

## WATER QUALITY OF REICHE ZECHE MINE, FREIBERG/SAXONY, GERMANY

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### ABSTRACT

Reiche Zeche is a lead-zinc-silver deposit in Freiberg, Germany, that was mined for over 800 years. Since 1969, Reiche Zeche has been a teaching and research mine with numerous adits for dewatering large amounts of inflowing water. Infrequent metal water quality monitoring in the 1980-1990s and flooding of the mine in 2002 led to a lack of relevant data. New measurements were taken at different level adits and ore veins for comparison to historical values, revealing pH levels as low as 1.95, conductivity as high as 22000  $\mu\text{S}/\text{cm}$ , and an overall trend towards less acidic waters.

### INTRODUCTION

Reiche Zeche is part of the Himmelfahrt Fundgrube, a former iron ore mine in Freiberg, Germany, in the Erzgebirge mining region of Saxony. The polymetallic sulfide ore found in Freiberg was mined from 1168 to 1969, and though it is no longer producing ore, Reiche Zeche remains as a teaching and research mine for the Technische Universität Bergakademie Freiberg. The most important ore minerals mined were sphalerite, galena, pyrite, chalcopyrite, and silver, and important gangue minerals include calcite, fluorite, barite, siderite, and quartz (Zänker et al 2002). Over one thousand ore loads were mined from this region during operation, which was ceased in 1969 after the lower part of the 700 meter depth was flooded, leaving only the top 200 meters under the surface open for research and teaching.

Mined materials from this region can be separated into high grade ore and waste rock. High grade ore, composed of pyrite, sphalerite, galena, chalcopyrite, and arsenopyrite, was brought to surface for smelting during mine operation, and spaces were backfilled with waste rock, which is the primary site of sulfide oxidation and acid mine drainage (Haubrich and Tichomirowa 2002). The waste rock includes remnants of ore from ore loss, veins which were too small to mine, or ore minerals within host rock.

Waste rock is primarily composed of biotite gneiss, with sulfides including jarosite, gypsum, minor anglesite, scorodite, and sulfur (Haubrich and Tichomirowa 2002). When weathered, the gneiss forms clay minerals such as illite and kaolinite (Haubrich and Tichomirowa 2002).

The temperature inside the mine is a relatively constant 10-12°C, with a similarly constant humidity of 97-98% year round (Weyer 2015). High humidity is due to surface water and precipitation coming into the mine through faults and fractures in the overburden. This water then comes in contact with waste rock and produces acidic solutions with high concentrations of heavy metals. Areas within the mine without sulfide deposits do not produce acidic water. Previous studies have categorized metal levels in different parts of the mine. The purpose of this study is to generate a comprehensive map of mine water quality to provide a basis for current and future mine research needs.

### METHODS

#### Sample Locations

Samples were collected in June 2015, from 14 points within and around Reiche Zeche. These points were selected based on historical data, accessibility, and the need to understand how water quality changes between levels within the mine. Map locations of the sampling points are shown in figures 1-3. Based on water flow, samples were classified as still water or flowing water.

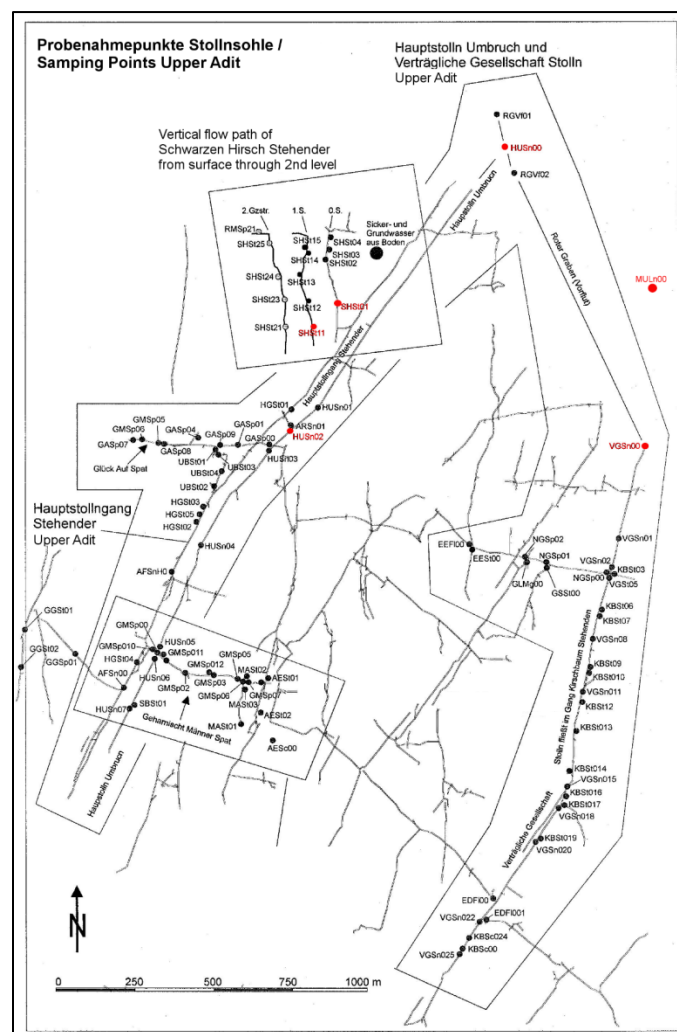


Figure 1. Upper adit sampling points (map from Baacke 2000).

## Field Analysis

Sample temperature, pH, redox potential, and conductivity were taken on site with a WTW Multi 3430 multimeter. The device had been calibrated prior to taking samples both days. A 50 mL sample from each site was collected for total inorganic (TIC) and total organic carbon (TOC) analysis. Samples were collected by submerging a glass bottle under water to ensure no oxygen was captured with the water sample. Three additional 50 mL samples from each site were collected and filtered through 0.2 or 0.45 µm Millipore syringe filters and stored in new plastic bottles. These additional samples were acidified with 0.5 mL of 69% HNO<sub>3</sub> on site for microwave plasma – atomic emission spectrometry (MP AES) or 0.5 mL of HCl for photometric analysis. MP AES and photometric analyses were performed at the Institute for Mining and Special Civil Engineering in Freiberg, Germany. TIC/TOC analysis was done at the Grundwasserforschungsinstitut Dresden GmbH in Dresden, Germany.

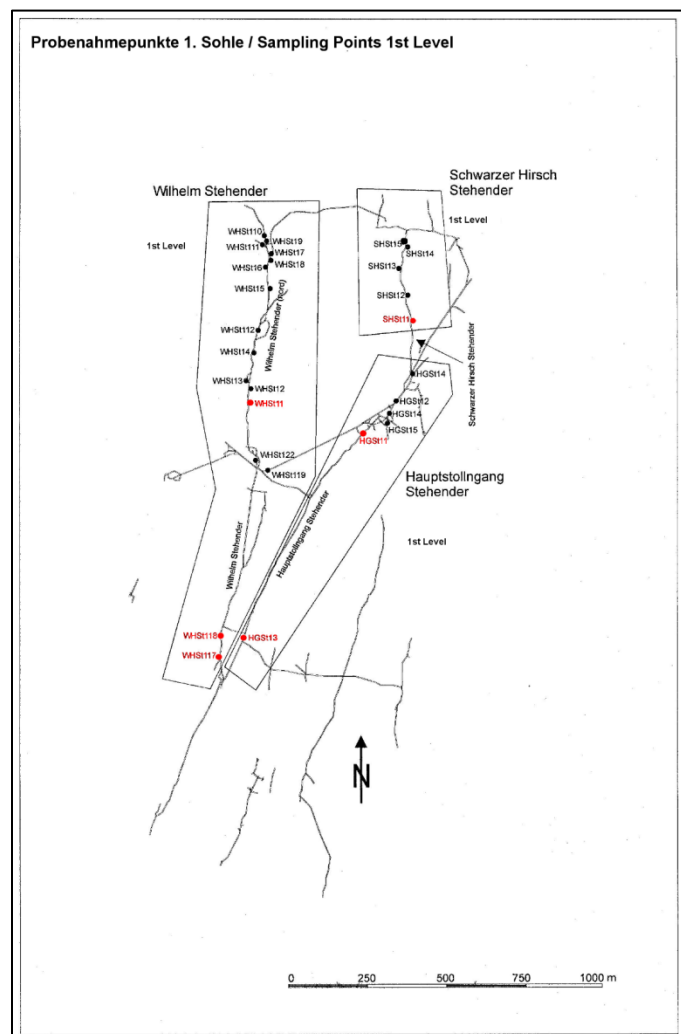


Figure 2. First level sampling points (map from Baacke 2000).

## Laboratory Analysis

Spectrophotometric analysis of Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> was done in the laboratory. Each ion was analyzed using preprogrammed standard methods on the HACH DR3000 spectrophotometer. The samples, which had been preserved immediately after sampling with 69% HNO<sub>3</sub> to remobilize sorbed or precipitated metals, were analyzed from lowest to highest conductivity, with higher conductivity samples generally demonstrating higher Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> concentrations.

Samples of low pH samples also correlate with higher conductivity, but it was evident without dilution that too many interfering species were present in the samples to obtain an accurate

measurement of Fe concentrations. Analysis of additional ion and metal concentrations was done using an Agilent 4200 MP AES at the Institute for Mining and Special Civil Engineering in Freiberg, Germany. Analyzed samples were filtered, therefore concentrations obtained are for dissolved complexes. This is critical to understand the fraction of metal that can be either taken up by biological organisms or sorbed onto surfaces.

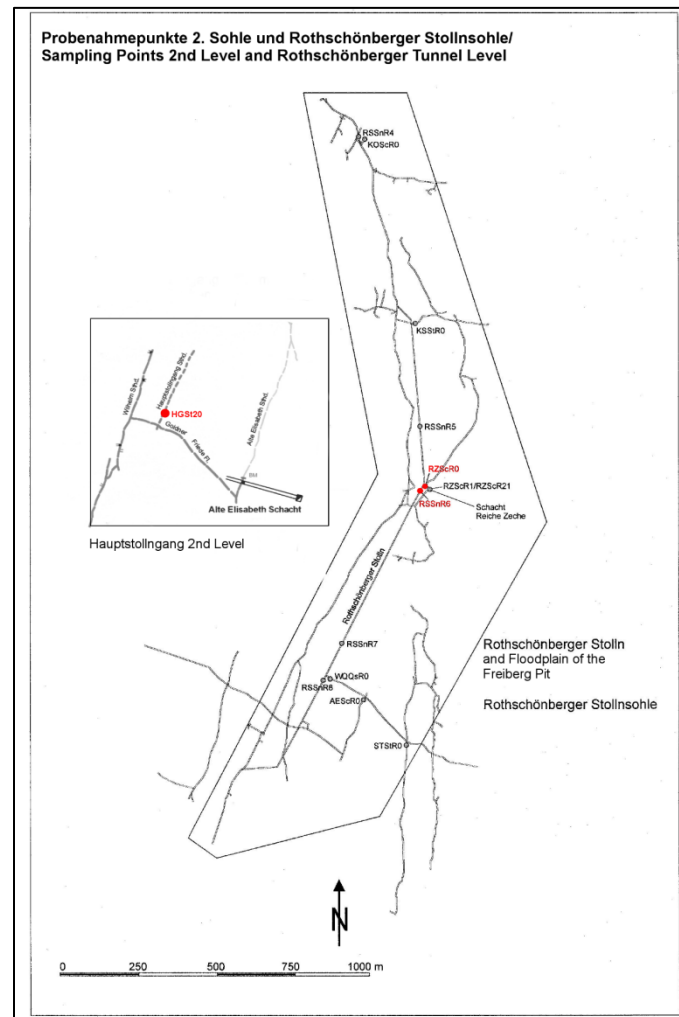


Figure 3. Lower level sampling points (map from Baacke 2000).

## RESULTS

### Schwarzer Hirsch Stehender

Schwarzer Hirsch Stehender is a section of the mine that was extremely productive and extensively studied in prior tracer test experiments. After mining, it was backfilled with waste rock. With a vein that is accessible on multiple levels, this area was sampled in order to determine how mineral concentration in the water changes as the water travels down through accessible levels of the vein. Locations SHSt01 and SHSt11, seen on Figure 1, were chosen to determine the changes in water mineralization between the upper adit and the 1<sup>st</sup> level. Both samples were still water samples, with no flow observed. Measured pH, conductivity, and redox levels were lower at SHSt11 compared to SHSt01 in the upper drift. This is likely due to water coming in contact with more dissolved minerals as it travels deeper into the mine. Results showed current concentrations were lower than historical averages.



**Figure 4.** SHSt01.



**Figure 5.** SHSt11.

Measured pH levels at both locations of around 2.5 revealed extremely oxidizing conditions, and Eh was 0.52-0.64 V. Mn is also present in dissolved form here, and with concentrations of 22-104 mg/L, likely exists as just as  $Mn^{2+}$ . Additionally, moderate levels of Al are coupled to the moderate Fe levels, leading to the conclusion that the water is oversaturated with aluminum iron hydroxides, since both Al and Fe are present in dissolved form at SHSt01.

#### Hauptstollengang Stehender

The vein Hauptstollengang Stehender and adit Hauptstolln Umbruch are connected, allowing mine water to flow out of Hauptstollengang Stehender through Hauptstolln Umbruch, reaching surface eventually at sampling point HUSn00 seen in Figure 1. Recently, clean and humid mine air flowing through Hauptstolln Umbruch has been allocated for use by the Freiberg hospital, when fans were installed to allow the 97-98% humidity and 10-12°C air to flow above ground into the hospital, where it is used for heating or cooling depending on seasonal needs.

Three sampling locations were chosen for Hauptstollengang Stehender, to trace metal concentration and water quality parameters through two accessible levels of the mine. HGSSt11 was near the battery loading station on the 1<sup>st</sup> level of the mine, and HGSSt13 was also on the first level, but collected from dripping water from the ceiling. HGSSt20 was collected from a 1.5 year old jug that was located on the second level, and is marked in Figure 3. There was a noticeable decrease in pH levels from 3.2-3.3 on the first level to 1.9 on the second level, as well as an increase in conductivity from 1300-1400  $\mu\text{S}/\text{cm}$  to 9720  $\mu\text{S}/\text{cm}$  from the first to the second levels. Redox levels increased from 0.5 V on the first level to nearly 0.7 V at the second level. Temperature change was not significantly different. The drop in pH and increase in conductivity with increasing mine depth is reasonable due to accumulating levels of dissolved metals as water flows down through the mine.



**Figure 6.** HGSSt11.



**Figure 7.** HGSSt13.



**Figure 8.** HGSSt20.

Not all ion and metal concentrations increased with depth. At HGSSt20, pH was lowest at 1.9 and concentrations were highest for most ions analyzed. Conductivity was 9720  $\mu\text{S}/\text{cm}$ , and the red water color precluded the extremely high concentration of iron that was recorded, which was over range for MP AES detection. HGSSt11 had the highest level of Ni recorded of the three sample areas. Interestingly, the following were present at higher concentrations at the dripping water location: Ba, K, Mg, Na, Sr, and pH. The highest pH level of 4.9 also was recorded here, and conductivity was 1298  $\mu\text{S}/\text{cm}$ , leading to the conclusion that cations are precipitating out of solution due to weak attachment to negatively charged clays. HGSSt20 and HGSSt13 were classified as still water, while HGSSt11 was flowing water.

High concentration of As at HGSSt20 is likely due to extremely high concentration of Fe, which was over the detection limit of the MP AES, as iron controls dissolved arsenic presence at pH <3, and pH at HGSSt20 was 1.9. However, as the sample was collected from a container that has been collecting drip water from the ceiling for 1.5 years, high concentrations of other metals such as Al and Zn, coupled with extreme Fe concentrations, require more thorough analysis to determine what compounds exactly are precipitating out at this location. Moderate levels of Al are coupled with extreme levels of Fe, leading to the conclusion that both metals are supersaturated as the water collects and sit for longer time at HGSSt20.

Hauptstolln Umbruch has been consistently sampled by Umwelt Sachsen since 1999. No exact historical sampling locations were found except for data from HUSn00. HUSn02, located within the air shaft supplying the hospital, was sampled to determine water quality and compare measurements to German groundwater, surface water, and drinking water standards. Water sampled here from 1990-2014 met threshold surface water criteria for  $\text{NO}_3$ , except for one outlying measurement in 2005.



**Figure 9.** HUSn00.



**Figure 10.** HUSn02.

Sampling in 2015 revealed that ion and metal concentrations coming out of the mine into the shaft used for hospital ventilation were all low, with a measured pH of 7.42 at the outflow of Hauptstolln Umbruch. None of the analyzed ions are monitored by surface water regulations, all applicable ions were within threshold levels for groundwater regulations, and most ions were even within threshold limits for drinking water regulations, signifying that this water is adequately buffered and neutralized by the time it exits the mine adit. Sampled metals were all below historical average values, and even minerals that were above historical average were still within historical range. Both sampling locations were flowing water.

#### Reiche Zeche Schacht and Rothschnbergerstolln

Reiche Zeche has exhibited pH levels all across the board, with lower pH levels perhaps attributed to upwelling of deep waters from the flooded levels of the mine nearly 700m under surface.

Rothschnbergerstolln (RSS), the deepest drainage adit, is supplied with water from the southern Erzgebirge mountains, which enters the Drei Brüder Schacht by way of the Constantinschacht, eventually flowing down into the RSS. Some of this water goes very deep within the flooded area, and when it comes back up again at the Reiche Zeche Schacht, it can carry traces of low pH level waters. This water then drains and is discharged 18 km north into the Triebisch and Elbe Rivers (Wolkersdorfer 2008). According to historical sources, flows coming into RSS from Rote Grube, Neue Schacht, and other



locations add up to roughly 400 L/s through RSS (Kuhnert, 2000). RSS outflow is 350-1000 L/s, depending on time of year, therefore any high ion or metal concentrations would be diluted.

The two sampling points at the Reiche Zeche Schacht were the deepest points sampled. Locations used were identical to those used by Baacke (2000). The sample *RSSnR6* exhibited slightly higher than historical average pH level of 7.07, and slightly lower than average levels of conductivity of 720  $\mu\text{S}/\text{cm}$ , and redox potential of 0.2 V. The Reiche Zeche sample *RZScR0* also exhibited a slightly higher than historical average pH of 6.55, conductivity of 1205  $\mu\text{S}/\text{cm}$ , and lower than average redox potential of 0.195 V. Present day *RSSnR6* ion concentrations were all lower than historical averages, with the exception of pH, which was still within the historical range. Present day *RZScR0* ion concentrations were mostly above average historical values, but also within historical ranges. Most ions analyzed were lower in RSS than in Reiche Zeche, with only Cu, Fe, and Pb slightly higher. Ions analyzed were not on the surface water monitoring list, all ions concentrations were within groundwater threshold levels, and most were even within drinking water threshold levels, with the exception of As, Cd, Ni, Mn, and Pb. However, as the water from RSS reaches the surface many kilometers to the north, this is not an issue. Both sampling locations were flowing water.



**Figure 11.** *RZScR0*.



**Figure 12.** *RSSnR6*.

#### **Wilhelm Stehender, Nord and Süd**

Wilhelm Stehender Nord was mined from 1937-1969, which leads to mine waters with incredibly high mineral concentrations due to backfill of waste rock after mining was finished.

Chosen sampling points were *WHSt11* in the north, and *WHSt118* and *WHSt117* in the south. A high pH of 4.90, low conductivity of 1131  $\mu\text{S}/\text{cm}$ , and low redox potential of 0.15 V were recorded in the southern *WHSt117*. With a low pH of 2.60, high conductivity of 14000  $\mu\text{S}/\text{cm}$ , and high redox of 0.428 V at *WHSt11*, water here flows from Wilhelm Nord to *WHSt118*, which had a low pH of 2.51, high conductivity of 22000  $\mu\text{S}/\text{cm}$ , and high redox potential of 0.469 V. *WHSt11* measurements were similar to values observed in 2014, which suggests that the sampling location was correct. Also, redox potentials were extremely high both at *WHSt117* and *WHSt118*, leading to the assumption that significant mineral leaching is occurring those areas.



**Figure 13.** *WHSt11*.



**Figure 14.** *WHSt117*.



**Figure 15.** *WHSt118*.

Results of the sampling analysis were surprising. As the water flows from Wilhelm Nord at *WHSt11*, south to *WHSt118*, one would

expect that it should get more concentrated, and *WHSt117* should not be influenced by the other two sampling points, as it has water flowing north from Wilhelm Süd. Therefore, concentrations should increase from *WHSt11* to *WHSt118*, and *WHSt117* should have a different profile. This assumption was true for the following analyzed parameters: pH, Ba, K, Na, Ni, Pb, and Sr. However, significant drops in Si and Zn concentration between *WHSt11* and *WHSt118*, and similar concentrations for between *WHSt11* and *WHSt117* leads to the assumption that those ions are preferentially sorbing to colloidal surfaces somewhere upstream of *WHSt118*. Additionally, the following ions are highest at *WHSt117*, and exhibit lower concentrations at *WHSt118* than *WHSt11*: Al, As, Ca, Cd, Co, Cr, Cu, Fe, Li, Mg and Mn. Of these, Ca, Fe, Li, Mg, and Mn concentrations are similar and high in *WHSt11* and *WHSt117*. Some sorption must be happening between *WHSt11* and *WHSt118* that the concentrations of these ions are so drastically reduced. Concentrations were not compared to drinking, surface, or groundwater threshold levels, as this water does not belong to any of those categories.

Sampled metal concentrations that were higher than average, but still within historical ranges were Al, Cd, Cu, Fe, while Pb was higher than average and above historical range. All other metals were lower than the historical average. All samples were classified as still water.

High concentrations of As at *WHSt11* and *WHSt117* are coupled with pH levels below 3, and Fe concentrations in excess of 2000 mg/L. s is likely precipitating out as excess  $\text{As}^{3+}$ , since most of the  $\text{As}^{5+}$  should be sorbing to the ferric oxides. It is likely that schwertmannite or jarosite are formed at some point between *WHSt11* and *WHSt118*, as precipitation of  $\text{Fe}^{3+}$  removes As from the system, and concentrations of both As and Fe at *WHSt118* are low or zero. *WHSt117* is low flow water that was classified as still water that comes from Wilhelm Stehender Süd. Concentrations of Fe and  $\text{SO}_4^{2-}$  at *WHSt117* are similar to those at *WHSt11*, leading to the same conclusion that As is present as  $\text{As}^{3+}$ .

Al levels were quite high in *WHSt117* and *WHSt11*, coupled with high Fe concentrations at both locations, which means that the water is oversaturated with aluminum iron hydroxides and both metals are present in dissolved form.

Additionally, TIC concentrations were quite high for all three locations, comparable to flowing water TIC concentrations. Though all three locations were classified as still water because the flow of water was slow, *WHSt11* had a high *in situ* alkalinity measurement of 28 mmol/L, which correlates to the high TIC concentration of 4.9 mg/L. *WHSt118* and *WHSt117* also had moderate levels of TIC at 2.3 and 3.5 mg/L respectively, but *in situ* alkalinity measurements did not correlate with these levels.

#### **Verträgliche Gesellschaft Stolln and Mulde**

The Verträgliche Gesellschaft Stolln is another main drainage adit of the mine, which ultimately drains to the Freiburger Mulde River. The Freiburger Mulde River, a tributary of the Elbe River, has been under consistent monitoring since 1999, with water quality data available online for download from the Sächsisches Landesamt für Umwelt, Landwirtschaft, und Geologie (LfUG). There is about a 24 hour delay between surface precipitation events and when the surface water penetrates down into the mine. Concentrations of metals should ideally be evaluated in accordance with precipitation events, but with limited and erratic data collection, this was is a difficult task.

Measurements taken in 2015 revealed a pH of 5.92, redox potential of 0.230 V, and conductivity of 655  $\mu\text{S}/\text{cm}$ . This pH level was above historical average, while redox and conductivity measurements were both significantly below historical averages. Except for Ba and Na, all ionic concentrations were higher at *VGSn00* than *MULn00*. Most compounds fell within drinking water standards of relevance, except for Cd, Ni, and Mn. Hardness in mg/L of  $\text{CaCO}_3$  at *VGSn00* was found to be 241, and 137 at *MULn00*, which were the lowest hardness concentrations of any sampling location, but comparatively hard for surface water. This decrease in concentration shows that  $\text{CaCO}_3$  precipitates out of solution as water moves downstream, diluting

concentrations in greater water volume. Both samples were flowing water samples.



**Figure 16.** VGSn00.



**Figure 17.** MULn00.

### CONCLUSIONS

The Reiche Zeche mine has been used by the Technische Universität Bergakademie Freiberg for research and teaching purposes since 1969. Historical water quality sampling has been inconsistent, therefore requiring an updated water quality analysis. Results show that concentrations of metals and ions both within and coming out of the mine have decreased over time. This is perhaps due to an 'armoring' of pyrite surfaces within areas of the mine. As pyrite oxidation is the primary mechanism by which sulfides are released, and since no fresh surfaces have been exposed in nearly 50 years, previously exposed sulfide surfaces have likely been weathered enough that no more oxidation is occurring, leading to decreases in minerals leaching from the ore.

Sampled locations were classified as either flowing or still water. Flowing water was categorized by an average pH of 6.4, average concentrations of 475 mg/L and maximum of 2000 mg/L of  $\text{SO}_4^{2-}$ , and average conductivity of 874  $\mu\text{S}/\text{cm}$  and maximum of 1298  $\mu\text{S}/\text{cm}$ . Still water was categorized by an average pH of 2.9, average concentrations of 10977 mg/L and maximum of 38000 mg/L of  $\text{SO}_4^{2-}$ , and average conductivity of 7774  $\mu\text{S}/\text{cm}$  and maximum of 22000  $\mu\text{S}/\text{cm}$ . These trends suggest that the weathered waste rock in Schwarzer Hirsch Stehender and Wilhelm Stehender Nord are still the primary sites of sulfide oxidation in the mine.

Iron is clearly one of the dominant systems controlling metal presence in the mine. In the still water samples which generally had pH <4.5, it is present in ferrous form and in high concentrations. In flowing water samples, it is generally present in ferric form and precipitating out of solution at pH >4.5 and high oxygen conditions, and was therefore detected at extremely low concentrations in flowing water. Iron was also the only metal for which an Eh-pH diagram was referenced, due to very low concentrations of As, Ba, Cr, Cu, and Pb at most sampling locations.

Aluminum concentration is dependent upon K, Na, or Pb based jarosites at pH <2.5. All locations where high Al was detected had pH <3.1, high concentrations of Fe, and low concentrations of K, Na, or Pb, which lead to the conclusion that jarosites in these acidic areas leach Al, which then likely forms  $\text{Fe}^{3+}$  hydroxides until the water is supersaturated, leaving excess Fe and Al to be present in dissolved form and high concentration.

Arsenic was detected in only three water samples – HGS20, WHSt11, and WHSt117. These locations also exhibited the highest Fe concentrations detected as well as pH <3, supporting the conclusion that Fe controls As mobility at extremely acidic pH levels.

The sulfate system is the other dominant system that controls metal presence in the mine. High sulfate concentrations were detected in still water samples, often in excess of iron concentrations as no natural process can fully eliminate sulfate from waters. Though temperature profiles and oxygen concentrations were not measured, sulfate concentrations were lower in flowing water samples, where oxygen concentrations were clearly higher, as were temperatures and pH levels, but concentrations of Pb, Fe, Zn, and Cu were all low. The reverse trend was seen in still water samples – higher concentrations of Fe, Zn, Pb, Cu at lower pH levels and temperatures.

The carbonate system must be discussed in conjunction with alkalinity and total carbon measurements. Greater alkalinity, which is

the sum of bicarbonate, carbonate, hydroxide ion and hydrogen ion concentrations, is correlated with greater overall concentration of hydrogen ions that can be buffered by the carbonate system. Total inorganic carbon is the sum of carbonic acid, bicarbonate, and carbonate ion concentrations. Fittingly, TIC levels in flowing

waters were higher on average than those in still waters, as natural waters have a better carbonate buffering system than mine waters.

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