Role of saturated covers as oxygen buffers in cold climates

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1. Introduction

There are numerous environmental ramifications caused by mine waste produced by mineral resource extraction (Pétel, 2017). Tailings in this paper's context refer to ore residue, which is the material left over from extracting the metal of interest from all other uneconomic material (Aubertin et al., 2009). Acid mine drainage (AMD) is a harmful byproduct of tailings. AMD occurs when sulfidic mine tailings react with water and oxygen to produce leachate, which is characterized by acidity, sulfates, and heavy metals (Ouangrawa, 2007). The equation to describe this reaction is summarized in equation 1:

Equation 1: Sulfidic mineral + O2 + H2O => Acidity (H^+) + Sulfate (SO_4^{2-}) + Me(Z^+)

In Canada, the preferred method of acid mine drainage reduction involves the use of oxygen barriers in the form of soil covers, aqueous covers, or saturated covers. Soil covers, also known as capillary effect barrier covers, limit both water and oxygen from reaching tailings by covering them with multi-layered soils that promote water retention. While this type of cover is effective in limiting the supply of oxygen and water from reaching tailings, it is not feasible in northern environments due to the lack of naturally occurring organic soil horizon present (Mbonimpa et al., 2011).

An aqueous cover involves excess pond water covering a tailings dam. Using water as an oxygen buffer is considered one of the best remediation methods for reactive tailings, and its efficiency is based on the maximum threshold for oxygen saturation within water being over thirty times less than in atmospheric conditions. However, water covers are best suited for climates with little to no extreme temperature fluctuations (Ouangrawa, 2007). The subarctic climate of Northern Canada, characterized by frequent freezing and thawing conditions, makes tailing dams more vulnerable to infrastructure failure due to the expansion and contraction of water as it freezes and melts (Mbonimpa et al., 2011).

To address this issue, this report explores a hybrid-applied solution: the use of saturated covers, which involve lifting an elevated water table into a tailing impoundment that maintains saturation within the tailing profile without allowing excess water directly along the surface of the embankment. The objective of this project is to evaluate the efficacy of saturated covers in Northern regions by testing oxygen diffusion in a series of experiments with two levels of saturation using an instrumented column. While there has been some research detailing the beneficial use of saturated covers, such as in the *Oxygen diffusion in saturated covers methodology and literature review* (Gagne Turcotte et al., 2020) completed prior to this lab scale study, the methodology used within this study relied heavily on prediction variables/models: De and Kr, but these proved to be more complicated than expected (Gagne Turcotte et al., 2020). Additionally, mine tailings by nature are rather unique and each sample of tailings has its own unique characteristics that need to be accounted for. Thus, the creation of this methodology occurred, with a specific emphasis on applied methods.

2. Materials and methods

This report presents the results of two sets of experiments focusing on the diffusion of oxygen into saturated covers. Two set-ups were investigated and will be referred to as set-up #1 and set-up #2, in the following document.

2.1. Cover material

To observe the effects of freeze and thaw in oxygen saturation in a saturated cover, without any additional variables introduced by unpredictable tailing material, the physical properties of real tailings, including material size, were mimicked in the two set-ups. Inert material was used instead of real tailings because real tailings are highly reactive which may interfere with the analysis of oxygen diffusion in this experiment (Gagne Turcotte et al. 2020). Using inert materials limits the introduction of additional chemical variables in oxygen diffusion.

In set-up #1, the cover material (silt to fine sand) was sourced from Long Lake, Whitehorse YT (60.74356°N 135.04684°W). The granulometry was controlled using a sieve ranging from 65 - 125 um to mimic tailing granulometry (Paralta 1997).

In set-up #2, synthetic silica flour (0.7 mm particle size, or 70 um) was used for the cover material in the column. The change of material was motivated by the limited access to the cover material used in set-up #1.

2.2. Column set-up

The column (figure 1 had a height of 71.1 cm and an inner diameter of 13.8 cm). The base and top of the column had a detachable lid and base plate, attached to the column using twelve detachable bolts. The top and bottom detachable pieces had holes drilled into the middle, where tubing was attached using a plastic bolt. In set-up #2, the tubing attached to the top of the column connected the column to a flowmeter for oxygen (99% pure) control. The tubing at the base of the column was closed off using a three-way-gas valve at the end.

The inside of the column was split into two compartments. The top section of the column was 44.1 cm from the top, and the bottom compartment was 27 cm from the base. These two compartments were separated by a circular piece of puck board with eight drainage holes, held up by four, 26 cm, 63 mm - PVC pipes. This inner shelf, creating the base compartment, was insulated with fiber glass to keep inert material out of the bottom section of the column, but still allow water and gas movement.

A small hole was created at the very base of the column using a ¼ inch drill bit, and 2m of Easy Heat Electric Roof De-icing Cable heat wire was pulled through the hole, into the bottom section of the column. The hole was then sealed off using marine epoxy. On the side of the column (at the base) opposite to where the hole for the heat wire was drilled, a circular hole was drilled and threaded to allow for the oxygen probe to be embedded into the wall of the column.

The three probes that recorded both temperature and unfrozen volumetric water were also embedded into the column at three different areas above the base-puck board compartment to further monitor temperature. The first temperature probe was 11 cm from the top, the second was 22 cm, and the third was 33 cm from the top of the column.

Six 3D pieces were designed to embed the temperature probes in the column, to reduce water from leaking from the columns, and to prevent damaging the temperature probes as much as possible. They were designed using Blender (Blender Foundation 2022). A hole the size of the body of the temperature probe was drilled into the three locations using a ¼ drill bit and a heated hand saw. A cm to the left and right, parallel to the column, two holes were drilled to hold a 3D printed piece inside and outside the column. Two pieces of two” rubber roof vent flashing cut outs were used to line the 3D parts pressed against the column; these were sealed using an ethylene-vinyl acetate (EVA) copolymer. The wire end of the 3D part on the outside, was sealed off using dental rubber dam, kneaded eraser, and construction grade sheathing tape.

One column was used throughout the entire experiment.

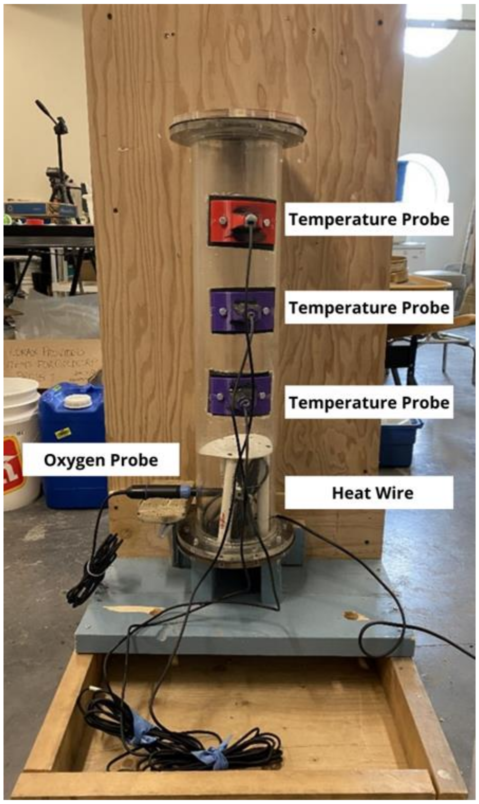


Figure 1. Instrumented column set-up with three temperature probes, and an oxygen probe wrapped in heat wire at the base.

2.3. Methods

2.3.1. Oxygen Probe Calibration and Oxygen Gas Set Up

The oxygen probe was calibrated the same way in each experiment. The dissolved oxygen probe was calibrated at 100% using oxygen saturated water, and at 0% using nitrogen purged water. For the 100% oxygen calibration, the methodology in the Oakton 420 dissolved oxygen operation instruction manual (Oakton 2022) was followed. The probe, fixed inside the base of the instrumented column, was covered with enough deionized (DI) water to submerge the oxygen probe (26 cm from the base). The DI water was then saturated with oxygen using 95% oxygen injected at the base of the column at a flow rate of 5L per minute, using tubing, and the calibration was done once the reading stabilized.

The 0% oxygen calibration was done in an equivalent manner, but instead of using 95% oxygen, Nitrogen was used to create a zero-oxygen calibration. Nitrogen gas was used to aerate the DI water for a minimum of 30 minutes, as recommended by standard procedure outlined by other gas-based calibration experiments (Bang et al. 2005, Sair et al. 2001 & Newby et al. 2005) until the reading stabilized. The 5TM probes and dissolved oxygen probe were set to record data every 10 mins. Every time the column was set up for an experiment, the sealed column was purged of oxygen using the 3-way valve at the base, with nitrogen until reaching a 0% measurement (calibration 0%) in the entire column to ensure the column was free of oxygen prior to starting a freeze and thaw cycle.

After calibration was completed:

- Set-up #1: 15L of pure oxygen (> 99%), measured using an oxygen regulator that output oxygen in liters per minute, was added to the top of the column. Another 15L of pure oxygen was added later in the column (before thawing, see later for details). The two additions of pure oxygen were chosen because lab testing indicated that this volume consistently allowed for 100% saturation in an empty column. 15L is also more than the total inner volume of the column.
- Set-up #2: A constant flow of oxygen was attached to the top of the column at a flow rate of 2.5 ml/min. The flowrate was set up to allow for the column to freeze without significantly altering the pressure within the column.

The second set-up was designed to better fit the needs of the industrial partners. A schematic of the two experimental set-ups is presented in figure 2.

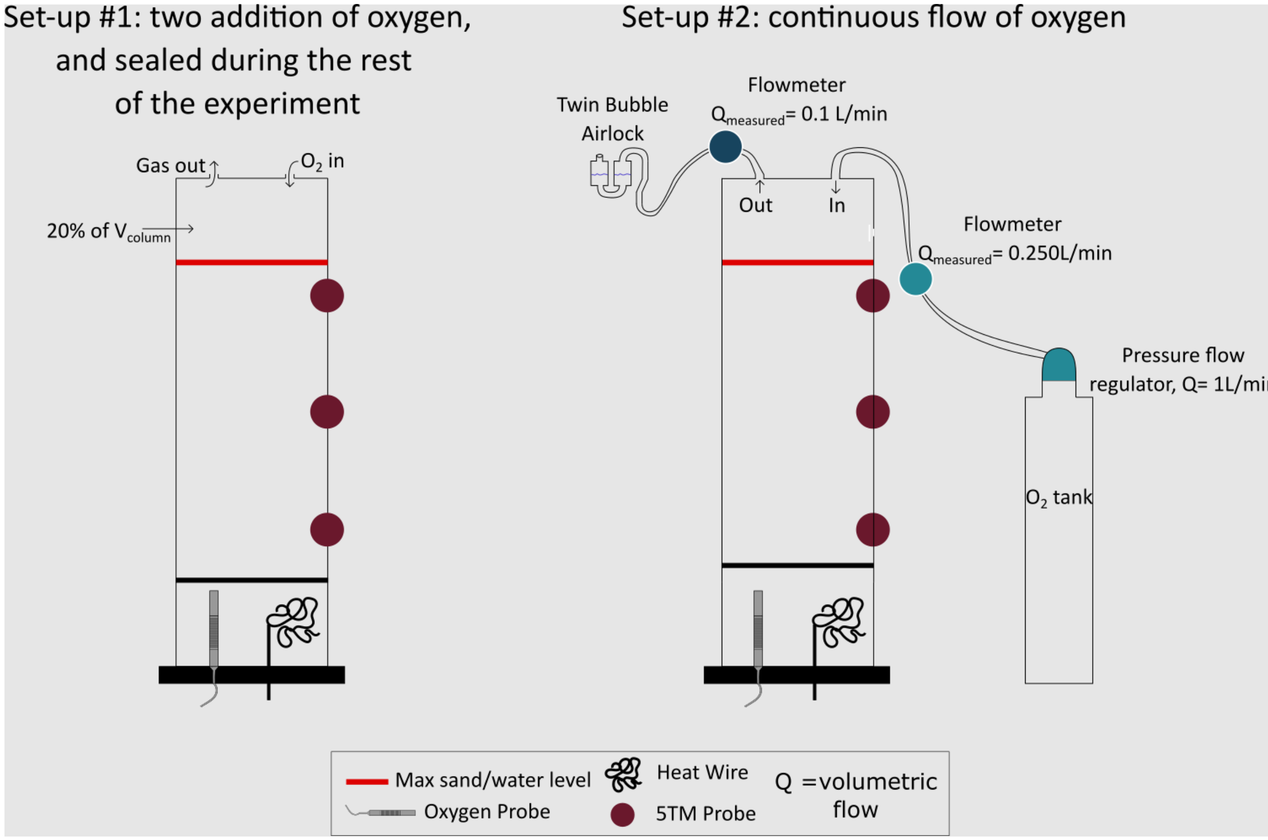


Figure 2. Schematic of the two experimental set-ups.

2.3.2. Experimental Conditions

For the two set-ups, there were three controls as shown in figure 3: an empty column, a column filled with DI water and a column filled with inert material. There were two water saturation levels: high level saturation (all inert material fully saturated), and a mid-level saturation (half of the inert material saturated).

In set-up #1, all these columns were subject to one freeze-thaw cycle. The experiment started when the first oxygen addition was performed, and the column was placed inside the freezer. When the column was frozen, the column was removed from the freezer, the second addition of oxygen was occurring, and the column was placed at ambient temperature. The time of the experiment was only dependent on the time it took to freeze and thaw the material present inside the column.

In set-up #2, all these columns were subject to separate temperature conditions for a given time (120h or 5 days). The experiment's time was based on the amount of oxygen consumed and the time it took to saturate the oxygen probe (16 mg/L) in the empty column at ambient temperature. The diffusion of oxygen saturation was evaluated in ambient conditions (120h at approx. 25°C), thawing conditions (columns is frozen, and then the oxygen is attached to the column when it is undergoing thawing – 120h with temperature going from -15°C to +20°C), and in freezing conditions (120h at approx. -20°C).

In the rest of the document, when set-up #1 or set-up #2 is not specified, it means that the experiment was performed similarly with both set-ups.

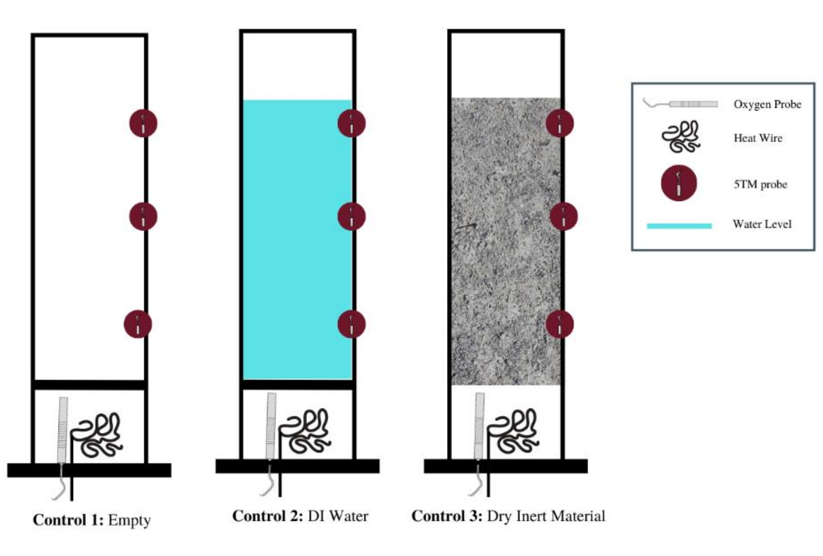


Figure 3. Controls schematic.

2.3.3. Control One: Empty column

The next three sections will discuss the controls performed to assess the oxygen diffusion through the mediums (water, air, and inert material), used in the actual experiments (mid-level water saturation and high-level water saturation). In the first control, the entire column was empty (aside from the DI water covering the oxygen probe, figure 5). The calibration and oxygen inputs were done following section 2.3.1.

Figure 4. Empty column at ambient temperature.

2.3.4. Control Two: Water filled column

This control was used to see the rate and quantity of oxygen saturation in a column filled with just DI water. The top section of the column was filled with DI water, filled to reach 62 cm from its base (figure 5). The calibration and oxygen inputs were done following section 2.3.1.

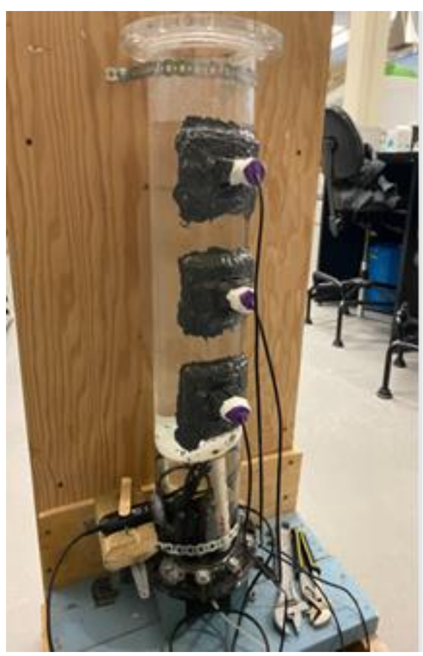


Figure 5. Control two at ambient temperature.

2.3.5. Control Three: Dry inert material column

This control was used to see the rate and quantity of oxygen saturation in a column filled with just inert material. The column was filled with inert material, until the three temperature probes were covered. No DI water was added into this control (aside from the DI water covering the oxygen probe, figure 6). The calibration and oxygen inputs were done following section 2.3.1.

Figure 6. Control three at ambient temperature.

2.3.6. Mid-water saturation

The following two sections describe the setup of the two saturation levels, the unsuccessful mid-water saturated column, and the successful fully saturated column. In this section, the setup of the first saturation level is discussed; inert material saturated with water to the halfway point in the column (figure 7). Half saturation was added to the saturation levels to examine whether the results observed in the fully saturated column were conditional upon the level of saturation or just the presence of some saturated media.

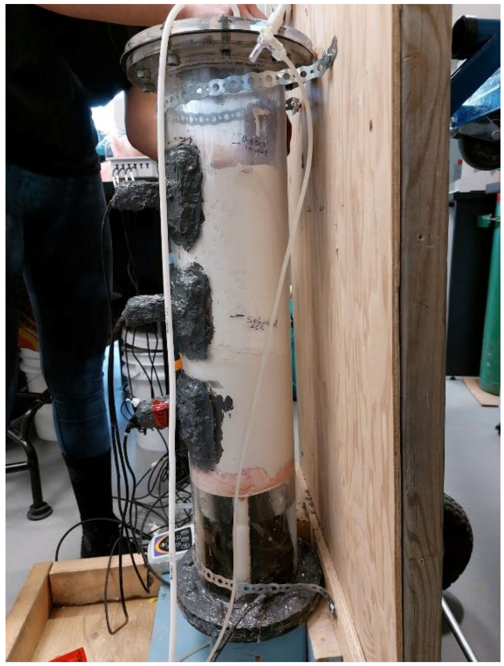


Figure 7. Mid-level water column at ambient temperature.

There were a few different methods attempted when trying to create a column where only half of the inert material in the column was saturated, and the remaining was left dry. This was difficult due to capillary action carrying the DI water up the sides of the column, whilst leaving the center dry.

For set-up #1: To uniformly saturate half of the inert material, the column was filled halfway with inert material, it was saturated (with 6L of water), then, the rest of the column was filled with dry inert material until the three temperature probes were covered. After this point, the column lid was affixed, and nitrogen was attached to the base to allow the nitrogen purge to occur. The remainder of the calibration and oxygen inputs were done following section 2.3.1.

For set-up #2: There were numerous different methodology versions attempted to create a successful mid-level saturation column, including the one presented for set-up #1. Unfortunately, we were not able to develop a packing method that allows us to obtain stable material undisturbed by the continuous flow of oxygen. One of the key issues was the appearance of consistent gaping between column material and column walls observed in midwater saturation (figure 8). The bottom half of the inert material was set up to be saturated, while the top half remained dry. Between the 24-hour and 48-hour mark, something occurred that caused the dry material at the top of the column and some areas in the saturated part of the column to pull away from the column walls. This separation, as preferential pathway, caused major spikes in oxygen saturation, and inaccurately portrayed saturation results in mid-level saturated inert material. A few trials were run, with increased saturation gradients, with lower flow rate, with slower packing, and longer column rest time (trials up from a day of rest up to a week of rest time before starting the experiment), still, the column did not behave appropriately. This issue was observed to be occurring within the mid-level water saturation set up as well as the water filled control in thawing conditions and may have been due to material contraction occurring as excess water in the saturated portion of the column was absorbed into the dry material at the top.

Figure 8. Mid-level saturation.

2.3.7. High-water saturation

This section looks at the setup of the second saturation level; all inert material saturated with water. Water saturated inert material (2:1), was added until all three temperature probes were covered (figure 9). The rest of the calibration and oxygen inputs were done following section 2.3.1.

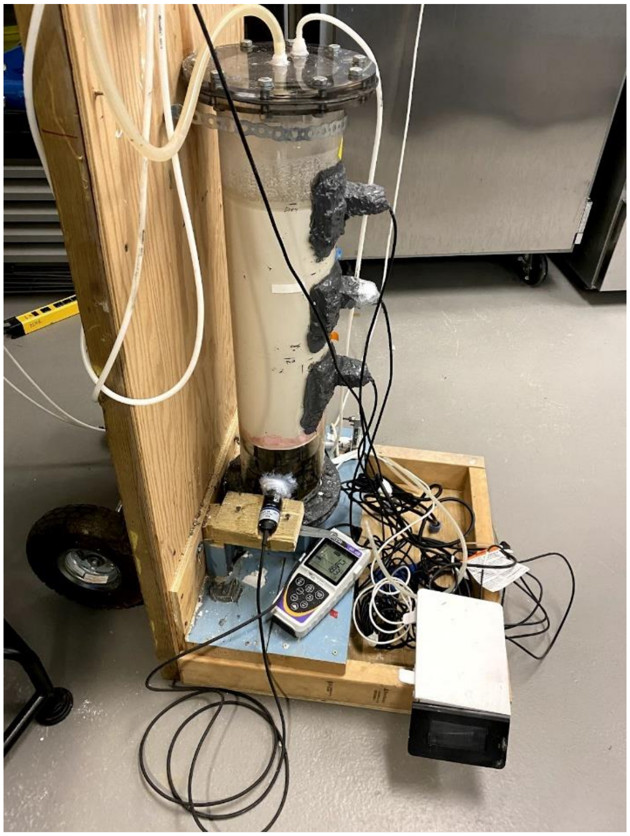


Figure 9. High-level water column at ambient temperature.

A schematic of the various levels of water saturation is presented in figure 10.

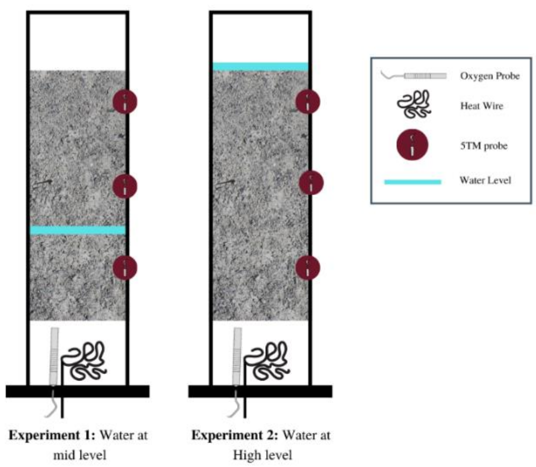


Figure 10. Mid-level water and high-level water schematic.

3. Results for set-up #1

3.1. Control One: Empty Column

The results obtained for control one, the empty column, presented in Figure 11 displays the oxygen concentration (mg/L), at the bottom of the column, as a function of time. The temperature is plotted on the secondary y-axis, as a function of time. The temperature plotted corresponds to an average of the three temperatures measured by the 5TM temperature probes inside the column and does not correspond to the temperature inside the freezer that was fixed at -20°C. The two-oxygen addition is plotted as black lines on the charts. The second black line corresponds to the column being placed at ambient temperature. For set-up #1, the data are presented similarly in this report.

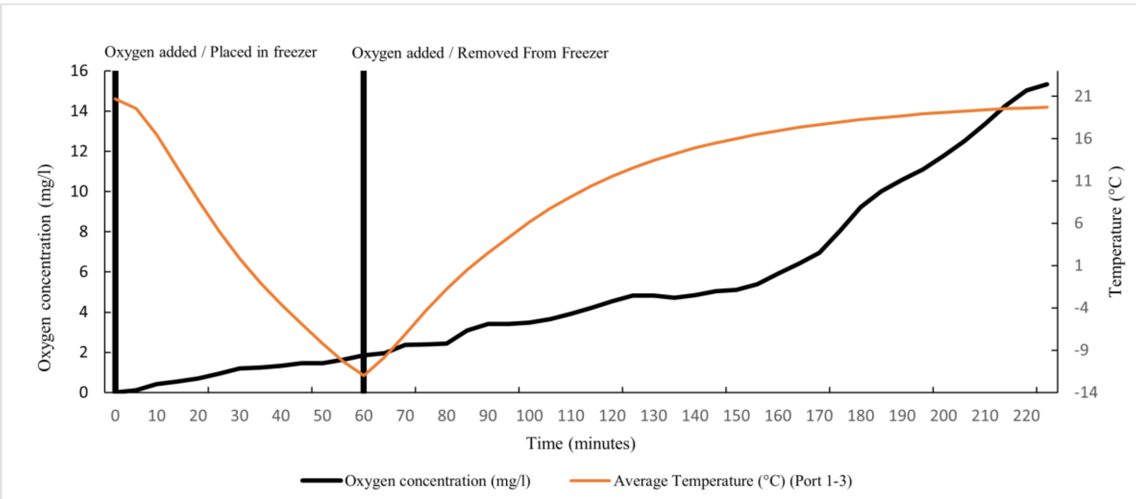


Figure 11. Oxygen concentration (mg/L) and temperature (°C) as a function of time in control one (empty column) for a full freeze-thaw cycle.

The freeze and thaw cycle for control one started at a temperature of 20.7°C and oxygen concentration of 0 mg/L. The column was injected with 15L of oxygen and placed in the freezer at the start of the experiment. The oxygen concentration increased steadily to 1.9 mg/L as the temperature declined to the freezing point at -12°C. At this point, an additional 15L of oxygen was added, and the column was removed from the freezer. During the thaw of the column, the temperature increased until reaching ~20°C, and an oxygen concentration of 15 mg/L. The increase in oxygen concentration was relatively steady over the first 170 minutes of the experiment. From 170 minutes to the end of the experiment (225 minutes), which corresponds to temperatures superior to 16°C, the slope increased, highlighting the importance of the highest temperatures in favouring greater oxygen diffusions. In an empty column, with two additions of pure oxygen at ambient temperature, the length of the experiment was 3h45 hours (225 minutes).

3.2. Control Two: water-filled column

The results obtained for control two, the water-filled column, are presented in Figure 12.

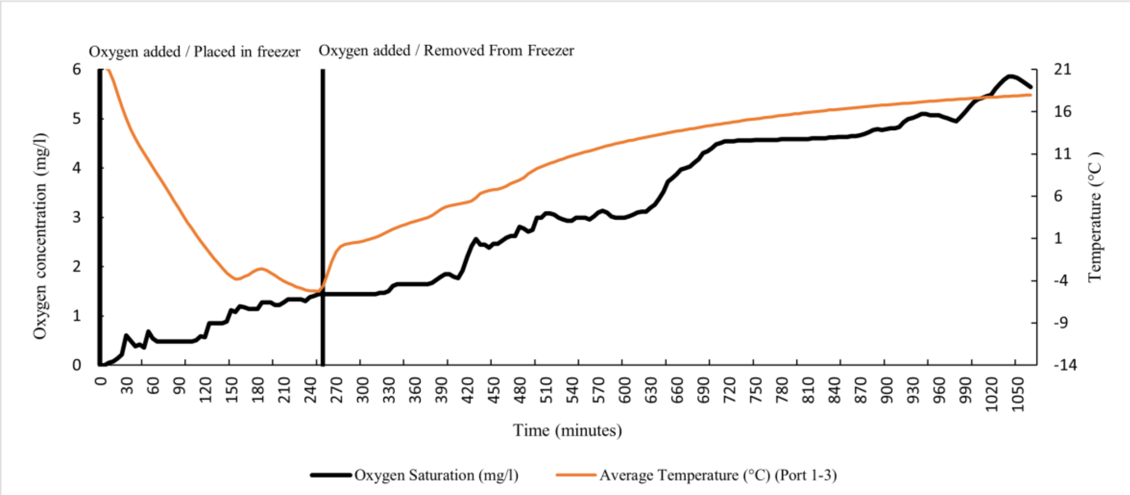


Figure 12. Oxygen concentration (mg/L) and temperature (°C) as a function of time in control two (water filled column) for a full freeze-thaw cycle.

The start of the freeze and thaw cycle for control two started at a temperature of 21°C and oxygen concentration of 0 mg/L. The column was injected with 15L of oxygen and placed in the freezer at the start of the experiment. The oxygen saturation increased as the temperature declined to the freezing point at -5°C. At this point an additional 15L of oxygen was added, and the column was removed from the freezer. During the thaw of the column, the temperature steadily increased until reaching ~20°C, and an oxygen concentration of 6 mg/L. The concentration in oxygen measured at the end of the freeze-thaw cycle is more than twice lower than the one measured in the empty column (control one), even though the length of this experiment was longer (1080 minutes vs 225 minutes in control one). This observation is in agreement with the literature review and the lower coefficient of diffusion of oxygen in water compared to air. From minutes 240 to 330, which likely corresponds to the water being fully frozen inside the column, the increase in oxygen concentration at the bottom of the column stopped. This result was expected since a full body of frozen water will leave no air space for oxygen to diffuse. Except for this interruption, the concentration of oxygen increased relatively steadily over time.

The water-filled control took longer than the empty column (18 hours vs. 3.45 hours) to complete the freeze and thaw cycle. More specifically, the freezing time was 4 times longer and the thawing part 4.25 times longer than in the empty column. This is due to the presence of water in the column. The large body of water present in the column took longer to freeze due to the lower freezing point of water. It is also possible that the heating wire at the base of the column (used to keep the oxygen probe at room temperature) influenced the temperature of the water in the column. Contrary to control one, where above 16°C the concentration of oxygen increased faster, no specific change had been observed in the speed of oxygen diffusion above this temperature.

3.3. Control Three Data

The results obtained for control three, the inert material filled column, are presented in Figure 13.

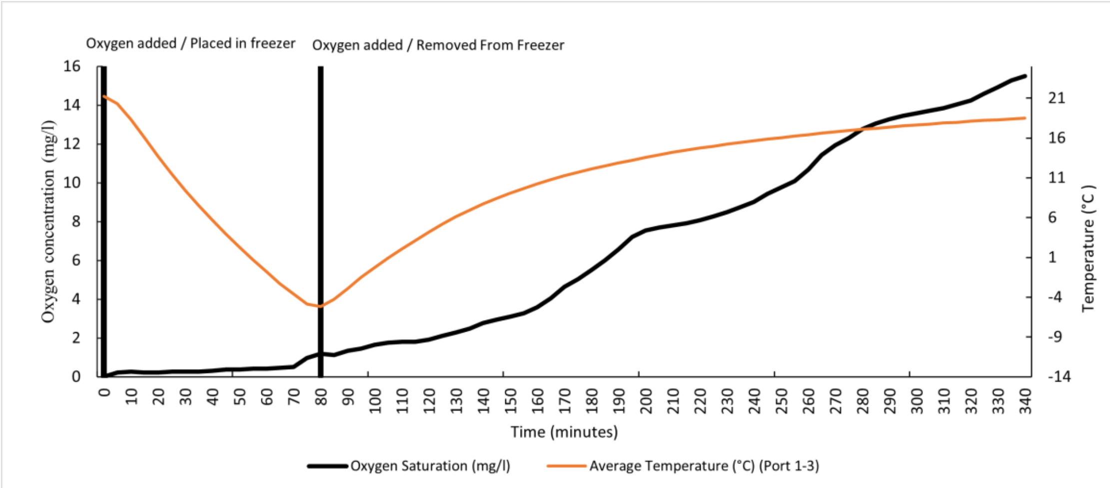


Figure 13. Oxygen concentration (mg/L) and temperature (^oC) as a function of time in control three (dry inert material) for a full freeze-thaw cycle.

The start of the freeze and thaw cycle for control three started at a temperature of 21^oC and oxygen concentration of 0 mg/L. The column was injected with 15L of oxygen and placed in the freezer at the start of the experiment. The oxygen saturation increased steadily up to 1.7 mg/L as the temperature declined to the freezing point at -5.2^oC. At this point, an additional 15L of oxygen was added, and the column was removed from the freezer. During the thaw of the column, the temperature steadily increased for 5.45 hours until reaching ~20^oC, and an oxygen concentration of 16 mg/L, a value similar to the one measured in the empty column. The increase in oxygen concentration at the base of the column in the freezing part of the freeze-thaw cycle was steady but slower than in the thawing part. This result highlights the role of temperature in the diffusion of oxygen.

The length of the freeze-thaw cycle is comprised between control one (3.45h) and control 2 (18h) with 5.45h. The time to freeze the column was 80 min, really similar to the one in control one (60 min). This small difference is likely due to the higher amount of material present in the control with the inert material compared to the empty column.

3.4. Discussion on controls' results

Control one (empty) and three (dry inert material) reached 15 mg/L and 16 mg/L respectively, by the end of the freeze-thaw cycle, despite the difference in time to complete one freeze-thaw cycle between the two controls (3h45 vs. 5h45). This is an indication that even though the presence of dry inert material impacts the freezing and thawing length, and thus the diffusion of oxygen (longer time to reach similar values), it does not strongly inhibit oxygen diffusion, and do not prevent to reach similar concentration than in an empty column.

The increase in oxygen concentration at the bottom of the column in control two reached only 6 mg/L, compared to the 15-16 mg/L in the two other controls. This validates the observation of previous studies showing the capacity of water to limit oxygen diffusion, due mostly to the lower coefficient of diffusion for oxygen in water.

The increase in oxygen concentration in control two presented oscillations not presented in the other controls. This might be due to the freezing point of DI water, the interference of the heat wire at the base of the column and/or the variable refrigerant cycle in the freezer used.

Interestingly, the lowest temperature reached inside the column is lower in the empty column compared to the two other controls (-12.5°C vs. approx. -5°C). This difference is likely due to the presence of water and inert material in control two and three that have different thermal properties (higher heat capacity for example) than air.

Finally, all three control reached around ~1.5 mg/L oxygen concentration at the coldest temperature measured in the experiment (independently of the time it took to reach this temperature), indicating that oxygen diffuse during the freezing period, but in all case at lower speed (smaller increase in oxygen concentration) than during the thawing period, which is coherent with the smaller diffusion of oxygen at lower temperature (in both air and water).

3.5. Water at Mid-Level Results

The results obtained for the column with water at mid-level are presented in Figure 14.

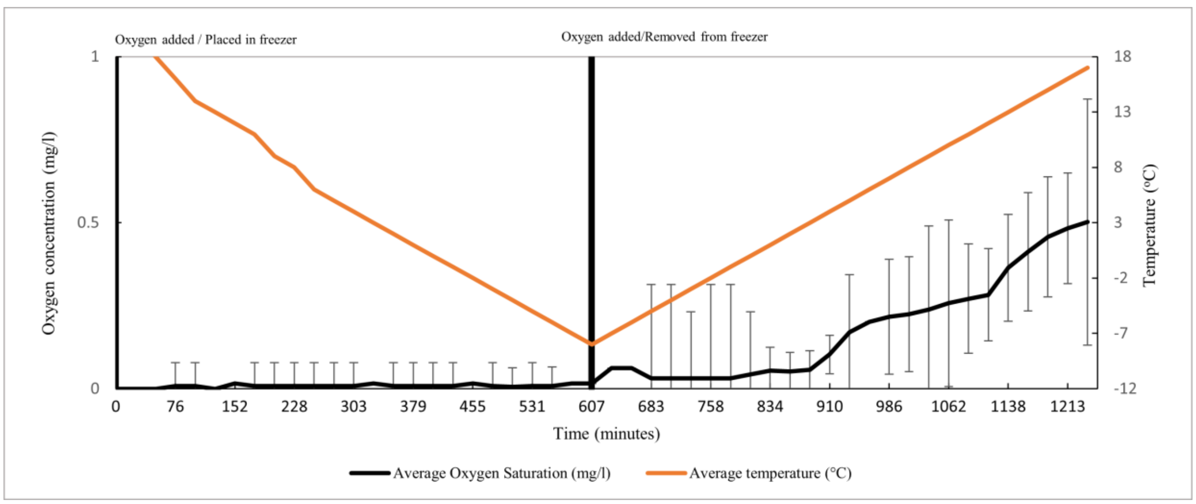


Figure 14. Oxygen concentration (mg/L) and temperature (°C) as a function of time for water at mid-level experiment for a full freeze-thaw cycle.

The freeze and thaw cycle for the saturated column with water at mid-level started at a temperature of 21°C and oxygen concentration of 0 mg/L. The column was injected with 15L of oxygen and placed in the freezer at the start of the experiment. The oxygen concentration fluctuated between 0 and 0.02 mg/L from the start of the experiment until the freezing point at –8°C after 430 minutes (7h). Upon reaching -8°C, an additional 15L of oxygen was added, and the column was removed from the freezer.

After the second oxygen injection, there was a jump in saturation going from 0.02 to 0.06 mg/L from -8°C to -5°C. This jump may have been due to the movement caused by the pressure change from the oxygen injection. After the slight jump, the oxygen saturation went back down to 0.02 mg/L. During the remaining thaw of the column, the temperature steadily increased up to around

17 ^{o}C, and the oxygen concentration increased to 0.5 mg/L. The increase in oxygen was not steady, with two notable jumps in oxygen concentration, from 4^{o}C to 5^{o}C, the oxygen concentration increased from 0.06 to 0.17 mg/L, and from 12^{o}C to 16^{o}C it increased from 0.28 to 0.36 mg/L. The overall length of the experiment is 1250 minutes (20h50), with the length of the freezing and thawing being relatively similar (610 and 640 minutes). It is interesting to note here that the length of the experiment is relatively similar to control 2 (18h), showing the role of water in controlling length of freeze-thaw cycles.

Another characteristic of note, seen in Figure 15, was the pocket of ice that formed as a divide between the saturation point and the remainder of the dry inert material. This ice pocket appeared in each replicate of the mid-level water column. This ice pocket is referred to as ice lenses in literature and corresponds to the formation of ice structures in soil systems, or similar systems. During freezing, negative pore-water pressures are created when water transitions from liquid to solid and promotes water movement toward the freezing front. The formation of the freezing front favours the formation of these ice lenses. These ice lenses occurred in the direction of least resistance, so usually upward, as observed here. The formation of ice lenses results in large volume expansion in soil, or here the saturated cover, called frost heaves. Systems made of silty to sandy particles, such as here, are most sensitive to the formation of ice lenses, and subsequently to the formation of frost heave (Nyameogo et al., 2020, Mend 1.61.5c). The formation of frost heaves could limit the utilization of saturated covers in the north, as it has been observed before (Mend 1.61.5c) and need to be considered in the design and utilization of saturated covers.

Compared to the control, the concentration of oxygen at the freezing point (0.02 mg/L) was significantly inferior (approx. 1.5 mg/L in the controls). The final concentration in oxygen after the freeze-thaw cycle was also largely inferior to the controls with a concentration of 0.5 mg/L versus 15-16 mg/L for controls one and two and 6 mg/L for control two.

The result of this experiment with mid-water level indicated a good ability of the saturated cover to limit oxygen diffusion compared to the controls: reduction by 97% compared to control one and two, and a reduction of 91.5% compared to control two. The diffusion of oxygen was largely smaller during the freezing phase of the experiment than during the thawing phase, and smaller than in the three controls. However, diffusion of oxygen during the freezing phase of the cycle was occurring since we observed a small increase in oxygen concentration at the bottom of the column.

Figure 15. Ice pocket between the saturation point and dry inert material.

3.6. Water at High-Level Results

The results obtained for the column with water at high-level are presented in Figure 16.

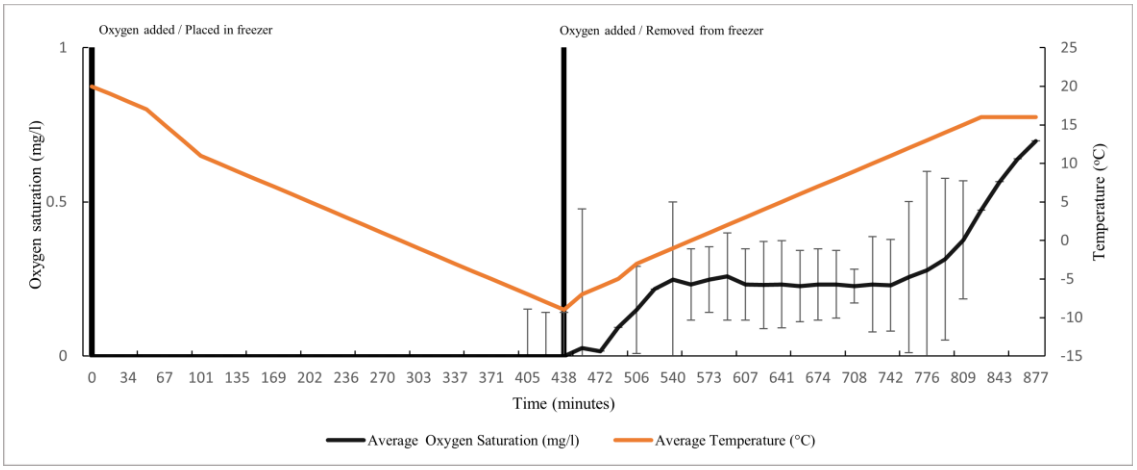


Figure 16. Oxygen concentration (mg/L) and temperature (^oC) as a function of time for water at high-level experiment for a full freeze-thaw cycle.

The start of the freeze and thaw cycle for the saturated column with DI water at high-level, started at a temperature of 20^{o}C and oxygen concentration of 0 mg/L. The column was injected with 15L of oxygen and placed in the freezer at the start of the experiment. The oxygen concentration remained at 0 mg/L until –6^{o}C, with a slight increase to 0.01 mg/L at the freezing point at -9^{o}C. Upon reaching -9^{o}C, an additional 15L of oxygen was added, and the column was removed from the freezer.

As seen in the mid-water level oxygen saturation, there was also a jump in oxygen concentration in the data around the same time the second oxygen injection was administered. There was a slight jump from 0.01 mg/L at -6^{o}C to 0.02 mg/L at -7^{o}C, back down to 0.01 mg/L at -8^{o}C. Then, the oxygen concentration jumped from 0.01 mg/L up to 0.26 mg/L at -1^{o}C. There are a few things that may have caused this jump: a pressure shift caused by the oxygen injection, a shift in saturated material caused by the thaw or a pressure shift caused by the refrigerant cycle in the freezer. From 0^{o}C to 8^{o}C, the oxygen saturation remained at 0.2 mg/L, before steadily increasing to 0.7 mg/L by the end of the thaw. When the temperature in the column reached 10°C, the increase in oxygen concentration was faster than before. This was also observed in the mid-saturated experiment, with a change in the slope of the oxygen concentration function of the time curve at approx. 10°C. This temperature value may thus correspond to a threshold in saturated cover, in these experimental conditions.

The oxygen concentration measured in control two (the water column) after the freeze and thaw, was 6 mg/L, and the final oxygen concentration monitored in control three (the dry inert material column) after the freeze and thaw, was 16 mg/L. With half of the inert material saturated (mid-level water), the oxygen concentration after the freeze and thaw cycle was 0.50 mg/L. For full saturation of inert material (high-level water), the oxygen concentration after the freeze and thaw was 0.7 mg/L. Similar oxygen concentration were measured at the freezing point for mid-level (0.02 mg/L) and high-level (0.01 mg/L).

Interestingly, for the first 440 minutes, and until reaching -5°C, the concentration of oxygen in the high-level water experiment stayed at 0 mg/L, while for the mid-level water experiment, the concentration of oxygen started to increase highly in the first 76 minutes. While the start in oxygen concentration increase is later in the high-level water experiment, the final concentration of oxygen reached after the freeze and thaw cycle is higher than in the mid-level water experiment. In addition, the time needed to reach 0.7 mg/L in the high-water level experiment is shorter (880 minutes) than the time needed to reach 0.5 mg/L in the mid-level water experiment (1250 minutes). Overall, these results seem to indicate that the high-water level would be more efficient during the freezing period to completely stop the diffusion of oxygen, while the mid-water level would be more efficient to slow down oxygen diffusion during thawing. The degree of saturation of systems similar to saturated cover is known to be a critical parameter in controlling the diffusion of oxygen, and thus more studies focusing on water-level and freeze-thaw cycles are needed (Bussières et al., 2007, Demers et al., 2009).

Similar to the mid-level saturation, high-level saturation of the inert material showed promising results in term of oxygen diffusion limitation, since the concentration in oxygen at the bottom of the column at the end of the experiment was smaller by 96.5% compared to controls one and three and 89% for control two. The time it took to freeze the high-water level experiment is similar to the time it took to thaw, similarly to what was observed in mid-level water experiment. Interestingly, while mid-water level presented higher length of experiment compared to the three controls, the experiment at high-water level is shorter by approx. 200 minutes than control two and approx. 400 minutes for mid-water level experiment.

It is to note, finally, that in both saturation levels, the concentration in oxygen rose faster during the thawing period, which could result in interaction between oxygen and the tailings, and thus acid mine drainage.

4. Results for set-up #2

4.1. Control 1, empty column, function of ambient, thaw, freeze conditions.

Figure 17 illustrates the results of oxygen concentration evolution in an empty column in ambient, thawing, and freezing conditions. Full oxygen concentration occurred the fastest in ambient conditions, then in thawing conditions, with the slowest being in frozen conditions. Specifically, full column concentration (15 mg/l) occurred at hour 42 in ambient conditions, at hour 49 in thawing conditions, and at hour 53 in freezing conditions. The shape of the curves was rather similar, a fairly linear increase with little to no significant peaks and valleys, though it is important to note that in the first 6 hours, the concentration in the frozen condition was the highest (by ~0.2 mg/L). After hour 6, the ambient temperature increased to have the highest concentration, with thaw and freeze having similar concentrations until hour 17, after which the frozen concentration remained the lowest until the experiment's completion.

The oxygen concentration results may have been temperature-dependent in an empty column, as the full concentration values were achieved at varying rates in ambient, thaw and frozen conditions. These results were also in agreement with what was observed in the literature, the oxygen concentration evolution at the base of the column seems to be temperature-dependent with lower diffusion through the column at lower temperature. The results in an empty column were rather important as the data established an important baseline for the following investigations into oxygen diffusion in various mediums.

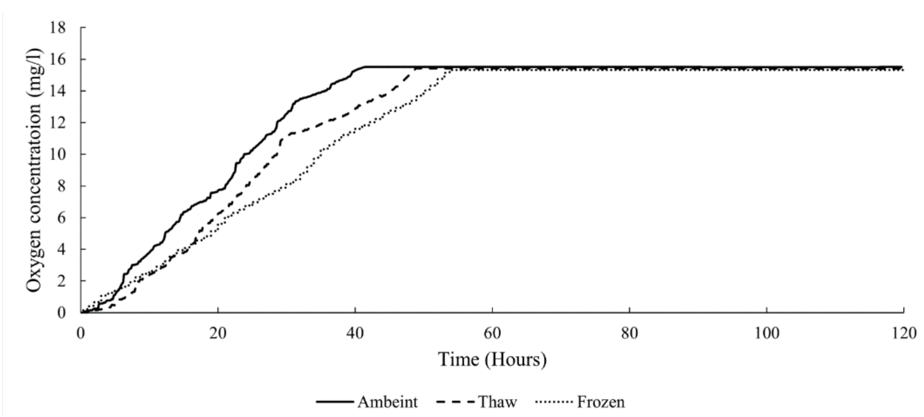


Figure 17. Control 1 – empty column.

4.2. Control 2, water column, function of ambient, thaw, freeze conditions.

Figure 18 illustrates the results of oxygen concentration evolution in a water filled column in ambient, thawing, and freezing conditions. Full oxygen concentration occurred the fastest in thawing conditions, then in ambient conditions, with no increase in oxygen concentration detected in frozen conditions. Specifically, full column concentration occurred at hour 96 in thawing conditions, and at hour 116 in ambient conditions. In the first 45 hours (about 2 days) of the experiment, the ambient column was observed to have the highest total oxygen concentration (higher than in the thawing experiment by ~1.0 mg/L), after the 45-hour mark, the thaw experiment consistently had the higher oxygen concentration (by ~2 mg/L).

Based off the results provided in the empty column, it was expected this column would also provide a similar trend of the ambient concentration reaching the highest concentration the fastest, then the thaw, and the frozen. While the results of the frozen conditions were as expected with no diffusion of oxygen through the column since frozen water does not have the pore space for the oxygen to move though the water to the oxygen probe. The results of the thawing experiment were a bit unexpected. Specifically, in the thawing experiment, as long as the temperature in the body of the column remained below 4°C, no oxygen diffused to the bottom, which was coherent with the results obtained for the frozen conditions. Once this threshold was surpassed, oxygen concentration at the bottom of the column began to increase, indicating oxygen diffusion had occurred.

There are several explanations for the observed differences in oxygen diffusion rates in the water-filled control column under ambient and thawing conditions:

- The formation of air pockets during the thawing process may have allowed for faster diffusion of oxygen through the column.
- The presence of ice crystals in the thawing column could have contributed to variations in the diffusion rate of oxygen, as they may have created channels that affected the diffusion process.
- The thawing column may have experienced a change in water density or viscosity, which may have impacted oxygen diffusion.

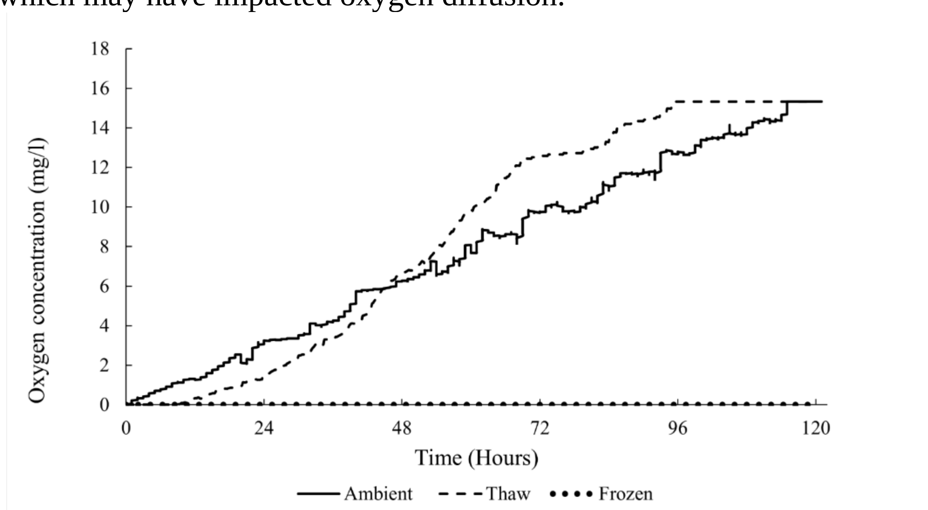


Figure 18. Control 2 – water filled column.

4.3. Control 3, dry inert material column, function of ambient, thaw, freeze conditions.

Figure 19 illustrates the results of oxygen concentration evolution in a -column in ambient, thawing, and freezing conditions. Full oxygen concentration occurred the fastest in ambient conditions, then in thawing conditions, with the slowest being in frozen conditions, similar to what was observed in the empty column control. Specifically, full column concentration occurred at hour 54 in ambient conditions, at hour 58 in thawing conditions, and at hour 110 in freezing conditions. The shape of the curves was rather similar, a fairly linear increase with little to no significant peaks and valleys, though it is important to note that in the first 17 hours the concentration in the frozen condition and the thawing condition were similar (off by 0.1mg/L). After this point, the frozen concentration remained the lowest until the experiment was finished.

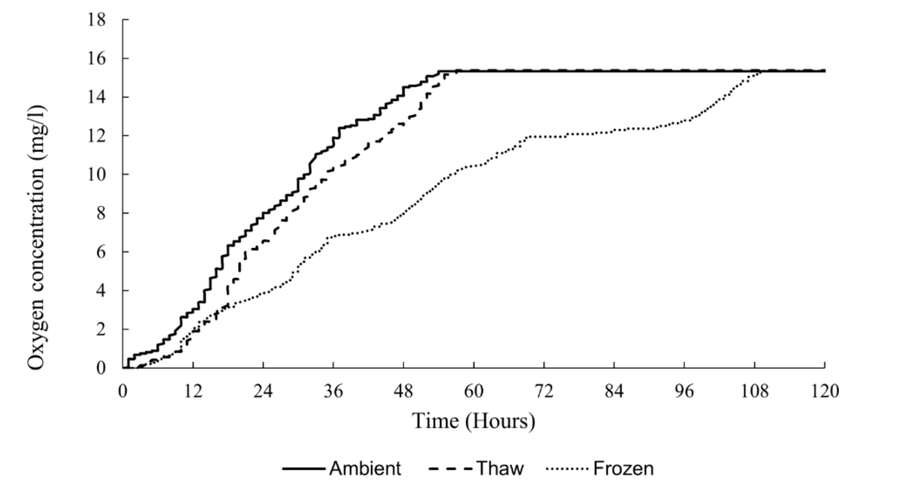


Figure 19. Control 3 – dry inert material.

4.4. Discussion about controls' results

In conclusion, the three control experiments provided valuable insights into the oxygen diffusion in different mediums under varying temperature conditions. The results indicated that temperature had a significant impact on oxygen concentration, with ambient conditions leading to the fastest full oxygen concentration, followed by thawing conditions, and frozen conditions being the slowest. The experiments also highlighted the importance of the medium, with dry inert material and empty columns showing similar trends, while water-filled columns demonstrated some unexpected results. Specifically in the water filled thawing experiment, oxygen did not diffuse to the bottom of the column as long as the temperature remained below 4°C, consistent with results from frozen conditions. However, when the temperature exceeded 4°C, oxygen diffusion occurred and the concentration of oxygen at the bottom of the column increased. These findings served as an important baseline for the investigation into oxygen concentration in the fully saturated column experiment.

4.5. Experiment, fully saturated material column, function of ambient, thaw, and freeze conditions.

The data obtained for the fully saturated column (figure 20) in ambient, thawing, and frozen temperature conditions showed some interesting results. The results produced in the ambient and frozen conditions were expected, given that the introduction of water in the dry inert material reduced pore space for diffusion. The ambient experiment provided a final concentration value of 0.014mg/L, and the frozen experiment remained at 0.000mg/L.

However, the results for the thaw experiment were surprising. Despite the fully saturated cover being initially efficient, the increase in oxygen concentration detected was greater (by ~0.34ml/L) than that obtained for ambient temperature until reaching a plateau. The data also indicated that in thawing conditions the oxygen concentration did not start to increase until hour 15, which is twice the time it took for in the water column thaw experiment (~ 10 hours). At this hour (15), the oxygen concentration increased very slowly for 60 hours (about 2 and a half days) before reaching a plateau.

There are a few reasons why the thaw results may have deviated slightly:

- The process of contraction/dilatation during the thawing might have disturbed the settlement of the fully saturated materials with changes in the evolution and distribution of the ice front within the column's pores and micropores.
- The thawing process may have created thermal gradients within the column, which could have influenced the rate of oxygen diffusion through the water and the fully saturated materials.

Regardless of the results, the overall oxygen concentration in all temperature conditions remained below 0.35mg/L. This indicated that the combination of water with the dry inert material (fully-concentration) increased the capacity of the water cover to stop or delay the increase in oxygen. These results suggest that the fully saturated cover played a significant role in controlling oxygen diffusion.

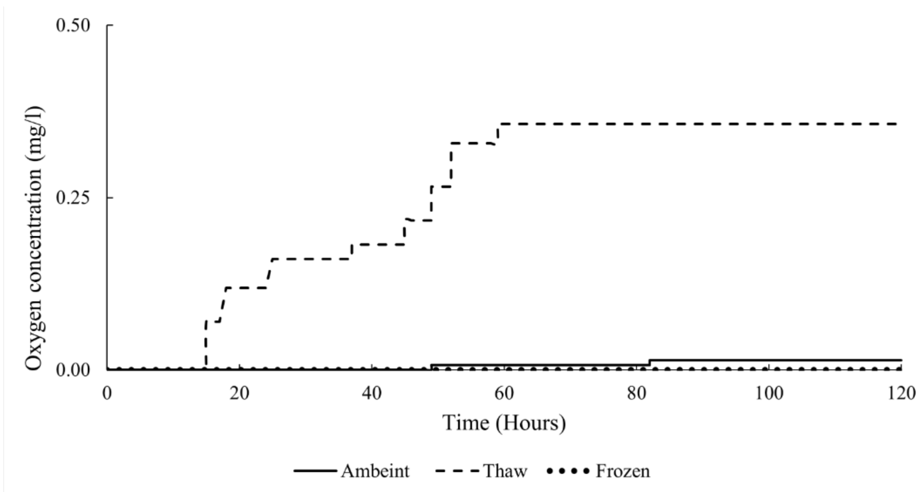
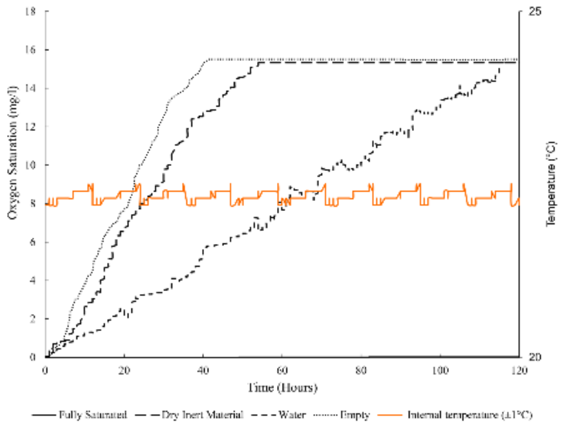


Figure 20. Experiment 1 – fully saturated cover.

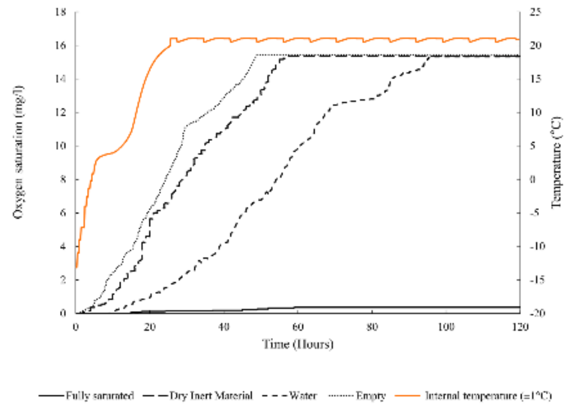
4.6. Results in ambient, thaw and frozen conditions

The experiments conducted in ambient, thaw, and frozen conditions provided valuable insights into the rates of oxygen diffusion in different mediums. This following section illustrates the results obtained from each experiment, examining the evolution of oxygen concentration over time and how it may have been influenced by varying temperature conditions.

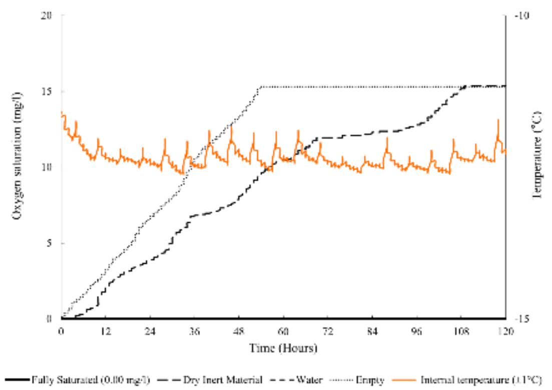
The results (figure 21) obtained for different media including empty, water, dry inert material, and fully saturated cover showed that the fully saturated cover was the most effective in limiting oxygen diffusion, even at ambient temperature. The same was found to be true for thawing conditions as well. Under frozen conditions, the fully saturated cover and water were more effective at limiting oxygen diffusion than dry inert material and empty column. These results suggest that the fully saturated cover is a viable solution for controlling oxygen diffusion in all temperature conditions. Overall, understanding the behavior of different media under different temperature conditions is crucial for effective oxygen diffusion control.



A



B



C

Figure 21. Ambient (A), thaw (B) and freeze (C) results (oxygen concentration and temperature) in empty, water filled, dry cover filled and saturated columns.

5. Conclusion

The studies of the controls experiment in both set-ups #1 and #2 showed that water may have been the most effective component in limiting oxygen diffusion in the column, but the combination of dry inert material and water to form fully saturated conditions consistently demonstrated superior results in all temperature conditions and set-ups evaluated, compared to the control group. The mid-water level gives comparable results to the high-water level in set-up #1, which could indicate that variation in the saturation level of the cover will not strongly impact the capacity of the saturated cover to limit oxygen diffusion. Unfortunately, the experimental conditions did not allow us to perform the mid-water level experiment in set-up #2. Synthetic material packed within an acrylic cover consistently caused far too many bubbles and disturbances in the nitrogen purging and oxygen gas (injection process). The absence of results for mid-water level in set-up #2 could also be an indication of the higher sensitivity to disturbance of the saturated cover when not fully saturated: something that should be considered when designing such systems.

The study based on set-up #2 indicated that the thawing period caused the most disturbance to the fully saturated cover, possibly due to the sequence of temperature creating alterations throughout the freezing and thawing periods and contraction/de-contraction inner column movement, which could be a potential area for future research in the form of natural observation over months or years, or in a column undergoing multi-succession freeze-and-thaw cycles.

While the two set-ups are difficult to compare due to their different designs, and more importantly the different oxygen injection systems, our results suggest that fully saturated covers have significant potential in limiting oxygen diffusion in northern conditions. However, further studies are needed. More specifically, the impact of thawing on the saturated cover needs to be carefully studied, and studies with different water levels (from highly disturbed systems with low saturation to variable saturation levels) need to be investigated in regard to several freeze-thaw cycles.

Based on this work, the utilization of pilot-scale column filled with desulfurized tailings exposed to freeze-thaw cycle (e.g., Yukon climate) with open access to atmospheric oxygen and strictly monitored for several years would be the best option to fully determine the role of saturated cover in limiting oxygen diffusion in northern Canada.

6. Citations

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