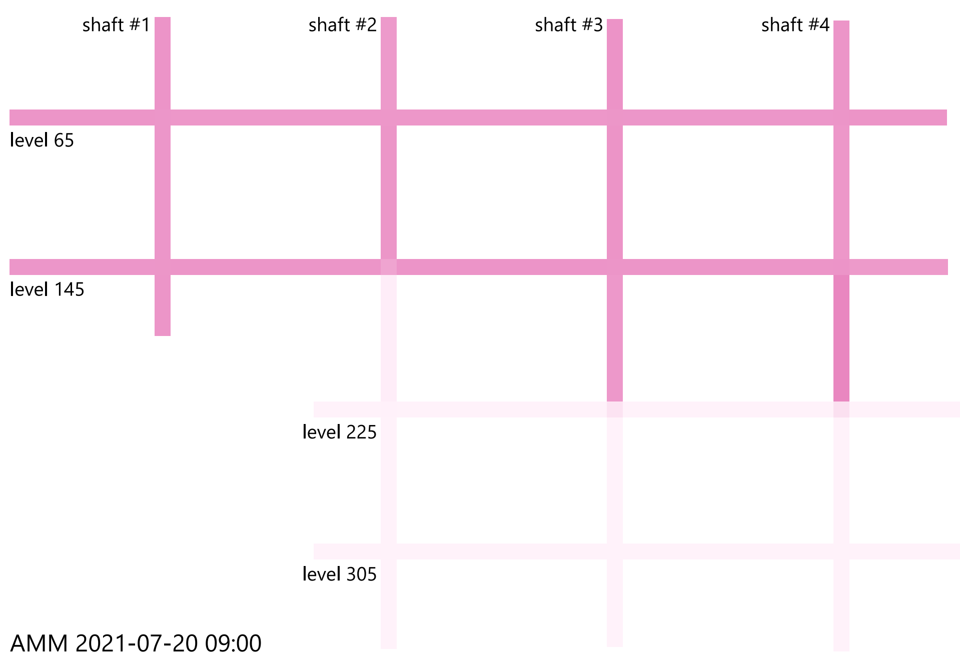

Fig. 11 Sulforhodamine B dye distribution prior to the commencement of the flushing experiment. Lighter colours indicate a concentration of 0.15 µg/L, the darkest colour 367 µg/L

WM water body had a concentration of 0.14 µg/L, showing that two distinct water bodies still existed even though the model mine was flushed.

At the cessation of the flushing experiment after 860 min, the average SRB concentration was 50 µg/L in the WM water body and 0.14 µg/L in the CF water body. There was still an SRB concentration of 475 µg/L in Sect. 4C (supplementary Fig. S-3), a concentration of 218 µg/L in Sect. 1E and a concentration of 310 µg/L in Sect. 4A. Therefore, the flushing of the AMM compromised all sections of subvertical shafts except 4C. These situations can also be expected for flooded mines, where some mine voids are not fully hydraulically connected to the point of discharge. This will result in long tails of the potential pollutant concentrations, as often observed in first flush curves that don't flatten to the background concentrations, as can be seen for the Schlema–Alberoda (Figs. 5, 6) and Straßberg/Harz mines (Fig. 9).

A characteristic first flush curve (Fig. 12) depicting the concentration of the SRB dye at the discharge point shows a steady drop in concentration from 110 to 630 min. There are two peaks from 640 to 680 min and at 750 min due to water flowing from legs 4C and 4E to the point of discharge. As the flushing continued, the concentration at the point of discharge dropped until it reached 3 µg/L. A breakdown of the density stratification in the AMM could not be observed by the flushing of the model. This is also supported by the fact that the average NaFl concentration in the CF water body remained at the background concentration of 0.1 µg/L. Yet, if the discharge position were below or within the WM water body, the stratification would have broken down. A more detailed description of the experiment is published in Molaba (2022).

Conclusions

After the discharge of MIW, the mine water quality commonly changes over time. This applies to the water quality in the mine pool and the mine water discharge and has profound effects on mine water management. When planning a mine water treatment plant, the first flush must be taken into consideration, as the changing water quality affects the demands on the plant. Therefore, for example, an active plant that is necessary at first, can sometimes be replaced by a passive plant after a few years. If the water quality improves considerably over time, mine water treatment might not be necessary anymore at all. For each mine, a first flush curve can be estimated based on the discharging water parameters, although this is only a rough estimation. It is recommended to take water samples from the upper water body as early as possible during flooding to allow for first predictions about the quality of the discharging mine water and the first flush. In most mines, density stratification occurs in the mine pool, which is why additional sampling from the entire water body is important. Furthermore, it needs to be considered that the first flush takes place in the entire mine water pool. Man-made interference, for example through pumping activities, can disturb the density stratification and the first flush, thus disrupting an improvement in water quality over time. In addition, the mine should be flooded as fast and early as possible, as this will improve the water quality more quickly and prevent pyrite oxidation.

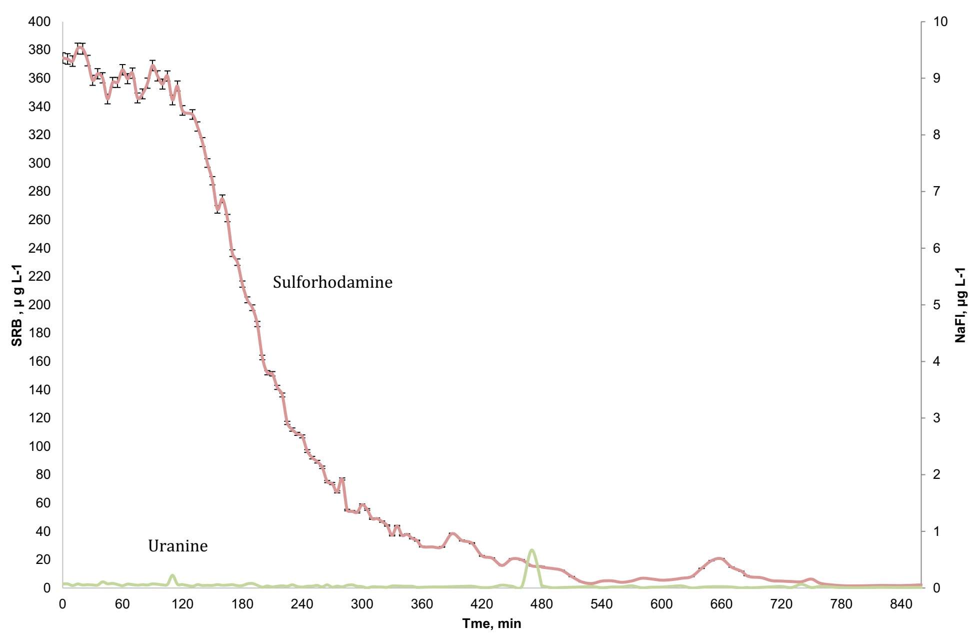

Fig. 12 First flush curve, illustrating the concentration of sulforhodamine B (from the CF water body) and uranine concentrations (µg/L, from the WM water body) in the AMM vs. time in minutes at the discharge point (Sect. 3E); error bars ± 1%

On the other hand, large fluctuations in the mine water level (mine water beach), for example through temporary pumping, should be avoided, as this leads to increased leaching, and can even briefly worsen the discharging water quality again. The authors' aim in the future is to find an empirical formula that allows a more precise prediction of the water quality development. An empirical formula that is easier for the end user to apply and requires less data about the mine's hydrogeological conditions would be advantageous. In particular, it should be possible to predict the time and concentrations of the peak, as well as the time and concentrations when the curve flattens out. An interdisciplinary research approach should be applied to obtain better predictions of mine water quality. The results of analogue modelling must be compared with long-term field measurements and numerical modelling to develop the best possible prediction tools.

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