



# Article Impact of Variability in Precipitation Patterns on the Geochemistry of Pyritic Uranium Tailings Rehabilitated with Saturated Cover Technology

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**Abstract:** Increasing variability in precipitation patterns is expected to result from climate change in Canada. This effect has the potential to affect the performances of saturated covers in inhibiting acid rock drainage (ARD) and metal leaching (ML) processes. Because ARD and ML may cause the release of deleterious chemical species into the environment, such climate-change-driven impact was investigated using trickle leach columns. The physical, chemical, and mineralogical characteristics of the tailings as well as chemical composition of the leachate were measured before and after the column study. Results from the experiment showed that higher variability in precipitation regimes could enhance leaching of uranium. Leaching ranged from 67.1 to 90.1% of the total amount of U, with greater values associated with higher variability in precipitation patterns. Lower water levels and prolonged drought periods led to higher oxygen fluxes to the U tailings and dissolution of carbonate-bearing minerals. The release of carbonates could have enhanced uranium leaching through the formation of stable uranium-carbonate complexes in solution. Overall, this study shows that water level variation caused by varying precipitation patterns can significantly affect the drainage chemistry of saturated cover systems for which the level fluctuates freely near the tailings–cover interface.

**Keywords:** acid rock drainage; metal leaching; saturated cover; climate change; uranium; mining residue; trickle leach column

# 1. Introduction

Sound management of potentially acid-generating mine wastes typically involves the implementation of preventive methods based on the exclusion of at least one parameter responsible for the formation of acid rock drainage (ARD) (water barrier, oxygen barrier and sulfur removal) and/or the reduction in factors that cause increased acidity production rate (neutralization or bacterial activity reduction) [1].

Water covers, a type of oxygen barrier, are common in temperate climatic regions of Canada and northern US, where climatic and topographic conditions are often favorable for underwater disposal of mining waste and for providing and maintaining a cover of suitable depth [2]. The ability of water covers to prevent ARD is primarily based on the low gas permeability and the poor solubility of gaseous oxygen in water. Although the efficiency of water covers is well accepted in the scientific community [3–5], one of the biggest challenges for this technology is to ensure the perpetual physical stability of the containment structures and consequently prevent spills from happening [6]. Physical stability is particularly precarious in northern environments, where freezing and thawing, thermal expansion and ice crystals formation in pore space can lead to erosion and subsequent weakening of the dams.



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**Copyright:** © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). In comparison, saturated covers are often considered as "second generation" water covers. This method involves raising the water table in a non-reactive cover material layer above the waste, either by modifying the water balance on site or by increasing the water retention capacity of the reactive wastes. Only a few sites in Canada have been rehabilitated using the saturated cover configuration, with most of these sites being left inactive and exposed for many years prior to their decommissioning. Among these sites are the Snip Gold mine tailings site (British Columbia), the Manitou tailings site (Quebec) as well as the Stanrock and Lower William Lake (LWL) Tailings Management Areas (TMAs), both located in the Elliot Lake (Ontario) region. Because the water level is raised within the cover material, the saturated water method does not present free surface water, and therefore does not require above-ground containment structures that pose a risk from a physical stability perspective. However, this method has features that make it sensitive to certain climate-change-driven impacts [7].

Numerous studies have demonstrated that the water level is one of the most critical parameters to ensure the effectiveness of the raised water table method [8–10]. As such, greater variation in the water table level caused by a change in the distribution and amount of precipitation, as well as longer drought periods, can reduce the saturation level of the reactive tailings, thereby also reducing the performance of saturated cover in preventing ARD [7]. Both phenomena are expected to become more frequent with climate change. According to Ouangrawa, to prevent oxidation of the sulfidic geological material, the depth of the water table from the waste–cover interface should be no less than half of the air entry value (AEV) of the reactive wastes [11].

Increased evaporation resulting from higher temperatures and prolonged drought periods also has a significant impact on the elevated water table method's efficiency in limiting the oxygen fluxes to the reactive wastes [12–14]. Evaporation leads to the desiccation of the cover material and reactive wastes and can therefore affect the water level. This is particularly true in the case of coarser granulometry. Recent modeling work demonstrated that, in addition to water table level, material properties and cover thickness can also greatly influence how the elevated water table cover method will perform when exposed to a small increase in precipitation combined with a significant increase in temperature [15].

A decrease in water table can lead to increased oxygen flux, which would result in the partially saturated tailing been more oxidized. Oxidation conditions could subsequently affect the mobility of redox sensitive species contained in the reactive material [13]. The main redox sensitive species in uranium mine tailings are iron, sulfur and uranium. Once released in the drainage,  $Fe^{3+}$  and  $SO_4^{2-}$  may precipitate as secondary minerals. The formation of an iron oxyhydroxide and/or hydroxysulfate layer (e.g., jarosite for a pH comprised between 1 and 2 and goethite for a pH above 2) may particularly affect the mobility of these ions as well as other dissolved species because this so-called "indurated layer" tends to cement the tailings' pores, thereby limiting the oxidation of the reactive particles and the diffusion of oxygen passing through the tailings [16,17].

Uranium is also a redox species of interest since significant amounts of U are typically contained in gold and uranium tailings [2]. The mobility of U is highly dependent on its oxidation state [18,19]. Uranium released from treated effluent in water and accumulated in sediment can be chemically toxic [20–22] to aquatic organisms and generate radioactive progenies such as Ra-226 and Po-210 [23,24], when accumulated over decades [25].

Although U tailings can contain appreciable amounts of thorium, the leaching of the latter is generally less of an issue because its mobility is very limited for most natural pH-Eh conditions [26,27]. Indeed, the strongness of Th-O liaisons (854 kJ/mol) explains the low solubility of thorium oxides [28]. Nonetheless, the presence of carbonates for pH > 4.5 proved to increase the solubility of this radioelement via the formation of  $Th(OH)_Y(CO_3)_Z^{4-Y-2Z}$  complexes [29].

Previous work investigating the performances of water covers showed that subaqueous storage of potentially acid-generating U tailings is an effective way to prevent U and Th mobilization [30–32]. Dissolved species profiles at these sites showed minor remobilization of U in the shallow zones, but progressively increasing concentrations with depth [31,32]. As expected, for these sites, the mobility of U is believed to be governed by the formation of stable dissolved U(VI)-carbonate complexes in equilibrium with its solid state [33]. Consequently, the increasing concentration of  $HCO_3^-$  in the porewater moderated by carbonate minerals, which are affected by pH variations was reported to increase U mobilization [34]. A geochemical investigation conducted at the Rio Algom Quirke cell TMA, where pyritic U tailings are kept under a shallow water cover, also demonstrated that the flooding of preoxidized tailings can lead to an initial important release of uranium from the tailings to the water column [35].

While some research has been conducted on water covers [30–35], there is a lack of data with respect to the mobility of U from sites containing pyritic tailings rehabilitated using the saturated cover method. Furthermore, to date, no study has been undertaken to evaluate the impact of climate-change-driven impacts, in particular water level fluctuations, on the behavior of uranium redox-sensitive species. Consequently, the purpose of this study is to investigate the performances of the saturated cover method subjected to variable precipitation patterns with respect to the mobility of uranium.

#### 2. Materials and Methods

# 2.1. Mineralogical and Physicochemical Characterization of U Tailings

#### 2.1.1. Tailings and Cover Material

Tailings were collected at a decommissioned U mine located in the Elliot Lake area (ON, Canada). The design of this experiment was based on the physico-chemical and hydrogeological characteristics observed at the LWL site, which was partially rehabilitated using the elevated water table method coupled with a monolayer cover following an accidental spill of uranium mine tailings in the 1950s. However, because the LWL site could not be accessed and sampled, tailings from another nearby decommissioned U mine were used instead.

Multiple core and bulk samples were obtained from the BHP Billiton (BHP) mine TMA, and were stored in a dry state. Before starting the study, tailings were manually homogenized, and later divided into 1 kg fractions using a sample divider (PT100, scientific ATS).

At the LWL site, the cover material is described as being composed of a mixture of coarse sand, gravel, till and organic debris, and does not appear to contribute significantly to oxygen consumption [36].

Silica (Unimin Canada LTD) was used in the current study to replace the abovedescribed cover material. The silica was grinded (Bico pulverizer MFD, Bico Inc., Burbank, United States) until a sandy soil texture was obtained and separated into equal fractions using the sample divider.

## 2.1.2. Physical Characterization

Particle size distribution of the cover material was determined using a series of square mesh sieves, ranging from 45 to 850 µm coupled with a vibrating sieve (Performer III ss-3, Gilson company, Lewis Center, OH, USA, 3600 vibrations per minute for 15 min). Tailings' granulometry was determined by laser diffraction (Horiba, Partica LA-950V2, Kioto, Japan).

The tailings' specific density of solid grains  $\rho_s$  was calculated using a gas pycnometer (Ultrapyc 1200e, Quantachrome Instruments, Boynton Beach, United States). Nitrogen was used as displacement medium in the expansion chamber. To obtain  $\rho_s$ , the mass of the sample introduced in the pycnometer was divided by the volume of the sample measured by the pycnometer. The porosity *n* was obtained from  $\rho_s$ , as per Equation (1) [37].

$$n = 1 - \frac{\rho_d}{\rho_s} \tag{1}$$

where  $\rho_d$  is the dry density of the sample, which was determined by establishing the ratio between the mass of the sample dried at 105 °C and its total volume in the wet state.

# 2.1.3. Mineralogy

The BHP tailings were selected for their mineralogical characteristics, similarly to those observed at the area of the LWL site studied in this document (Table 1). X-ray diffraction (XRD) patterns were obtained using a Rigaku D/MAX 2500 rotating anode powder diffractometer (Tokyo, Japan) with monochromatic CuK radiation. The measurement conditions consisted of the following: 2 angular range = 5–70, step size = 0.020, scan speed = 1/min, voltage = 40 kV, amperage = 200 mA. Mineralogical phases were identified using the JADE version 9.3 (Version 9.3, Materials Data, Livermore, United States) coupled with the ICSD and ICDD diffraction database.

Table 1. Comparison between the Lower William Lake and BHP Billiton tailings' mineralogy.

Average pyrite content5.9%5.5%Mineral phases (mass > 1%)Quartz, K-feldspar, albite, muscovite, monazite, Fe-oxyhydroxide, pyrite, chalcopyriteQuartz, muscovite, pyrite, orthoclase, anorthite, albite, calc kaersutite, hematite/magnetite	Mineralogical Characteristics	Lower William Lake (Core Identified as LWL-4-3 M-2) [36]	BHP Tailings
Mineral phases (mass > 1%)    Quartz, K-feldspar, albite, muscovite, monazite, Fe-oxyhydroxide, pyrite, chalcopyrite    Quartz, muscovite, pyrite, orthoclase, anorthite, albite, calc kaersutite, hematite/magnetite      Porocity    52.5%    42.1%	Average pyrite content	5.9%	5.5%
Porocity 52.5% // 12.1%	Mineral phases (mass > 1%)	Quartz, K-feldspar, albite, muscovite, monazite, Fe-oxyhydroxide, pyrite, chalcopyrite	Quartz, muscovite, pyrite, orthoclase, anorthite, albite, calcite, kaersutite, hematite/magnetite
1 0105ity 52.576 42.176	Porosity	52.5%	42.1%

Quantitative mineralogical analysis was carried out using TESCAN Integrated Mineral Analyzer (TIMA, TESCAN, Brno, Czech Republic). The combined backscattered (BSE) and energy dispersive (EDS) signals were applied for the phase identification. BSE signal was calibrated on Pt Faraday cup, while four EDS detectors were calibrated on the Mn standard. The accelerating voltage was 25 kV and the absorbed current was 5 nA.

# 2.1.4. Chemical Characterization

4-acid digestions (HCl, HNO<sub>3</sub>, HF, HClO<sub>4</sub>) were performed on 0.25 g of tailings following the protocol described by SGS [38]. A certified reference material (UTS-4, CANMET, Ottawa, ON, Canada) was also digested to ensure quality control. To achieve proper quantification in diluted digestate solutions, Al, Ba, Cd, Co, Cr, Cu, Pb, and Th were analyzed with an X-Series II ICP-MS (Thermo Fisher Scientific, Waltham, MA), while Al, Ca, Fe, Mg, Mn, Ni et U were analyzed using a 725 ICP-OES (Agilent Technologies, Santa Clara, CA, USA). Sample dilutions were performed with 2% HCl (Fisher Chemical, Trace Metal Grade) for ICP-MS and 4% HNO<sub>3</sub> (Fisher Chemical, Trace Metal Grade) for ICP-OES. An induction furnace (Eltra CS-2000) was used to measure total S and C in tailings.

## 2.2. Column Study

# 2.2.1. Static Testing

The Acidification Potential (AP) and Neutralization Potential (NP) of the BHP tailings were quantified using the Sobek et al. method [39] and the modified Sobek method by Lawrence and Wang [40] following protocols described in Price [41]. The net neutralization potential (NNP) was obtained using Equation (2) [39].

$$NNP = NP - AP \tag{2}$$

### 2.2.2. Column Set-Up

Eight cylindrical acrylic columns (height = 29 cm, internal diameter = 10 cm, wall thickness = 0.06 cm) were used for this study.

A total of 3 scenarios were tested, in duplicate, at ambient temperature: (1) the reference scenario, based on projected rainfall forecasts for the years 2085; (2) low variability of precipitation pattern; and (3) high variability in precipitation patterns. The last two of the eight columns consisted of the control and blank.

Except for the blank, each column was filled with 1 kg of dry BHP tailings. The blank column was left completely empty for the entire study. A piece of geotextile was placed under the tailings, on a perforated plate, to prevent the loss of material into the column's

double bottom, which served as a sampling reservoir. Tailings were first saturated with distilled water from the bottom to the top, to limit the occurrence of preferential channels (Figure 1).



Figure 1. Visual representation of the experimental set-up and initial saturation of the tailings.

After primary consolidation of the saturated tailings, 50 mL of a bacterial culture was poured on the upper surface of the tailings to simulate field conditions. This bacterial culture was prepared using tailings from the BHP decommissioned tailings, using the method described in McCready [42]. Each column was finally filled with an additional 1650 g of silica, except from the control column, where tailings were left exposed to the atmosphere.

The water level, controlled using a bottle connected to the bottom of each column, was initially raised until it slightly exceeded the interface between the cover material and the atmosphere. After 24 h, the columns were drained, and the leachate was analyzed for analytes of interest. To ensure proper consolidation of the solid materials, the columns were then left as is for 7 days prior to initiating the first wetting–draining cycle.

# 2.2.3. Predicted Climate Change Conditions

The volumes of distilled water to be added to each column are based on historical climate data, adjusted to reflect the predictions related to climate change in the LWL region. To do so, the ClimateWNA program (CFCG, 2014), which incorporates predictive climate change models to historical data for a given location, was used using the approximate coordinates of the site under study (46.4970894, -82.6289732). Numerous predictive models were tested (CanESM2\_rcp45; CanESM2\_rcp85; CNRM-CM5-rcp26; CNRM-CM5-rcp45; CNRM-CM5-rcp45; HadGEM2-ES\_rcp45). The CanESM2\_rcp85 model was ultimately chosen to establish the site reference conditions. Table 2 presents a comparative table of historical and model-projected mean precipitation for the years 2025, 2055 and 2085.

Table 2 shows that for the LWL site, climate change could lead to a marked increase in annual precipitation, in particular during the spring, fall and winter months. The forecast associated with the year 2085 was chosen to create the reference conditions for the column tests.

Each week, a predefined amount of distilled water was added to each column from the top, to simulate rainfall. Distilled water was preferred over synthetic rainwater in order to prevent any impact of rainwater alkalinity on drainage water. After 5 days of contact time, sampling was initiated by allowing the columns to drain freely for approximately 8 h. Weekly drainage collection was performed by inserting a quick disconnect hose barb insert into a coupling body, screwed into each double bottom of the columns.

	Average Precipitation (mm)				
Time Period	Annual	Winter	Spring	Summer	Fall
1961–1990	910	177	225	263	245
2025	936 (+2.9%)	195	221	248	272
2055	961 (+5.5%)	199	244	230	288
2085	960 (+5.5%)	215	250	190	305

**Table 2.** Historical and projected average precipitations for the years 1961–1990, 2025, 2055 and 2085 obtained using the CanESM2\_rcp85 model.

Table 3 presents the amount of water added to the different series of column on a cyclic basis, as well as the ratios between weekly and total precipitation volumes for each scenario tested. Cycles were repeated every three weeks for the entire 30 weeks of this study. Although the entire study is set to last longer, this paper only discusses the initial 10 precipitation cycles (30 weeks).

**Table 3.** Distilled water added to each set of columns as precipitation, and associated ratios between weekly and total (cyclic) volumes of added water (in parenthesis).

Time Period	Column 1 and 2 * Reference Scenario	Column 3 and 4 * Low Rainfall Variability	Column 5 and 6 * High Rainfall Variability	Control	Blank
Week 1	145 mL (0.33)	64 mL (0.15)	0 mL (0)	145 mL (0.33)	145 mL (0.33)
Week 2	145 mL (0.33)	145 mL (0.33)	113 mL (0.26)	145 mL (0.33)	145 mL (0.33)
Week 3	145 mL (0.33)	226 mL (0.52)	322 mL (0.74)	145 mL (0.33)	145 mL (0.33)
Total—per cycle (mL)	435 mL (1)	435 mL (1)	435 mL (1)	435 mL (1)	435 mL (1)

\* Column experiment were performed in duplicate.

The volumes of water to be added on a weekly basis to columns 1 and 2 (reference scenario), 7 (control) and 8 (method blank) were obtained by dividing the projected 2085 annual rainfall by 52, and then multiplying this value by the cross-sectional area of the column. No weekly variation in precipitation was simulated for these scenarios. On the other hand, as highlighted in Table 3, some precipitation pattern variability was included in the low and high variability scenarios.

#### 2.2.4. Leachate Analysis

Samples were collected in 200 mL High Density Polyethylene containers, soaked for 12 h in 10% HNO<sub>3</sub> and rinsed with distilled water beforehand. Using a pipette, each sample was separated into three aliquots. The first aliquot, intended for the analysis of the metals and radionuclides of interest by ICP-OES and ICP-MS, was filtered (Whatman, 0.45  $\mu$ m) and acidified with concentrated nitric acid until a pH lower than 2 was reached. A pH meter (Oakton PD 450, Metex Corporation Limited, Toronto, ON, Canada) was used to validate the reaching of this condition. The second aliquot, intended for the analysis of sulfate by ion chromatography, was also filtered (Whatman, 0.45  $\mu$ m), but not acidified. The remaining fraction was used as is for the measurement of pH, redox potential and conductivity. Samples collected for the analysis of metals, radionuclides and sulfates were stored for up to one week in a refrigerator at a temperature of approximately 4 degrees Celsius.

# 3. Results and Discussion

# 3.1. Characterization of BHP Tailings

The tailings' granulometric curve, presented in Figure 2, shows that particles are relatively coarse, having a loamy-sand texture.



Figure 2. Average particle size distribution of BHP tailings, in duplicate (n = 2).

Figure 3 shows the mineral phases identified by X-ray diffraction, and Table 4 presents the results obtained via modal analysis with the TIMA. The mineralogy is consistent with the chemical composition of the tailings, which is presented in Table 5.



**Figure 3.** XRD patterns for BHP tailings, the mineral formulae correspond to the reference phases from the databases ICSD and ICDD and do not necessarily represent the sample phases' exact chemical composition.

Mineral	Weight (wt% of the Phase)	Mineral	Weight (wt% of the Phase)
	55.9	Uraninite	0.29
Quartz Amphibole	9.7	Monazite	0.26
Orthoclase	4.7	Ilmenite	0.10
Muscovite	4.7	Pentlandite	0.08
Pyrite	4.6	Chalcopyrite	0.08
Anorthite	3.5	Zircon	0.07
Plagioclase	2.8	Anhydrite	0.06
Pyrrhotite	1.7	Apatite	0.05
Enstatite-(Fe)	1.0	Titanite	0.04
Albite	1.0	Allanite-(Ce)	0.03
Hematite/magnetite	0.64	Baryte	0.02
Calcite	0.41	Dolomite	0.02
Ankerite	0.34	Biotite	0.01
Ferrosaponite	0.33	Jacobsite	0.01
Rutile	0.32	Other	7.3

Table 4. Mineral phases quantified by TESCAN Integrated Mineral Analyzer (TIMA) analysis.

Table 5. Element concentrations measured in the BHP tailings.

Elements	Average Concentration
Majo	or elements (%)
Mg	$0.43\pm0.04$
Ca	$0.13\pm0.05$
Fe	$3.06\pm0.00$
Si	$31.81\pm0.81$
S (total)	$2.26\pm0.01$
C (total)	$0.16\pm0.00$
C (inorg)	$0.16\pm0.00$
Minor	elements (mg/kg)
Mn	$111.2 \pm 17.3$
Ni	$161.8\pm11.6$
Th	$122.1\pm4.9$
U	$378.0 \pm 19.1$
Sc	$4.8\pm0.3$
Y	$18.9\pm1.6$
La	$201.5\pm13.3$
Ce	$645.0\pm74.7$
Pr	$64.9\pm7.2$
Nd	$205.3\pm22.9$
Sm	$28.5\pm2.9$
Eu	$1.3\pm0.1$
Gd	$15.1 \pm 1.5$
Tb	$1.3\pm0.1$
Dy	$4.6\pm0.3$
Но	$0.6\pm0.0$
Er	$1.1\pm0.2$
Tm	$0.2\pm0.0$
Yb	$1.0\pm0.1$
Lu	$0.1\pm0.0$

Mineralogical characterization shows that the tailings are mainly composed of plagioclase feldspar minerals, amphiboles, mica, pyrite. Typical of these minerals, the diffraction pattern obtained via XRD shows a busy pattern, which makes it difficult to identify with certainty the various mineral phases. The results obtained are nevertheless consistent with those obtained with TIMA. This second mineralogical approach helped quantify the different mineral phases, showing a predominance for quartz, amphibole, orthoclase, muscovite and pyrite. Sulfur is mainly found in the form of pyrite, pyrrhotite, chalcopyrite, pentlandite, anhydrite and baryte.

Table 5 shows that significant amounts of uranium and thorium are still present in the tailings, equivalent to 378 mg/kg U and 122 mg/kg Th, respectively. In the literature, slightly different values were measured for pyritic uranium mine tailings. At Mary Kathleen mine, in Australia, concentrations between 7.2 and 42.7 mg U/kg and 133 to 257 mg Th/kg were measured [43], while for the Denison mine, which is located in the Elliot Lake region in Ontario, these values were approximately 67.1 mg U/kg and 204 mg Th/kg [44]. Another study performed with tailings from the Quirke Waste Management Area, also located in Elliot Lake, showed much lowered uranium concentrations, equivalent to 25 mg/kg [30].

Table 5 also shows that a significant portion of uranium is present as uraninite (0.29%). However, it should be pointed out that there are uncertainties on the modal proportion given by the TIMA related to sampling (homogeneity) and unideal polishing quality of specific small areas, pores and cracks of minerals, and grain boundaries analyses which comprise the "unclassified" line in Table 4. Considering the above-mentioned factors, it is possible that the uraninite proportion differs from the previously mentioned value. Figure 4 nonetheless presents some images of typical uraninite occurrences observed via backscattered electrons. Due to their chemical similarities to Rare Earth Elements (REEs), U and Th could also be present in REE-bearing minerals (e.g., monazite) through lattice substitution. A portion of these cations could also be adsorbed by iron and/or manganese oxides (such as hematite/magnetite, as identified in Table 4), which could have precipitated as secondary minerals in the TMA or as a result of sample transport and handling.



Figure 4. Typical uraninite occurrences observed via BSE in the BHP tailings samples.

Based on the acid-base accounting results, BHP tailings were classified as acid generating, since the PN/PA ratios obtained using the Sobek and Lawrence and Wang methods both showed values well below 1. Additionally, the neutralization potential of the carbonates ranged between 5.66 and 7.08. This implies that the tailings have good buffering capacities resulting from the strong reactivity of carbonates in acidic conditions.

# 3.2. Leachate Analysis

As mentioned previously, the leachate pH, oxidoreduction potential (ORP) and electrical conductivity (EC), as well as the major and minor element concentrations were monitored once a week.

# 3.2.1. pH, ORP and EC

pH measurements remained around circumneutral values (ranging from 6.5 to 7.5) during the entire study for all tested scenarios (Figure 5). pH range measured indicate that the entire study took place during the initial phase of acid mine drainage, when the neutralizing minerals (carbonate-, silicate- and hydroxide-bearing minerals) are not yet fully depleted and are in sufficient quantity to buffer the acidity produced by the oxidation of sulfur. This pH behavior is consistent with other column studies performed on acid-generating tailings. Indeed, multiple months and sometimes years can be necessary before a decrease in pH is observed for the leachate [13,41].



Figure 5. pH evolution for all tested scenario over the 30 weeks (10 cycles) of the experiment.

Decreasing ORP values were observed during the initial 4 weeks for all tested scenarios, although at different rates (Figure 6). These values then stabilized around weakly oxidizing values for the reference and low variability scenarios, and weakly oxidizing values for the high variability and control column. In another column experiment investigating saturated covers, slightly higher ORP values were observed for the entire experiment, in the range of 325–425 mV depending on height of the water table level. However, these higher values were generally higher because of the different frequencies at which the water was added and drained.

Finally, in regard to EC, values increased significantly for all scenarios, at variable rates, indicating mineral solubilization.

## 3.2.2. Leaching of Uranium

Figure 7 shows the cumulative amount of uranium extracted as a function of time. The results are presented on a cycle-basis, as cumulated mass extracted, to simplify comparison between the different scenarios tested despite the variability between the amount of water added between the different sets of columns.



Figure 6. ORP evolution for all tested scenario over the 30 weeks (10 cycles) of the experiment.



**Figure 7.** Cumulated mass of U collected in the leachate for each tested scenario. For the reference, low variability and high variability scenarios, results correspond to the average cumulated masses of the duplicates. Next to each curve is indicated the final cumulated mass of U extracted, expressed as percentage of total U in the pristine tailings.

Figure 7 shows that the columns associated with the highest variability scenario generated the greatest uranium leaching, followed by the low variability scenario, the control scenario, and the reference scenario. These results confirm that the variability in precipitation regimes has a significant influence on the quality of drainage water.

However, the significant quantity of U leached (with a leaching yield ranging from 61.7% to 90.1%) was unexpected, since uranium tends to form refractory oxides that are typically poorly soluble, and the mineralogical analysis had demonstrated that U was at least partially present as uraninite (UO<sub>2</sub>). Although it was demonstrated that the flooding of preoxidized tailings could cause an initial release of a significant amount of uranium to the water column, leaching yields are typically more in the range of a few %, and sometimes even less than a percent [35]. In a similar column study conducted using uranium mine

tailings from the Elliot Lake region, for example, the concentration in uranium in the leachate was under the detection limit (0.6 mg/L) for the entire column study, despite the tailings containing a significant amount of U [45].

The use of distilled water to simulate precipitations, rather than synthetic rainwater, could have artificially increased the leaching yields for U. Indeed, it is possible that the low ionic strength of the distilled water favors the dissolution of U into the pore water solution, thus leading to greater leaching yield of the elements contained in the tailings. However, it should be noted that this behavior was not as significant for other investigated refractory elements. Indeed, for La and Ce, the cumulative mass leached reached less than 3% of the total amount in the pristine tailings after 9 weeks, while for uranium, about one third of the total U had already been leached by that time. Similarly, the amount of leached Fe was often under the limit of detection despite the significant Fe content present in the tailings. Fe is further discussed in Section 3.2.5 below.

Another hypothesis would be that greater oxygen flux to the tailings associated with increasing variability in precipitation regime would cause an increasing dissolution of carbonate-bearing minerals. The carbonate therefore released would form very stable soluble complexes in solution.  $(UO_2)_2(OH)_3CO_3^-$  ( $log \ \beta_n = -18.63$ ),  $UO_2CO_3$  ( $log \ \beta_n = 9.68$ ),  $UO_2(CO_3)_2^{2-}$  ( $log \ \beta_n = 16.9$ ) and  $UO_2(CO_3)_3^{4-}$  ( $log \ \beta_n = 21.6$ ) [46,47], in particular, show the highest stability constants with  $UO_2^{2+}$ , higher than those of sulfates, nitrates and chlorides [19,46]. This hypothesis was further studied by analyzing the leaching behavior of carbonate-bearing minerals.

## 3.2.3. Carbonate Leaching

Mineralogical analysis showed that the tailings host multiple carbonate-bearing minerals. Such minerals have an intrinsic neutralizing potential, greater than hydroxides and silicates. According to Blowes and Ptacek, the relative reactivity of carbonates would follow the following order: Calcite > Dolomite > Ankerite > Siderite [48]. If silica-based mineral phases are excluded from Table 4, calcite, ankerite and dolomite can result in significant amounts of carbonates.

Other sources of carbonates are also present in the tailings but are associated with silicate minerals. Considering the low solubility of silicates at near-neutral pH, it is less likely that calcium-bearing silicates will release carbonates and then participate in the neutralization process. Given the rapid dissolution rate of calcite, sufficient to maintain quasi-equilibrium conditions and buffer the pH of pore waters, it is likely that this mineral played a major role in buffering drainage waters and mobilizing uranium.

Post-experiment mineralogy work confirmed the hypothesis stated above. Table 6 presents a summary of the main mineral phases identified in the tailings before and after the 10 precipitation cycles (30 weeks).

Uraninite was observed in the pristine tailings at a concentration of 0.3 wt%. However, in the leached sample uraninite could not be found by manual investigation, liberal analysis nor bright particle analysis.

Calcite, present at 0.4 wt% in the pristine sample, also appears to be entirely leached. Apatite and anhydrite also decreased, suggesting that these carbonate-bearing minerals were also partially leached.

Monazite, zircon, allanite, and pentlandite were found in the pristine and leached samples at concentrations suggesting that they were relatively not affected by the leaching process. The relative increase in the concentration of these mineral phases in the leached samples could be partially attributable to the dissolution of other minerals, as well as sampling heterogeneity.

Minerals	Pristine Tailings (wt% of the Phase)	Leached Tailings (wt% of the Phase)
Quartz	55.9	62.6
Amphibole	9.7	7.6
Orthoclase	4.7	3.9
Muscovite	4.7	5.0
Pyrite	4.6	4.7
Anorthite	3.5	2.0
Plagioclase	2.8	1.7
Pyrrhotite	1.7	0.9
Enstatite-(Fe)	1.0	0.8
Albite	1.0	0.8
Hematite/Magnetite	0.64	0.59
Calcite	0.41	0.00
Ankerite	0.34	0.21
Ferrosaponite	0.33	0.19
Rutile	0.32	0.30
Uraninite	0.29	0.00
Monazite	0.26	0.44
Ilmenite	0.10	0.09
Chalcopyrite	0.08	0.04
Pentlandite	0.08	0.26
Zircon	0.07	0.12
Anhydrite	0.06	0.01
Apatite	0.05	0.02
Titanite	0.04	0.02
Allanite-(Ce)	0.03	0.05
Baryte	0.02	0.05
Dolomite	0.02	0.00
Biotite	0.01	0.01
Jacobsite	0.01	0.02
Unclassified	7.3	7.5
Total	100.0	100.0

**Table 6.** Mineral phases quantified pre and post experiment by TESCAN Integrated Mineral Analyzer (TIMA) analysis.

## 3.2.4. Leaching of Thorium

Concentrations below the detection limit  $(2.7 \,\mu g/L)$  in the leachate were observed for Thorium. However, this result was expected, since Th is known to be relatively immobile and poorly influenced by redox changes, unlike U. The possibility that Th was not measured in the samples due to its adsorption on the sampling containers was nonetheless investigated. To do so, random samples were collected in Nalgene bottles containing enough concentrated nitric acid so that the final sample would have a HNO<sub>3</sub> concentration of at least 3 moles per liter. Despite the very acidic conditions, concentrations below the detection limit were observed regardless of the precipitation scenario and sampling week. This suggests that Th was either not solubilized or was adsorbed on iron, aluminum and/or manganese oxides that formed inside the columns. Indeed, Fe, Al and Mn oxides have the potential to adsorb metals and radionuclides via their OH functional groups, which can develop pH dependent variable charges. Even in small quantities, these oxides can play a critical role in geochemical processes due to their high reactivity [41].

## 3.2.5. Dissolution of Iron Sulfide Minerals

Over the course of the experiment, minimal iron levels, frequently below the ICP-OES detection limit (0.23 mg/L), were measured in the leachate. Nonetheless, Table 6 highlights that a significant portion of pyrrhotite was solubilized. The elevated sulfate contents measured in the leachate, depicted on Figure 8, also confirm that iron solubilization took place. Indeed, by performing a mass balance, it was found that even if barite and anhydrite



(the only two sulfide minerals that do not contain iron) were entirely solubilized, sulfate contents would not have reached those observed levels, ranging above 7000 mg.

**Figure 8.** Cumulated mass of  $SO_4^{2-}$  collected in the leachate for each tested scenario. For the reference, low variability and high variability scenarios, results correspond to the average cumulated masses of the duplicates. Next to each curve is indicated the final cumulated mass of sulfate extracted, expressed as percentage of total sulfate in the pristine tailings.

These results suggest that most of the solubilized Fe could have precipitated in the form of Fe oxide, inside the column itself. Visual observations made at the end of the study also pointed in this direction, as an orange layer formed at the tailings–cover interface in all columns. This layer, likely composed of secondary oxidation products such as goethite, jarosite or ferrihydrite, was significantly thicker in the control column. Due to the absence of a cover on its tailings, the control scenario was the most oxygenated scenario.

The prominence of this layer in the control column could explain why this scenario did not leach as much U as the low or high variability scenarios despite of its higher oxygen flux reaching the tailings. Indeed, tailings' reactivity can be reduced by the formation of an indurated layer, which can fill and cement the particles' pores. As mentioned above, secondary minerals such as iron hydroxides, also have the potential to influence the drainage geochemistry via co-precipitation and/or adsorption. As such, it is also possible that a greater quantity of U was solubilized in the control column, but that this element was immobilized in the indurated layer. To validate this hypothesis, the mineralogy and chemical composition of this layer should be investigated; however, this was not evaluated as part of the current study because the column experiment was pursued and sampling the indurated layer could have greatly disturbed the system.

# 3.2.6. Precipitation Patterns and Oxygen Flux

The results presented above show that greater variability in precipitation patterns can have an impact on contaminant loadings in the drainage waters. An explanation could be that a greater variability in precipitation patterns would periodically bring low water levels, subsequently leading to increasing oxygen fluxes available for tailings oxidation. The coarseness of the cover material is insufficient in preventing oxygen diffusion when the water level is below its lower interface, since the water content of the cover material remains close to its residual water content in this configuration. This was validated using a volumetric water content probe installed in the cover material (Decagon 5TM). Water levels below the tailings–cover interface were observed periodically for the low variability scenario (every first week of each cycle) and high variability scenario (every second week of each cycle).

Additionally, prolonged drought periods can lead to increased evaporation and subsequent desiccation of cover material and tailings. A prolonged drought period was imposed periodically to the high variability scenario (every first week of each cycle). Ultimately, observed changes in oxygen availability caused by precipitation pattern variability resulted in greater oxidation of the tailings, which enhanced U mobilization, a redox sensitive species.

Finally, it should be emphasized that this study greatly simplified field conditions. Indeed, to better isolate the consequences of increasing precipitation pattern variability, this study incorporated numerous simplifications (e.g., no temperature/seasonal variation, utilization of distilled water rather than natural or synthetic rainwater, no snow cover, etc.). As such, the obtained results do not provide accurate prediction of the future drainage chemistry, as the field parameters listed above could significantly influence reaction kinetic. This is a common challenge experienced with column studies. Nonetheless, the obtained results can provide useful information on mineral weathering as well as secondary mineral precipitation.

## 4. Conclusions

To date, no study has been undertaken to evaluate the impact of climate-change-driven water level fluctuations on the behavior of redox-sensitive species for sites rehabilitated using the saturated cover method. The fate of uranium, in particular, should be of prime interest as most of the sites currently rehabilitated using this technique host uranium-bearing tailings. Consequently, the purpose of the current study was to investigate the performances of the saturated cover method with respect to uranium mobility and precipitation pattern (and therefore water level) variability.

The current study showed that saturated cover systems for which the water level fluctuates freely near the tailings–cover interface could be sensitive to an increase in precipitation patterns variability. Indeed, such phenomenon could enhance the mobility of uranium from the reactive tailings to the pore water and subsequently to the drainage water. A total of three scenarios were tested in this laboratory scale column study: a reference scenario, based on projected rainfall forecasts for the years 2085; a low variability of precipitation pattern scenario; a high variability in precipitation patterns scenario. Uranium leaching yield ranging from 67.1 to 90.1% were observed over the first 30 weeks of the experiment, with greater values associated with higher variability in precipitation pattern. A mineralogical investigation showed that these very high leaching yields could be at least partially explained by carbonate-bearing mineral dissolution, and subsequent carbonate released, which would have formed very stable soluble U-CO<sub>3</sub><sup>2-</sup> complexes in solution.

In addition to this, it is believed that the fluctuation of the water level caused by the variability of the precipitation regimes generated redox changes in the pore water, which favored the dissolution of uranium redox-sensitive species. To validate this hypothesis, it would be interesting to investigate the leaching of other redox-sensitive species to verify whether their mobilization is also influenced by the variability of precipitation regimes and episodes of drought in the same way as for uranium. The use of thermodynamic modeling could also be a promising avenue to answer the questions raised during the leach column tests, in particular as it relates to the leaching of uranium and predicting the fate of other deleterious species.

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