

## Impact of temperature on the leaching of sulphate, Co, Fe, Mn, Ni and Zn from the Ballangen tailings deposit, Norway: a laboratory column experiment

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### ABSTRACT

Temperature is an important factor affecting the leaching of contaminants from waste deposits, especially in the Nordic region where temperature change is more drastic than other areas. In this study, the impact of temperature variation in the leaching of sulphate, Co, Fe, Mn, Ni and Zn from the Ballangen tailings deposit, northern Norway, was investigated using a column leaching experiment. Unoxidized tailings were fed into four columns, which were subsequently put into four wine fridges set at 5, 10, 14 and 18 °C, respectively. The columns were filled with 600 mL of deionized water from the top every second week. Leachate was collected at the bottom and tested for pH, conductivity and concentrations of  $\text{SO}_4^{2-}$ , Co, Fe, Mn, Ni and Zn. The saturation index for ferrihydrite and the activity of  $\text{Fe}^{2+}$  in the leachate were calculated with PHREEQC. The results showed that the conductivity and leachate concentrations of  $\text{SO}_4^{2-}$ , Co, Fe, Mn and Ni were highest at 14 and 18 °C, and lowest at 5 °C, which showed high tailings oxidation and subsequent leaching of contaminants at higher temperatures. X-ray photoelectron spectroscopic (XPS) analysis of the residual material confirmed the oxidation of sulphides and leaching of many elements. Ferrihydrite was supersaturated in the leachate from the 14 and 18 °C columns, which showed the oxidation of pyrrhotite and olivine and the precipitation of ferrihydrite. The cumulative mass of Zn leached out was highest at 10 °C, which might be the threshold temperature for the leaching of Zn.

**Key words:** Ballangen deposit, column experiment, leaching, oxidation, temperature

### HIGHLIGHTS

- Temperature is an important factor in the leaching of contaminants from the tailings deposit.
- High oxidation and leaching of contaminants from tailings were observed at a higher temperature.
- 10 °C is suggested to be the threshold temperature for the leaching of Zn.

## 1. INTRODUCTION

Waste rock and tailings from mining operations can cause a potential risk to the surrounding environment when directly exposed to weathering. Especially waste rock and tailings containing high concentrations of sulphides are notorious for their potential production of acid rock drainage (ARD) and subsequent leaching of contaminants to the local environment (Avilla *et al.* 2008). The leaching of contaminants from tailings deposits has been reported in many studies (Besser & Rabeni 1987; Yukselen 2002; Mendoza *et al.* 2006). High concentrations of  $\text{SO}_4^{2-}$  (280–29,500 mg/L), As (<0.01–12 mg/L), Fe (0.025–2,352 mg/L), Mn (0.1–732 mg/L) and Zn (<0.025–1,465 mg/L) have been observed in the acidic leachate from the tailings impoundment in Taxco, Southern Mexico (Mendoza *et al.* 2006). The leaching of contaminants from a tailings deposit in Northern Cyprus has been reported (Yukselen 2002). The leaching of contaminants from abandoned lead mine tailings deposits in southeast Missouri, USA, and the subsequent accumulation of contaminants in aquatic invertebrates have been studied (Besser & Rabeni 1987). In addition, the leaching of contaminants from tailings deposits to stream sediment and stream waters has been reported in previous studies (Concas *et al.* 2006; Avilla *et al.* 2008).

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The quality of mine drainage water is affected by many factors such as the geology/mineralogy of the ore deposit, the climate, mining and mineral processing methods, waste management and the particle size of mill tailings (Parviainen *et al.* 2012). Sulphide minerals, especially pyrite and pyrrhotite, are the main contributors to acid generation, while carbonate minerals, especially calcite, are the main neutralizers (Sherlock *et al.* 1995; Jurjovec *et al.* 2002). Olivine and plagioclase are also known to contribute to the neutralization process; however, their reaction rate is slower than pyrite–pyrrhotite reaction rates (Schulz *et al.* 2014), although they may effectively raise the pH due to their large abundance in some mine waste material.

Various physical and chemical factors play an important role in the distribution of trace element concentration in the surrounding environment of a tailings deposit, including proximity to the tailings pile, grain size variations, variable Al, Fe, Mn and S concentrations, pH, weathering, and the general reactivity of elements under oxidizing and acidic conditions (Bhattacharya *et al.* 2006). The effect of different parameters on the leaching of contaminants from tailings deposits has been investigated in many studies. The effect of leachant ionic strength, pH, leachant residence time and buffering ability on the leaching of metals from silver mine mill tailings has been investigated in a column leaching experiment (Doepker 1991). The effect of organic amendments on the leaching of Cd, Pb and Zn from mine tailings has been investigated in previous studies (Burckhard *et al.* 1995; Schwab *et al.* 2007). The effect of redox conditions on the stability of As in water from a tailings wetland, the effect of pH and phosphate on the mobility of metal from soils of a lead smelting site and the effect of solid–liquid contact time and aeration on the dissolution of metals from mine tailings have been studied in previous research (Doepker & Drake 1991; Impellitteri 2005; Beauchemin & Kwong 2006). The effect of parameters such as pH, temperature, particle size and contact time on the leachability of heavy metals from mine tailings of the Dexing copper mine in China has been investigated in a series of laboratory batch experiments (Guo *et al.* 2013). The effect of temperature, initial pH and pulp density on the bioleaching of As from mine tailings has been studied by bioleaching tests (Park *et al.* 2014).

Of these different parameters, temperature is one of the most important. The effect of temperature on the leaching of contaminants from tailings deposits has been determined in several previous studies (Guo *et al.* 2013; Chen *et al.* 2014; Park *et al.* 2014). Although there have already been previous studies in this field, the temperature they investigated is not practical in natural conditions as those studies required an additional heating process. In addition, most of the previous studies were conducted in a non-Arctic region. There is limited information on the effect of temperature on the leaching of contaminants in the Arctic region at present, where ARD processes take place naturally (Dold *et al.* 2013). In addition, few studies discuss the effect of temperature in the context of global climate change, although temperature is one key parameter of global climate change. This is extremely important especially for the Arctic region, since the climate change is more drastic in the Arctic region than that in non-Arctic regions (Parry *et al.* 2007).

In this study, the effect of temperature variation in the leaching of sulphate, Co, Fe, Mn, Ni and Zn from the Ballangen tailings deposit, Nordland county, Northern Norway, was investigated using a column leaching experiment. The aim was to find out whether a continuous temperature increase in the context of global climate change would have a significant effect on the leaching of contaminants from waste deposits in the near Arctic region.

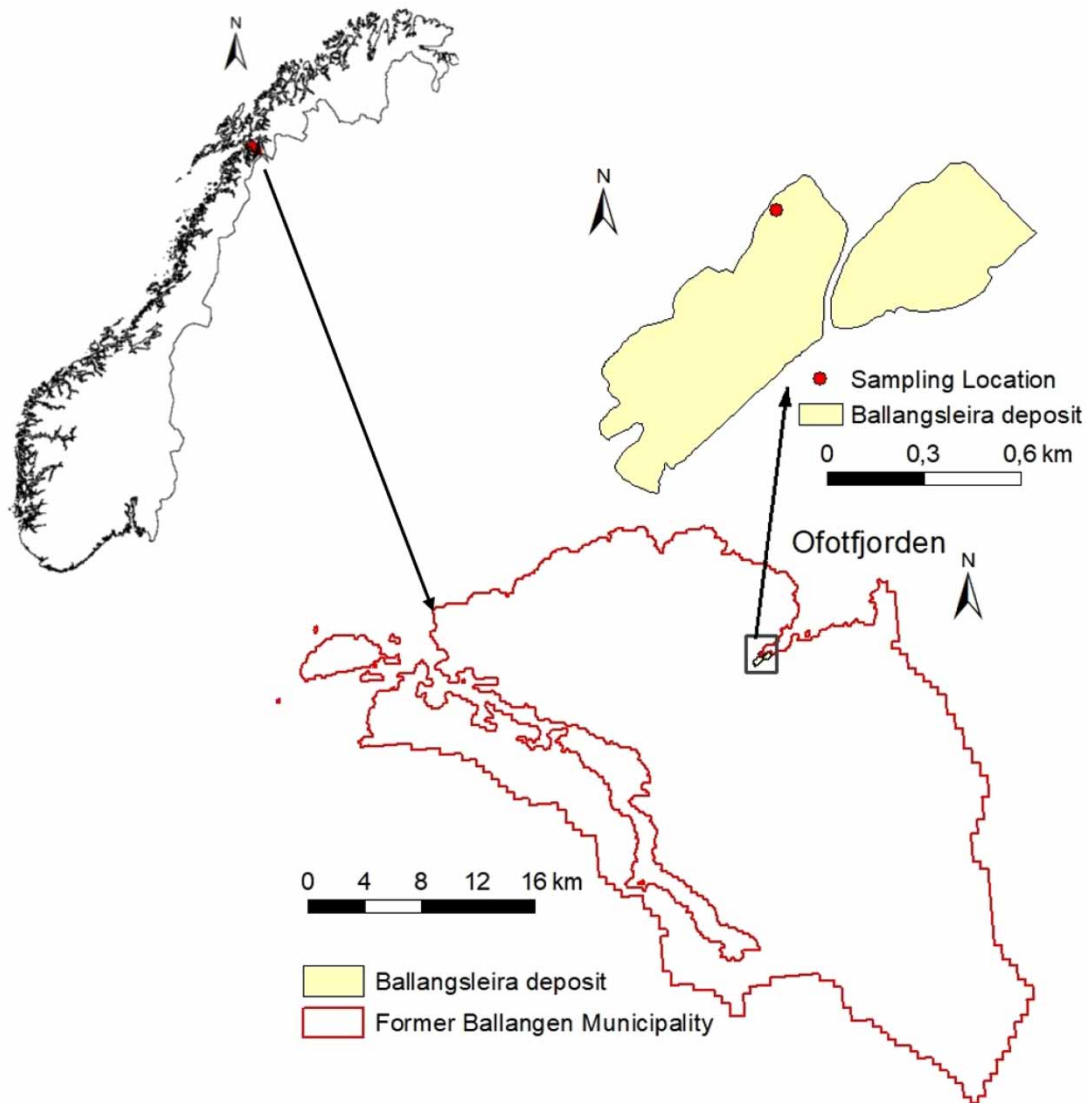
## 2. STUDY AREA

The Ballangen tailings deposit is located in the former Ballangen municipality in the north of Norway (Figure 1). The tailings in the deposit originate from processing the Råna nickel–olivine mine and were deposited at two sites: Ballangsløira (Figure 1) and Fornes deposit. The tailings mainly consist of mafic minerals and plagioclase, with minor to trace amounts of pyrrhotite and traces of chalcopyrite (Embile *et al.* 2018, 2019). A 10–20 cm of soil cover was put over the tailings to prevent their weathering and oxidation. However, the soil cover is not effective in the prevention of the tailings oxidation and the subsequent leaching of metals to the surrounding environment (Segalstad *et al.* 2006; Embile *et al.* 2018; Lu *et al.* 2021), which has been observed in a previous study (Embile *et al.* 2018). Therefore, this study selected the Ballangsløira deposit as the study area to investigate the impact of temperature on the leaching of contaminants from tailings.

## 3. METHODS

### 3.1. Sampling and analysis of tailings

The unoxidized tailings from the Ballangsløira deposit were collected with a plastic spade into several plastic buckets in June 2016, which were covered with a lid after sample collection. The collected samples were transported to the Kjeøy Research and Education Center laboratory at Kjeøy, Vestbygd, Norway, and stored at 4 °C for analysis.



**Figure 1** | Tailings deposit and sampling location (Lu *et al.* 2021).

The tailings were sent to the ALS Laboratory Group AS for the analysis of whole rock major and trace element composition. For mineralogical analysis, the tailings sample was dried and ground to a fine powder. X-ray diffraction (XRD) measurement was performed using a Rigaku Smartlab diffractometer with a Co lamp (40 kV, 135 mA). The XPS measurements were carried out for unoxidized tailings and tailing samples collected after the column study. XPS spectra were obtained using a Thermo Fischer Scientific ESCALAB 250Xi with a monochromatic Al K $\alpha$  source (1,486.6 eV). The charge correction was performed by setting the binding energy (BE) of adventitious carbon to 284.8 eV.

### 3.2. Column leaching experiment

Column and batch leaching experiments have been widely used to investigate the release of heavy metals from solid materials (Fan *et al.* 2016). There are several guidelines and standard testing methods for performing these tests (ASTM International 2001; NASI 2012, 2013). The column experiment method has the advantage of simulating a long-term release process and detecting temporal variations in heavy metal release from solid materials compared with the batch experiment method (NASI 2013; Fan *et al.* 2016). A column leaching experiment was performed on the unoxidized tailings. The unoxidized tailings were fed into four columns and then placed into four wine refrigerators, which were set to four different temperatures of 5, 10, 14 and 18 °C. The temperature settings were based on local monthly average temperature statistics between –3.9 and

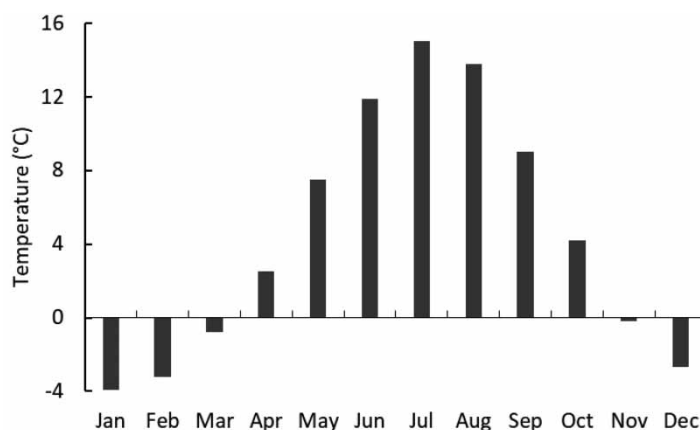
15 °C (Figure 2) (Weather2visit 2020). The temperature below freezing point (0 °C) was not selected because the freezing of the materials will restrict the leaching. The temperature of 18 °C, which was above the highest monthly average temperature, was selected to investigate the impact of increasing temperature in the future under global climate change.

There are no local data that show how the air temperature affects the soil/tailings temperature. However, the impact of air temperature on soil/tailings temperature has been studied before. A high correlation between mean yearly air temperature and soil temperature has been found in a study in southern China (Zhan *et al.* 2019). A slow increase in soil temperature as a response to an increase in air temperature has been observed in several studies, for example the soil temperature data obtained at the Armagh Observatory. Ireland shows a warming trend of 0.04–0.25 °C/decade (Garcia-Suarez & Butler 2006). A similar warming trend has also been observed at two-thirds of the monitoring stations across Canada, with an increase of 0.26–0.30 °C/decade in the springs of 1958–2008 (Qian *et al.* 2011). The variations in soil temperature do not respond to the air temperature on a rapid basis, and air temperature variations have less effect deeper in the soil. However, oxidation normally takes place in the upper 1–2 m; therefore, it is within the range of the air temperature effect. The microbial effect on sulphide oxidation becomes minor below 4 °C; therefore, this range of temperature is applicable for the selected site. Consequently, the real temperature in the tailings deposit was properly reflected in the current study.

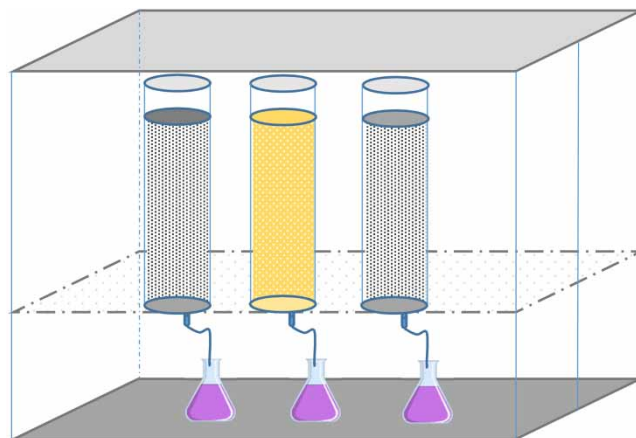
The columns were filled with 600 mL of deionized water with a shower from the top every 2 weeks. The addition of 600 mL water volume was calculated based on the maximum monthly precipitation of 80 mm/month and the diameter of the column (140 mm), which combined would give a daily addition of 41 mL or approximately 600 mL/14 days. The water was added in bulk at one time because the infiltration rate was low. The leachate was collected at the bottom of the column. Water continued to drip out for up to 72 h after the addition of water (Figure 3). The collected leachate was tested for pH, conductivity and alkalinity on the day of collection, with further analysis of the concentrations of sulphate, Ca, Co, Fe, Mn, Ni and Zn afterwards. After collection of the leachate, an addition of the same volume of deionized water was made to the columns from the top again after 2 weeks. The leachate was collected at the bottom again. The drainage time for the water through the columns increased over time. The columns were set up in October 2016, and 21 leaching cycles were performed. In total, 84 leachate samples were collected. The column experiment was designed and run at Kjeøy Research & Education Center. The analysis of the leachate was partly performed at Kjeøy Research & Education Center (pH, conductivity, temperature and TDS were analysed with a probe immediately; alkalinity was measured by titration using a Metrohm Titrand; the sulphate concentration was analysed using an IC Metrohm 870 and concentrations of Ca, Co, Fe, Mn, Ni and Zn were analysed by ICP-AES). Some leachate samples were sent to ALS Laboratory Group AS for the analysis of Co, Fe, Mn, Ni and Zn by ICP-AES or ICP-MS. After the column leaching tests had terminated, residual tailings samples were collected from different heights of the column bed (top and middle) and dried. XRD and XPS analyses were carried out for the residual tailings samples as described in Section 3.1. The information of each column is listed in Table 1.

### 3.3. PHREEQC program

The open source PHREEQC geochemical modelling program, developed and maintained by the U.S. Geological Service (Parkhurst & Appelo 2013), was used to evaluate the saturation indexes (SI) of the potential secondary minerals gypsum



**Figure 2** | Average monthly temperature for Ballangen (Weather2visit 2020).



**Figure 3** | The design of the column experiment set in refrigerators with glass doors.

**Table 1** | Column information

Column number	Weight of column (g)	Weight of tailings + column (g)	Weight of tailings (g)	Temperature (°C)
C2	1,224	5,207	3,981	5
C5	1,220	5,426	4,206	10
C8	1,222	5,625	4,403	14
C11	1,227	5,264	4,037	18

and ferrihydrite. SI is a parameter to measure how far from equilibrium a mineral is, based on the solution chemistry (species activity and ionic strength) and the physiochemical parameters. The concentration of species in solution multiplied by the activity coefficients for the species gives the species activity. The activity coefficient is calculated with the extended Debye–Huckel equation. In addition, the activity of ferrous iron ( $\text{Fe}^{2+}$ ) in the leachate solution was calculated with PHREEQC and the MinteqV4 database integrated into PHREEQC. The calculated SI for ferrihydrite and the redox potential measured immediately after leaching were used to calculate the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ratio.

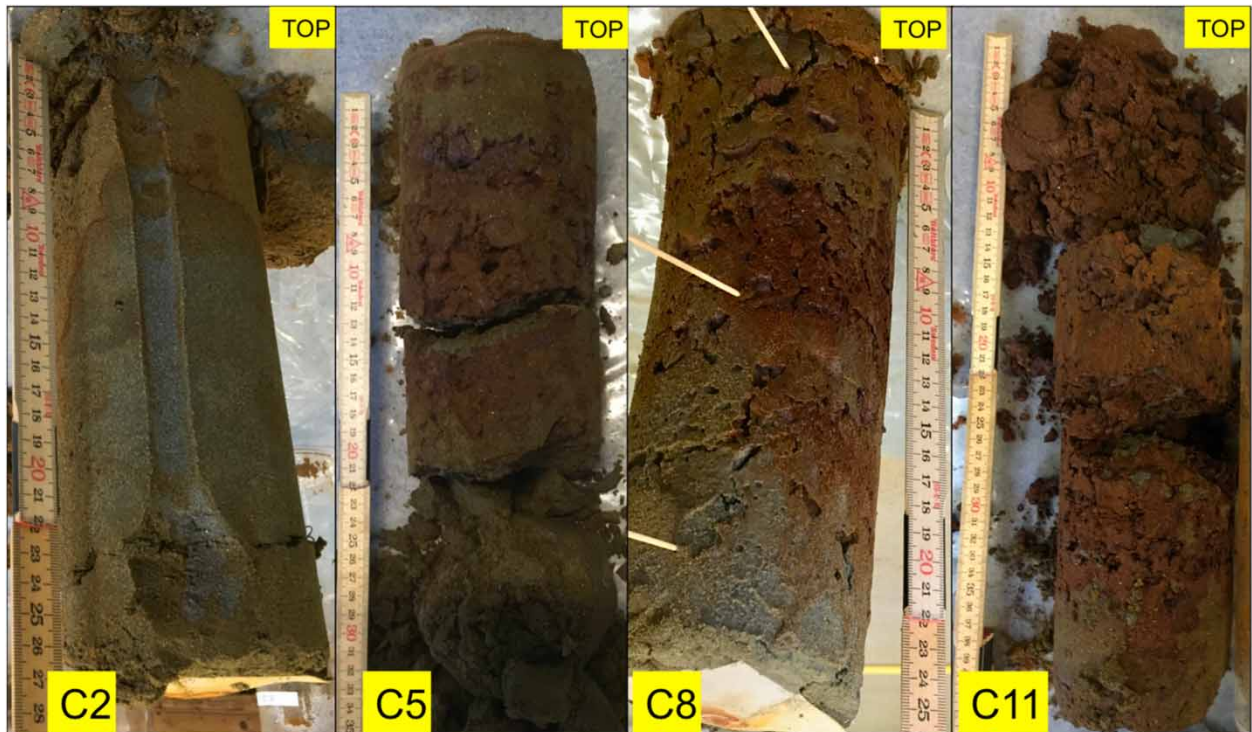
## 4. RESULTS

The columns after the leaching experiment are shown in Figure 4. The tailings were observed to be oxidizing in all four columns, showing a transition from grey to red-brown colour over time. The top 5–10 cm of column C2 showed clear iron staining with a light brown colour, while, below 50 cm, the column was primarily grey with some areas of iron staining. Column C5 had the same light brown staining on the top 5–10 cm as column C2, but there was red-brown staining further down in the column. Only the bottom third of the column showed a primarily grey colour. The red-brown staining extended further down in column C8 compared with columns C2 and C5. Column C11, with the highest leaching temperature of 18 °C, showed red-brown staining throughout the column with spots of grey to light brown.

### 4.1. Mineralogical characteristics of tailings before and after column studies

The tailings were all grey before the leaching experiments, while at the end of the study the surface of the columns had changed to a brown-red colour. When the column materials were taken apart, we found semi-round sections within the columns that still showed the grey colour.

XRD analysis showed that the unoxidized tailing was mainly comprised of silicates with the major mineral being forsterite (ferroan). This is in line with previous studies (Segalstad *et al.* 2006). Minerals from the amphibole, plagioclase and phyllosilicate groups were also present and tentatively identified as tremolite, albite, chamosite, siderophyllite, vermiculite and clinocllore. In addition, enstatite and pyrrhotite may have been present.



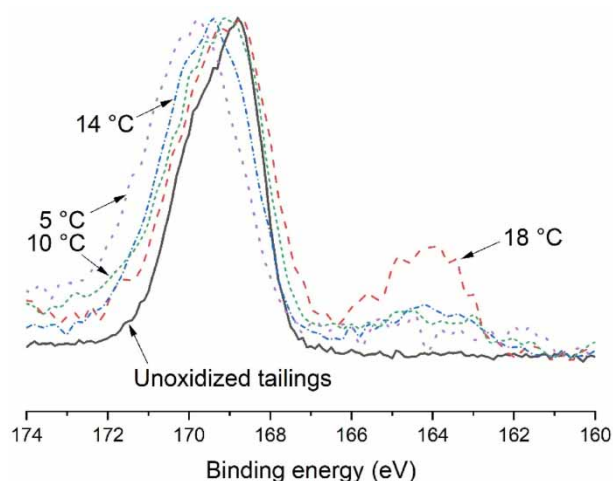
**Figure 4** | Photos of the tailings from columns C2, C5, C8 and C11 after 42 weeks of leaching.

The XPS survey scan showed the presence of oxygen, magnesium, iron, sulphur, silicon, sodium, chlorine and aluminium on the surface of tailing samples (Table 2), whereas high-resolution scans additionally confirmed potassium but did not confirm other metals clearly (Co, Cu, Ni, Mn and Zn). The C 1s spectrum of unoxidized tailing (spectrum not shown) showed adventitious carbon at 284.8 eV and carboxyl groups at about 288.3 eV (Pinto *et al.* 2014). The S 2p spectrum of the unoxidized tailings (Figure 5) revealed that sulphur was in the sulphate form (S 2p peak located at about 169 eV) (Wang *et al.* 2018; Gogoi *et al.* 2019).

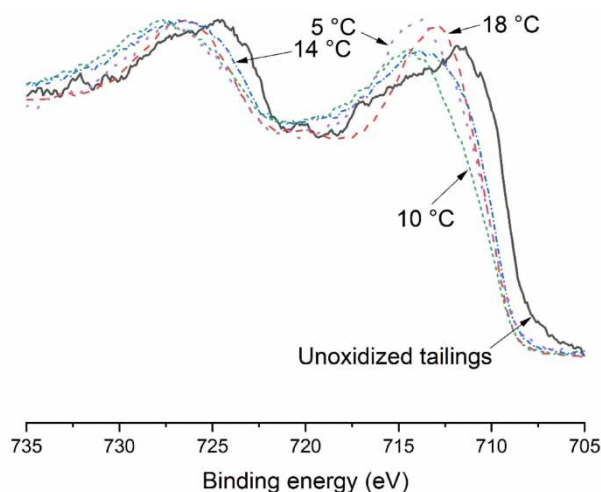
The samples collected after the column studies showed some changes in the surface composition (Table 2). Sodium and chloride had leached out from all the samples, except for a small amount of sodium observed at the top of the 5 °C sample. Magnesium and sulphur were also present in much lower amounts on the surface. The proportion of iron increased significantly on the surface as a consequence of the leaching of elements. The Fe 2p<sub>3/2</sub> peak in the column samples was found clearly at a higher BE in comparison with the unoxidized tailings (Figure 6).

**Table 2** | Surface elemental composition (weight %) of unoxidized tailing and residual tailings from columns

	Unoxidized tailings	18 °C medium	18 °C top	14 °C medium	14 °C top	10 °C medium	10 °C top	5 °C medium	5 °C top
O 1s	45.7	46.1	46.6	45.1	47.8	44.7	46.2	49.1	51.0
Mg 1s	10.6	1.7	1.6	4.4	2.0	2.0	4.2	4.5	4.5
Fe 2p	10.3	33.5	33.3	26.3	26.9	31.0	26.2	18.7	21.9
S 2p	9.8	4.2	4.7	8.3	8.1	5.7	7.3	3.1	7.9
Si 2p	8.5	7.0	8.6	8.7	9.7	10.5	9.8	17.3	9.6
Na 1s	5.8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.2
Cl 2p	4.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C 1s	2.7	6.8	5.0	6.4	5.0	5.6	6.3	5.0	4.8
Al 2p	2.4	0.0	0.0	0.0	0.0	0.0	0.0	2.2	0.0
N 1s	0.0	0.7	0.4	0.9	0.6	0.6	0.0	0.0	0.0



**Figure 5** | S 2p XPS spectrum of unoxidized tailings and samples collected from the column operated at different temperatures (samples from the middle of the column are shown; the same trend was observed in the top samples). The spectra have been scaled to have the same intensity range.



**Figure 6** | Fe 2p XPS spectrum of unoxidized tailings and samples collected from the column operated at different temperatures (samples from the middle of the column are shown; the same trend was observed in the top samples). The spectra have been scaled to have the same intensity range.

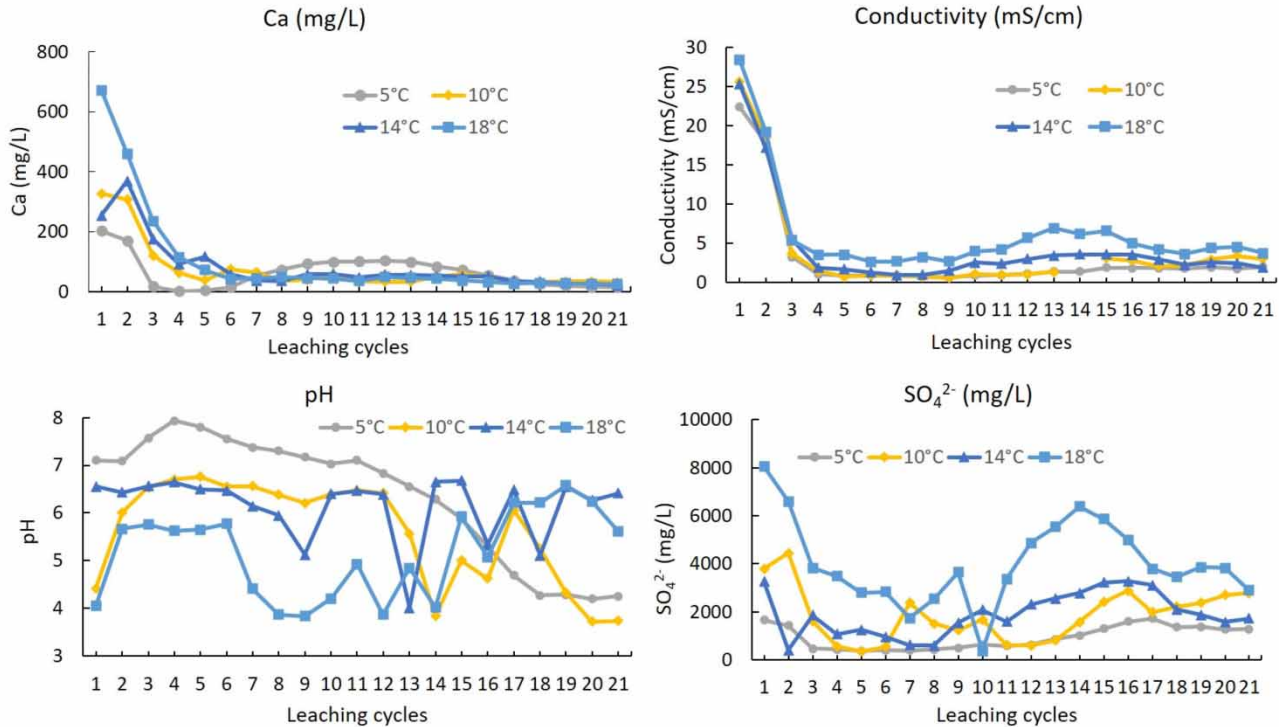
As mentioned above, the unoxidized tailings contained sulphur only in the form of sulphate on the surface, which was also the case for the column samples treated at a low temperature (5 and 10 °C) (Figure 5). On the other hand, column samples treated at the highest temperature (18 °C) showed additionally a clear peak at about 164 eV (Figure 5), which could be attributed to some sulphide species or elemental sulphur (Leiro *et al.* 2003; Krylova & Andrulevicius 2009). The samples treated at 14 °C showed a smaller peak.

## 4.2. Column leaching results

The leachate analysis results from the columns at each temperature are presented in the following sections.

### 4.2.1. Leachate pH

The pH of the leachate throughout the leaching cycles is shown in Figure 7. In the first 14 leaching cycles, the pH of the leachate was highest at 5 °C, and lowest at 18 °C. After the 14th leaching cycle, the pH of the leachate at the leaching



**Figure 7** | Evolvement of conductivity, pH and concentrations of Ca and sulphate ( $\text{SO}_4^{2-}$ ) in the leachate (one outlier result for conductivity was removed and is not shown in the figure).

temperature of 5 °C showed a decreasing trend and the pH of the leachate at 18 °C showed an increasing trend. The leachate at 18 °C was acidic throughout the leaching process, which indicates the oxidation of the tailings and production of acidic leachate. The pH of the leachate at 5 °C was neutral or slightly alkaline in the first 11 leaching cycles and decreased afterwards. The results indicate that, in the first 14 leaching cycles, an increase in temperature accelerated the oxidation of tailings, and thus the production of acidic leachate. A low temperature of 5 °C inhibited the oxidation of tailings from the short-term perspective. However, as leaching proceeded, the oxidation of tailings started to initiate even at the low temperature of 5 °C. In contrast, the oxidation of tailings at the leaching temperature of 18 °C was highest at the beginning of leaching and slowed down after a while.

#### 4.2.2. Concentration of Ca and conductivity of the leachate

The evolvement of the conductivity and concentration of Ca in the leachate throughout the leaching cycles is shown in Figure 7. The conductivity and concentration of Ca was highest in the first leaching cycle and decreased substantially in the first three to four leaching cycles, becoming fairly stable afterwards. This indicates that both easily soluble secondary minerals and initial water with potentially high conductivity were present in the tailings at the start of the experiments. The high concentrations of Na, Cl, Mg and Ca in the leachate in the first few leaching cycles indicate that (windblown) seawater was included in the tailings.

Generally, the conductivity was highest at the leaching temperature of 18 °C and decreased as the temperature decreased. The highest conductivity monitored at 18 °C was 28.4 mS/cm. This indicates that there was higher mineral dissolution at 18 °C due to higher oxidation rates of tailings, which therefore resulted in acidic conditions at this temperature. Most salts are more soluble in acidic conditions. XPS also confirmed that leaching of salts had occurred (Table 2).

#### 4.2.3. Leachate concentrations of $\text{SO}_4^{2-}$

The leachate concentrations of  $\text{SO}_4^{2-}$  throughout the leaching cycles are shown in Figure 7. Generally, the highest and lowest leachate  $\text{SO}_4^{2-}$  concentrations was observed at leaching temperatures of 18 and 5 °C, respectively. The highest  $\text{SO}_4^{2-}$  concentration at 18 °C indicates the highest oxidation of sulphide in the tailings at this temperature, which corresponds to the acidic

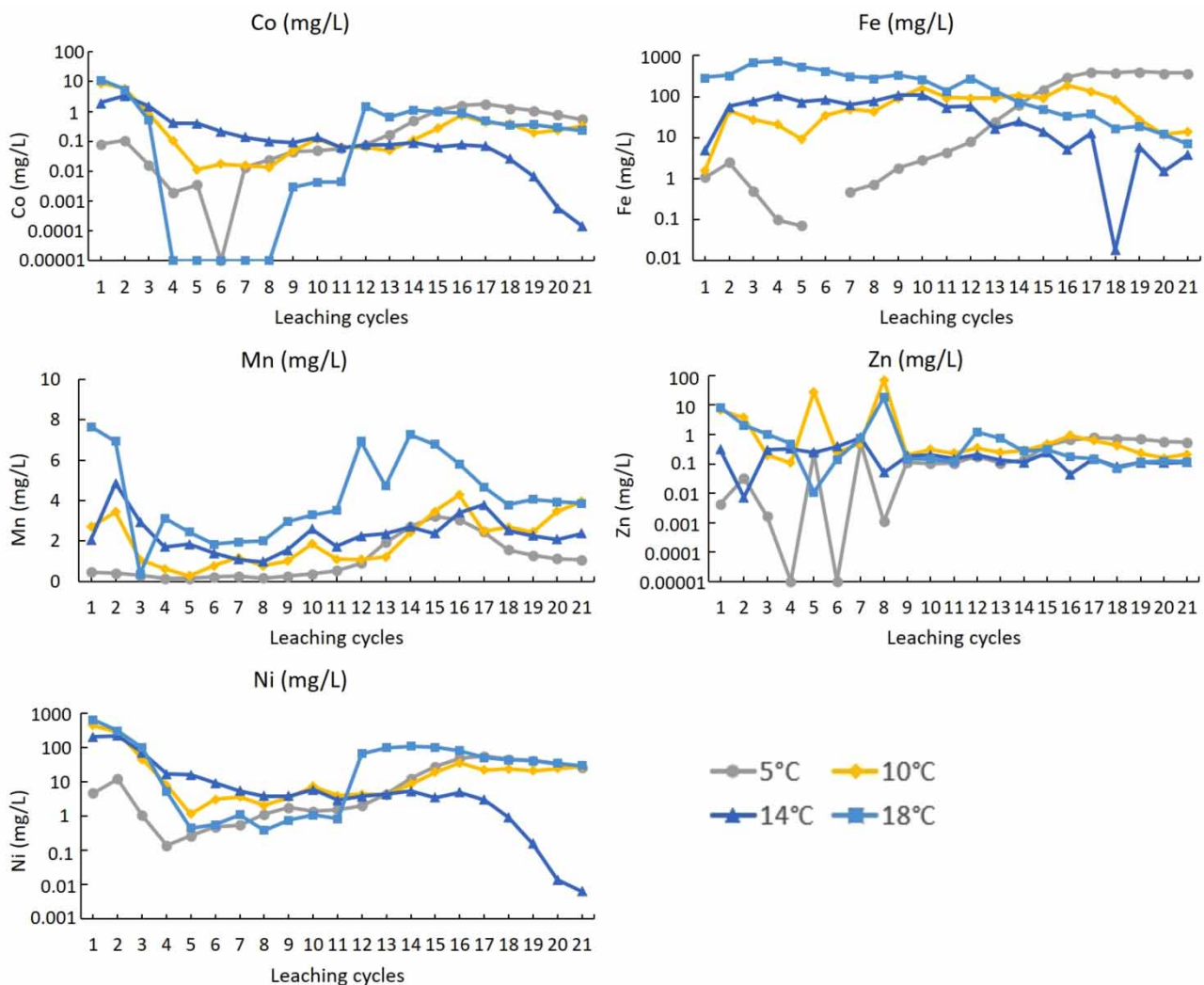


pH throughout the leaching cycles and the lowest pH in the first 14 leaching cycles. The leachate concentration of  $\text{SO}_4^{2-}$  at 5 °C remained fairly stable in the first 14 leaching cycles, except for a slight decrease at the beginning of the leaching and a slightly increasing trend after the 14th leaching cycle, which corresponds to the decrease in pH towards the end of the leaching.

The leachate concentration of  $\text{SO}_4^{2-}$  was 8,052 mg/L in the first leaching cycle and decreased significantly afterwards. The lowest level throughout the leaching was 370 mg/L, observed in the 10th leaching cycle. The concentration increased again after the 10th leaching cycle and reached the second peak value of 6,390 mg/L in the 14th leaching cycle. After the 14th leaching cycle, the concentration decreased again, which corresponds to the increase in pH after the 14th leaching cycle.

#### 4.2.4. Leachate concentrations of Co, Fe, Mn, Ni and Zn

The leachate concentrations of Co, Fe, Mn, Ni and Zn throughout the leaching cycle are shown in Figure 8. In the first 14 leaching cycles, the leachate concentration of Fe was highest at the 18 °C leaching temperature and lowest at 5 °C, which is similar to the trend for pH. After the 14th leaching cycle, the leachate concentration of Fe was highest at 5 °C and lowest at 18 °C. Generally, the leachate concentration of Fe showed a decreasing trend throughout the leaching at 14 and 18 °C and an increasing trend at 5 °C after the 5th leaching cycle. The highest and lowest leachate concentrations of Fe were 743.7 mg/L (observed at 18 °C) and 0.07 mg/L (at 14 °C), respectively.



**Figure 8** | Concentrations of Co, Fe, Mn, Ni and Zn in the leachate.

The leachate concentration of Mn generally showed a similar trend to that of  $\text{SO}_4^{2-}$ . The concentration was generally highest at the leaching temperature of 18 °C and lowest at 5 °C. At 18 °C, the concentration was highest in the first leaching cycle at 7.65 mg/L and decreased significantly in the first three leaching cycles, with the lowest concentration observed in the third leaching cycle, at 0.37 mg/L. The concentration increased continuously afterwards until the 14th leaching cycle, where the second peak concentration of 7.26 mg/L was observed. After the 14th leaching cycle, the concentration decreased again. At a leaching temperature of 5 °C, the concentration was fairly stable in the first 11 leaching cycles, and then increased until the 15th leaching cycle, where the highest concentration of 3.22 mg/L was observed. After the 15th leaching cycle, the concentration started to decrease again.

The leachate concentrations of Co and Ni showed a similar trend. Their concentrations were highest at the leaching temperature of 14 °C in the first 11 leaching cycles. From the 11th to 15th leaching cycle, the highest concentrations of Co and Ni were observed at 18 °C. After the 15th leaching cycle, the concentration of Co was highest at the leaching temperature of 5 °C, and the concentration of Ni was highest at the leaching temperatures of 18 and 5 °C. At 14 °C, the concentrations of Co and Ni showed a significant decreasing trend after the 15th leaching cycle, whereas their concentrations were fairly stable at other leaching temperatures after the 15th leaching cycle.

In the first eight leaching cycles, the leachate concentration of Zn was highest at the leaching temperature of 10 °C followed by 18 and 14 °C, with the lowest concentration observed at 5 °C. The leachate concentrations from leaching cycles 9–11 were similar at different leaching temperatures. The concentration was higher at 14 °C than that at 5 °C in the first nine leaching cycles, with similar levels in the leachates from the 9th–11th leaching cycles. In leaching cycles 12–14, the concentration of Zn was highest at the leaching temperature of 18 °C, followed by 10 °C, with similar concentrations at 5 and 14 °C. After the 14th leaching cycle, the concentration was highest at 5 °C, followed by 10 °C, with similar concentrations at 14 and 18 °C. In general, the leaching concentration of Zn was highest at 10 °C.

#### 4.2.5. Cumulative mass of elements leached out

The cumulative amounts of Co, Fe, Mn, Ni and Zn leached out from the tailings were calculated and are shown in [Figure 9](#). Generally, the highest cumulative leached amounts of Co, Fe, Mn and Ni were observed at 18 °C. The lowest cumulative masses of Co, Mn and Ni were observed at 5 °C. The leaching curves of Co and Ni showed a similar trend, with the highest leaching rate observed at 18 °C, followed by 10, 14 and 5 °C. The leaching curves of Fe and Mn also showed a similar trend. For Mn, the cumulative mass leached out decreased as the temperature decreased.

The cumulative mass of Zn leached out showed a different trend than that of the other elements. The highest cumulative mass of Zn leached out was observed at the leaching temperature of 10 °C, followed by 18 °C, with the lowest observed at 5 and 14 °C. This seems to indicate that 10 °C is the threshold temperature for the leaching of Zn.

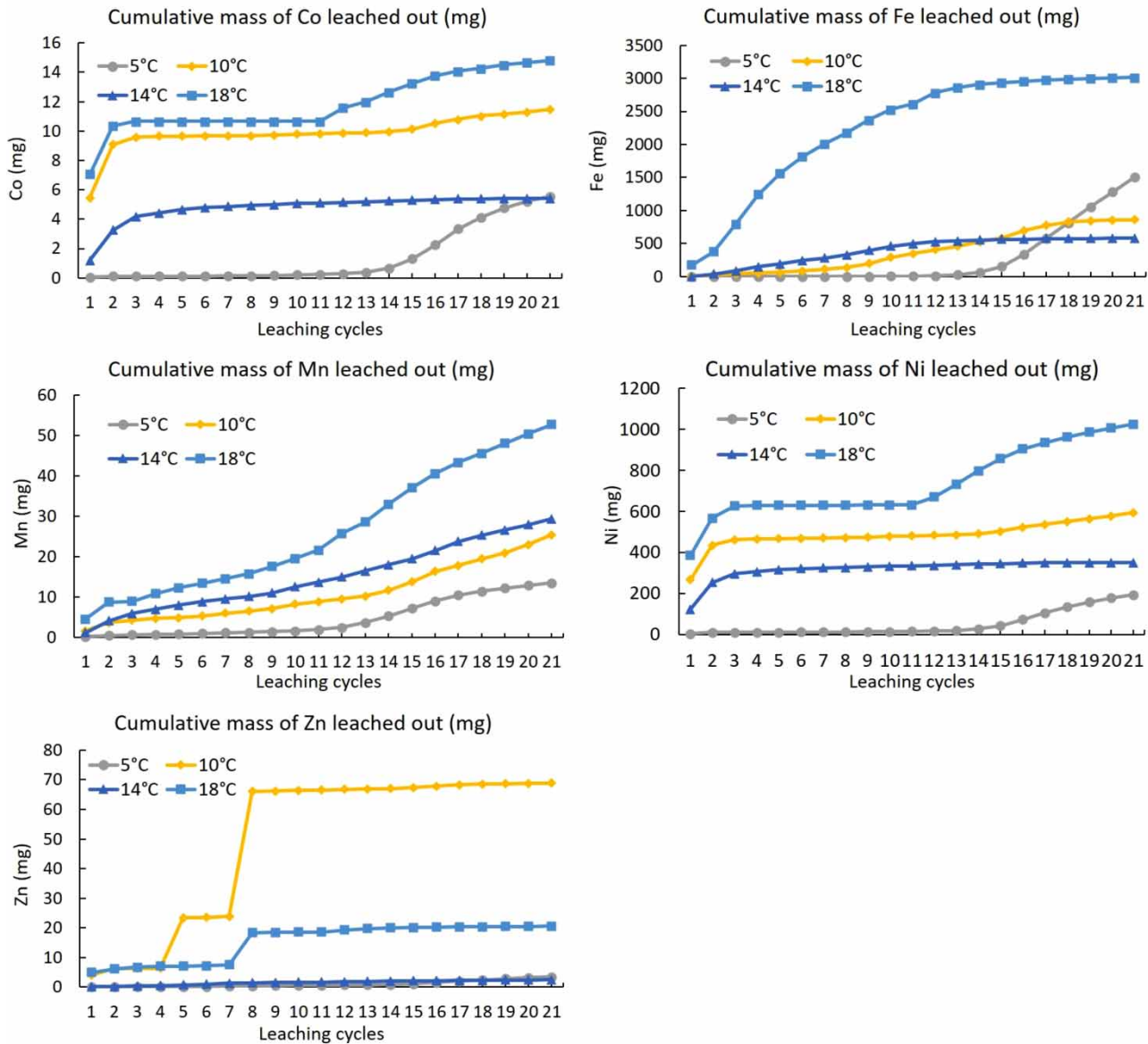
## 5. DISCUSSION

### 5.1. Reliability of the results

The original tailings material was collected from an area of tailings that did not seem to have been oxidized due to its grey colour. Within the column, the material was exposed to air during both watering and the drying periods. Even though the mass of material and the volume of water added every week was the same, the two-weekly leaching rates were not fully consistent between the columns. This could have been an effect of the different flow in the columns and thereby the variable and different amounts of material that were subjected to oxidizing conditions. In addition, the two-weekly addition of water probably did not rinse the same amount of material on a weekly basis, as iron hydroxide was precipitating in the columns and thereby changed the flow path.

The calculated SI for gypsum indicates that gypsum was undersaturated throughout the whole leaching period, except for the first leaching at 10, 14 and 18 °C ([Figure 10](#)). This would again indicate that the main source of sulphur and calcium through the leaching process was not gypsum. In the early cycles, when the pH was weakly acidic to neutral, the calcium source could have been calcite, in addition to seawater.

The activity of the  $\text{Fe}^{2+}$  vs. log SI for ferrihydrite is shown in [Figure 11](#). At the pH observed in the leachate, the oxidation of the  $\text{Fe}^{2+}$  released from the oxidation of pyrrhotite and olivine will precipitate as ferrihydrite rather than stay in solution as  $\text{Fe}^{3+}$ . At the leaching temperatures of 5 and 10 °C, ferrihydrite is undersaturated in the leachate. The undersaturation may indicate firstly that the oxidation of the  $\text{Fe}^{2+}$  released from the oxidation of pyrrhotite and olivine was not rapid enough, and secondly, the further precipitation of iron as ferrihydrite. In contrast, at the leaching temperatures of 14 and 18 °C,



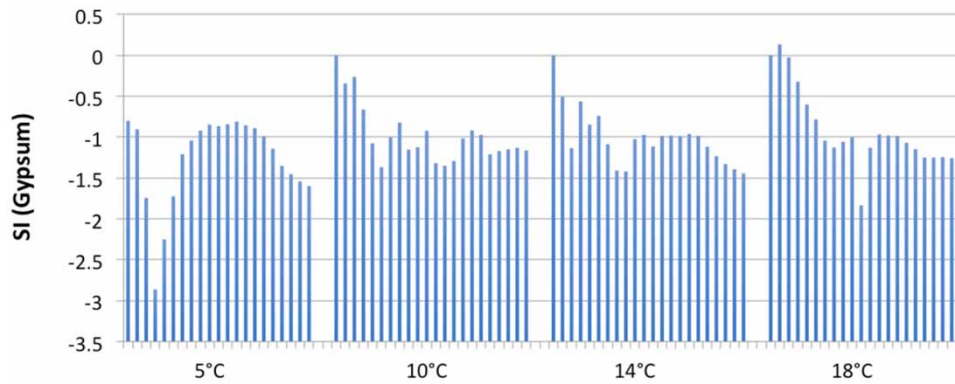
**Figure 9** | Cumulative mass of Co, Fe, Mn, Ni and Zn leached out from tailings.

especially at 18 °C, ferrihydrite is supersaturated in the leachate and the  $\text{Fe}^{2+}$  activity is high, which indicates the release of  $\text{Fe}^{2+}$  from the oxidation of pyrrhotite and olivine, and the subsequent oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  and precipitation of  $\text{Fe}^{3+}$  as ferrihydrite. This corresponds to the low pH and high concentrations of  $\text{SO}_4^{2-}$ , Co, Fe, Mn and Ni in the leachate.

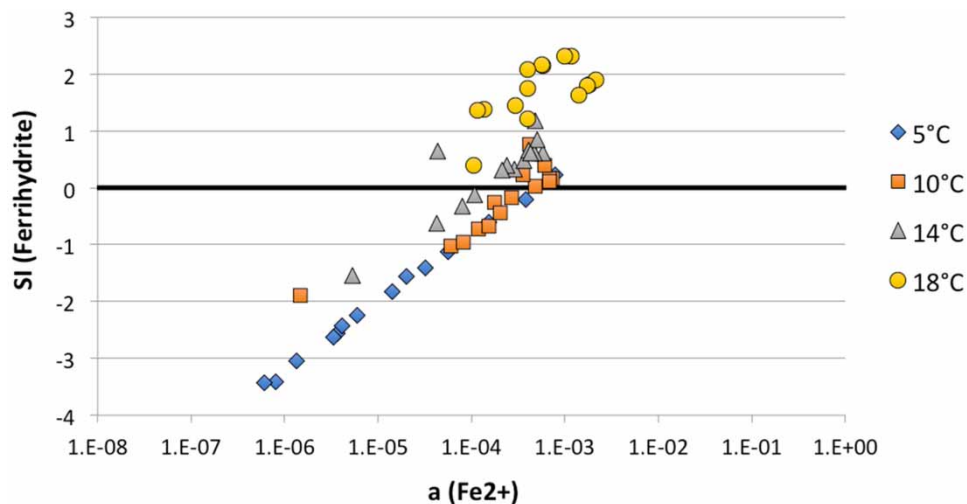
## 5.2. Effect of temperature on leaching

The observation of the colours of the tailings material after 42 weeks of leaching showed an increase in iron staining from the low temperature to the higher temperature. The middle temperatures were similar in the amount of iron staining, while the tailings exposed to the highest temperatures clearly showed much more sulphide oxidation.

The  $\text{SO}_4^{2-}$  concentration was highest at the leaching temperature of 18 °C and lowest at 5 °C in the first 14 leaching cycles. This agrees with the pH, which was acidic throughout the leaching cycle. The results indicate higher oxidation of sulphides in the tailings at 18 °C than that at 5 °C; therefore, more sulphate is produced and leached out from the tailings. Due to the acidic conditions of the leachate at 18 °C, leachate concentrations of Fe and Mn were also highest at the leaching temperature of 18 °C and lowest at the leaching temperature of 5 °C. The concentrations of Co and Ni showed a similar trend and were higher at



**Figure 10** | SI for gypsum for all the leaching cycles in the four temperature settings. SI = 0 is at saturation, and positive numbers indicate supersaturation.



**Figure 11** | Activity of  $\text{Fe}^{2+}$  vs. log SI for ferrihydrite.

the higher leaching temperatures of 14 and 18 °C than those at lower leaching temperatures. The results indicate that an increase in temperature accelerates the oxidation of sulphides in the tailings and the leaching of certain elements into the surrounding environment. This agrees with previous studies. An increase in the temperature has an increasing effect on the oxidation of sulphides such as pyrite and pyrrhotite and the process follows the Arrhenius behaviour (Belzile *et al.* 2004). Oxygen is the ultimate oxidant of sulphide minerals in natural waters at pH > 4, which means that sulphide oxidation only occurs in areas where dissolved or gaseous oxygen is present (Belzile *et al.* 2004). A significant increase in the oxidation rate of pyrrhotite with an increasing temperature has been reported (Belzile *et al.* 2004). An increase in temperature can enhance the rate of oxygen diffusion and therefore the formation of ferric oxide and ferric sulphate products (Belzile *et al.* 2004). Since the predominant pH throughout the leaching experiment was above four, oxygen was the primary oxidant in the present leaching experiment. The temperature dependency of sulphide oxidation kinetics has been described using the Arrhenius relationship (Nielsen *et al.* 2004; Nielsen *et al.* 2006). The oxidation rate has been doubled with a temperature increase of 12 °C (Nielsen *et al.* 2004). The sulphide oxidation rate in tailings has been investigated at temperatures between 10 and 30 °C, with significant oxidation of tailings observed at 30 °C (Meldrum *et al.* 2001). At lower temperatures, the oxidation rate reduced substantially (Meldrum *et al.* 2001).

Unlike the other elements, the leachate concentration of Zn was, in general, highest at the leaching temperature of 10 °C. This shows that Zn may have a different leaching mechanism. When it comes to the cumulative mass of Co, Fe, Mn and Ni leached out from the tailings, the highest amounts of Co, Fe, Mn and Ni were leached out at 18 °C, and the lowest amounts of

Co, Mn and Ni were leached out at 5 °C. The highest cumulative amount of Zn leached out from tailings was observed at 10 °C. This suggests that 10 °C is the threshold temperature for the leaching of Zn. It is difficult to explain the differences in the leaching of Co and Ni, for example, relative to Zn. It may be the effect of temperature. Another study on the water extractability of Zn from compost waste showed also a different trend with a temperature change to that of Cu, Cd and Pb (Adekunle 2009). The distinct differences in release rates seen in these columns may also be an effect of the differences in water and air flow through the columns, where more sphalerite was exposed to oxidation and Zn transport in the 10 °C column.

The  $\text{SO}_4^{2-}$  concentration was high at the beginning for all temperatures and then dropped by one to two orders of magnitude. This indicates that there were secondary sulphate minerals within the material that dissolved at the beginning, whereas the later leaching rate was due to sulphide oxidation and release of sulphate. XPS also confirmed that the sulphur on the surface was predominantly present as sulphate and, being water-soluble, its amount decreased in all the column samples, revealing unoxidized sulphur at 18 °C. The lower concentration of sulphate in water and the higher amount of sulphur on the surface at lower temperatures indicate a lower sulphide reaction rate, which corresponds to reaction rate studies of pure minerals. The leaching rate at 5 °C was in the range of a quarter to a half of that at the 18 °C temperature setting. However, it also shows that, even at 5 °C, the oxidation of sulphides still occurs. Maintaining the temperature at 5 °C did not prevent sulphide oxidation. The results from another study have also revealed that biotic and abiotic sulphide oxidation proceeded at temperatures as low as –11 °C (Elberling 2005). The overall oxidation of pyrite is temperature-dependent, and both chemical and biological pyrite oxidation rates decrease with decreasing temperatures, as described by the Arrhenius equation (Elberling 2005). Several studies have confirmed that the Arrhenius equation is a valid approximation for the effect of temperature on sulphide oxidation rates (Elberling 2005). The temperature has a great influence on the oxidation rate as its value doubles with every 10 °C increase (Pozo-Antonio 2014).

As a result of the tailings oxidation and leaching of water-soluble species at higher temperatures, the surface became richer with iron minerals. The shift of the Fe 2p XPS peak refers to the fact that the iron in the column samples was to a greater extent in oxidized form, such as ferric silicates and ferric oxides. Dissolution of iron might also result in the precipitation of new iron oxide material on the surface (Schott & Berner 1983) due to oxidative and mild acidic-neutral pH conditions.

## 6. CONCLUSIONS

The oxidation of tailings and the subsequent leaching of sulphate, Co, Fe, Mn, Ni and Zn from the Ballangleira tailings deposit at four different temperatures, i.e. 5 °C, 10, 14 and 18 °C, were investigated in a laboratory column experiment. The conductivity and the leachate concentrations of  $\text{SO}_4^{2-}$ , Co, Fe, Mn and Ni were highest at 14 and 18 °C, and lowest at 5 °C, which indicate higher tailings oxidation and subsequent leaching of contaminants from tailings at higher temperatures. This is consistent with the observation of iron staining in the residual tailings after the leaching experiment, where the column at the leaching temperature of 18 °C showed red-brown staining throughout the column with spots of grey to light brown. High oxidation and leaching of contaminants at 18 °C were also confirmed by XPS analysis. The highest cumulative leached mass of Co, Fe, Mn and Ni was observed at 18 °C. The lowest cumulative masses of Co, Mn and Ni were observed at 5 °C. The highest cumulative mass of Zn leached out was observed at 10 °C. It seems that 10 °C is the threshold temperature for the leaching of Zn. Thus, temperature has an important impact on the leaching of contaminants from tailings deposits. Increased global temperatures due to climate change may, therefore, result in a greater release of metals from sulphide-containing mine waste material in the future.

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## DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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