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# **Effective oxygen diffusion coefficient of till and green liquor dregs (GLD) mixes used in sealing layer in mine waste covers**

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Abstract

Cover systems can efficiently limit acid mine drainage generation from sulfidic mine wastes by controlling oxygen diffusion. Their performance relies on their high degree of saturation, as oxygen diffusion is substantially reduced in water or saturated medium. However, natural soils available in the mine vicinities do not necessarily have the hydrogeological properties required for the construction of sealing layers. A common strategy is to improve the characteristics of local soils using bentonite amendment, but this usually induces high costs and environmental footprint. An alternative is to reuse (or valorize) waste materials, such as mine wastes or industrial wastes like green liquor dregs (GLD). Blends of till and GLD can have advantageous properties regarding water retention capacity and hydraulic conductivity. In this study, the effective oxygen diffusion coefficient $D_e$ of till-GLD blends was evaluated using 81 diffusion tests. Various quantities and different types of GLD were tested. The diffusion coefficient was found to vary greatly depending on the degree of saturation. Even though the GLD contained naturally a substantial amount of water, a high water content of the till was still required to reach a low $D_e$. Measurements were also compared to modified Millington-Shearer predictive model which could generally predict the diffusion coefficient within an acceptable range. Results also indicated that the till-GLD mixes should not be exposed to evaporation as significant performance loss may rapidly occur upon drying. Main experimental results are presented in this paper together with recommendations in terms of cover design using till-GLD mixes.

Key words

Oxygen diffusion, green liquor dregs (GLD), mine wastes, covers, sealing layers, acid mine drainage, reclamation

## 1. Introduction

Sulfidic mine wastes exposed to air and water can oxidize and generate acid mine drainage (AMD) characterized by low pH and high sulfate and metal concentrations (Blowes et al., 2014; Nordstrom, 2015; Lindsay et al., 2015). AMD remains today one of the main environmental challenges for the mining industry (Aubertin et al., 2016). One of the primary objectives of the reclamation of AMD generating mine sites is to prevent oxidation reactions at the source, by controlling the access of either oxygen or water to mine wastes (e.g. Aubertin et al., 1999, 2002, 2016). In humid climate, oxygen barrier covers can generally effectively prevent oxygen diffusion (Höglund and Herbert, 2004).

The objective of oxygen barrier covers is to limit the oxygen flux to the underlying reactive waste materials by maintaining a high degree of saturation even though they are sometimes placed well above the water table (e.g. Nicholson et al., 1989; Collin, 1998; Aubertin et al., 1999; Höglund and Herbert., 2004; Lottermoser, 2010). In multilayer covers, oxygen diffusion is controlled by the sealing layer (or moisture retaining layer, MRL). The sealing layer is typically placed between two coarser grain layers, which will develop capillary barrier effects, and prevent water loss by drainage and evaporation (Aubertin et al., 1999). The top coarse grain layer also acts as a drainage layer and can protect the sealing layer from root penetration, freeze-thaw action, and erosion (Aubertin et al., 2002). An organic-rich layer can be added on top to promote the establishment of vegetation (e.g. Guittonny-Larchevêque et al., 2017). This type of barrier is particularly suitable for humid continental and boreal climates with positive groundwater recharge, such as in Sweden (Lottermoser, 2010) or Canada (Aubertin et al., 2002, 2016). Current targets for sealing layers in Sweden are based on results presented in the MiMi research program (Höglund and Herbert, 2004) and suggest that the oxygen flux should be less than 1 mol $m^{-2}$ $yr^{-1}$, which is consistent with recommendations in other countries (e.g. Demers et al., 2009; Pabst et al., 2018).

Cover systems must be designed so they remain efficient for the indefinite lifetime of a reclaimed mine site (Vick, 2001), which is usually the reason for using natural mineral materials (Aubertin et al., 2016). Sealing layers are commonly made of clayey till (Höglund and Herbert, 2004) or other fine-grained materials (Bussière et al., 2007). However, reclamation of mine sites covering sometimes hundreds of hectares requires large quantities of natural materials which could significantly impact the environment if they had to be borrowed in the vicinity or transported over long distances. Moreover, natural materials close to the mine can be scarce, or highly variable and they sometimes do not have suitable properties for cover design. When local natural materials do not meet performance criteria for a sealing layer, other options are needed.

The addition of a small fraction of bentonite to the till (3-5 % on dry weight basis) can, for example, contribute to decrease the hydraulic conductivity and enhance the water retention capacity (e.g. Chapuis, 1990; or more recently and specifically for cover systems: Boulanger-Martel et al., 2015). Green liquor dregs (GLDs), a waste from the pulp and paper industry, are another potentially attractive mixing material because of their adequate hydraulic properties, their availability in some regions, and their low costs (Nigéus et al., 2018). GLDs are one of the largest waste streams generated by the pulp and paper mills using the sulphate production system and they are classified as non-hazardous waste and dispensed from landfill taxes in Sweden. Commonly, GLDs have a low hydraulic conductivity and high water retention capacity but also have a paste like consistency and low shear strength. Mixed in a limited amount with granular soil such as till, an increasing addition of GLDs have the capacity to improve the water retention capacity of the mixture, while keeping relatively good geotechnical properties. The success of the methods relies on an efficient mixing of the GLD in the matrix and a sufficient degree of compaction of the blend.

GLD are fine-grained and mostly inorganic wastes from sulfate pulp and paper industry (Nigéus et al 2018). The use of GLD is rather novel and previous studies have focused on the chemical, physical and mineralogical characterization of GLD (Martins et al., 2007; Hamberg and Maurice, 2013; Mäkitalo et al., 2014; 2016). Various mixtures containing GLD were tested in the laboratory (Villain, 2008; Jia et al., 2013; 2014; Mäkitalo et al., 2015a; 2015b; Nigéus, 2018) and pilot scale studies were carried out in the field (Chtaini et al. 2001; Ragnvaldsson et al., 2014; Jia et al., 2017). Results indicated that GLD, and especially mixes of GLD and till, had good properties for the construction of cover systems, including a high water retention capacity (Mäkitalo et al., 2015a; 2015b; Nigéus et al., 2018), thus potentially being able to efficiently reduce oxygen diffusion. Moreover, such mixes could contribute to valorize (i.e. re-use) GLD and reduce the volumes that need to be disposed of, thus promoting the concept of circular economy (Nigéus et al., 2018).

However, the effective capacity of the till-GLD mixes to control oxygen diffusion has not been experimentally validated so far. The main uncertainty concerns the difficulty to homogenize the mixes, particularly because of the "sticky" texture of (some) GLD which tend sometimes to agglomerate and form clumps (Virolainen, 2018). Oxygen transport though mine waste cover systems can occur through a combination of advective and diffusive processes in both the gas and aqueous phase of the porous medium. Molecular diffusion is generally the controlling transport mechanism in partly saturated fine-grained soils (e.g. Collin and Rasmusson, 1988). The oxygen flux is generally dominated by diffusion in the air phase, but, when saturation exceeds 85–90%, the air-filled pores becomes discontinuous, and the oxygen flux becomes controlled by the diffusion through water-filled pores (Aubertin and Mbonimpa 2001; Aachib et. al., 2004).

The oxygen flux from one-dimensional oxygen diffusion through a non-reactive material can be described by Fick's first law (Crank, 1975):

$$F(z,t) = -D_e \frac{\partial C\,(z,t)}{\partial z} \quad (1)$$

and the oxygen concentration C(z,t) at depth z and time t can be described by Fick's second law:

$$\frac{\partial}{\partial t}\left(\theta_{eq} C\right) = \frac{\partial}{\partial z}\left(D_e \frac{\partial C}{\partial z}\right) \quad (2)$$

where F(z,t) is the diffusive flux at position z and time t [M $L^{-2}$ $T^{-1}$], $D_e$ is the effective diffusion coefficient [$L^{-2}$ $T^{-1}$], and C(z,t) the concentration of oxygen at position z and time t, and $\theta_{eq}$ is the equivalent diffusion porosity [$L^3$ $L^{-3}$].

The effective diffusion coefficient ($D_e$) is governed by the grain size, porosity, tortuosity and degree of saturation of the material (Aubertin et al., 1995). $D_e$ can be determined by field (Elberling et al. 1994; Dagenais et al., 2012) or laboratory measurements (Yanful, 1993; Demers et al., 2009). However, as measurements can be difficult and time consuming, several empirical relationships based on geotechnical properties were developed. Predictive models can be useful during preliminary stages of a project, or in numerical models (once calibrated). For example, the predictive model proposed by Aachib et al. (2004) was developed from earlier models proposed by Millington and Quirk (1961), Millington and Shearer (1971), and Collin and Rasmusson (1988). Aachib et al. (2004) model is a dual-phase diffusion models which considers diffusion through both water and air. The modified Millington-Shearer model (MMS) for predicting the $D_e$ can be expressed as:

$$D_e = \frac{1}{n^2}\left(D_a^0 \theta_a^{p_a} + H D_w^0 \theta_w^{p_w}\right) \quad (3)$$

where H is Henry's equilibrium constant (0.032 at 25°C), $\theta_w$ and $\theta_a$ are the volumetric water and air contents respectively, $D_w^0$ is the free diffusion coefficient in water ($L^2$ $T^{-1}$; $1.76\times10^{-5}$ $m^2$ $s^{-1}$ at 25°C), $D_a^0$ is the free diffusion coefficient in air ($L^2$ $T^{-1}$; $2.1\times10^{-9}$ $m^2$ $s^{-1}$ at 25°C), n is the porosity, and $p_a$ and $p_w$ are constants related to tortuosity. Aachib et al. (2004) showed that $p_a$ and $p_w$ could be approximated by the following relation:

$$p_{a,w} = 1.201\theta_{a,w}^3 - 1.515\theta_{a,w}^2 + 0.987\theta_{a,w} + 3.119 \quad (4)$$

Authors also suggested that $p_a = p_w = 3.4$ was a good estimate (Aachib et al., 2004). MMS predictive model and Aachib equations were, however, developed for natural and uniform materials, and the applicability to material mixes have not been validated.

The aim of this study was to evaluate the effective oxygen diffusion coefficient of till-GLD blends to assess their performance as a material for sealing layers. The water content, the types and quantities of GLD in the blends were the variables studied in the experimental design. Both the initial water content and the behaviour of the materials subjected to drying was tested in the laboratory. A total of 81 diffusion tests were carried out in the laboratory on various till-GLD blends. Based on laboratory results, the performance of MMS predictive model to accurately determine the effective diffusion coefficient of till-GLD blends was evaluated.

## 2. Methodology

### 2.1. Materials

Four samples of green liquor dregs (GLD), one till, and a field blend of till and GLD were tested in this study. The four GLD were selected to cover a variety of properties encountered in the industry and were obtained from four pulp and paper mills located in Sweden: Billerud (B), Smurfit Kappa (SK), Iggesund (I), and Vallvik (V)(Figure 1):

1) Smurfit Kappa: black with white fragments (mesa, calcium carbonate and hydroxide), crumbles and clumps, moist and sticky.
2) Billerud: grey, small crumbles, perceived as relatively dry, similar to Vallsvik but with smaller aggregates.
3) Iggesund: dark grey paste, very wet with a lot of bleeding water, very sticky.
4) Vallvik: grey, sharp smell, medium-coarse crumbles, perceived as relatively dry.

GLD properties can vary significantly depending on the process and production rate at the pulp mill (Nigéus et al 2018) so these samples were not necessarily representative of the typical GLD generated at these mills or elsewhere. However, they were sufficiently different to give some insights about typical behaviours.

The till was collected from a till quarry producing material for mine waste covers. It was dried at room temperature for 48 h and sieved to a maximum particle size of 2 mm. This till was actually also used for reclamation on a mine site, but its saturated hydraulic conductivity exceeded sealing layer requirements (i.e. $10^{-8}$ m/s) and improvement was decided. In field conditions, the till was sieved to 20 mm and mixed with 6.1% (dry weight) of GLD B to produce the final sealing layer material. The resulting material was sampled for this laboratory study, sieved to a maximum particle size of 2 mm (like other materials tested in this study) and tested in the laboratory (Field blend).

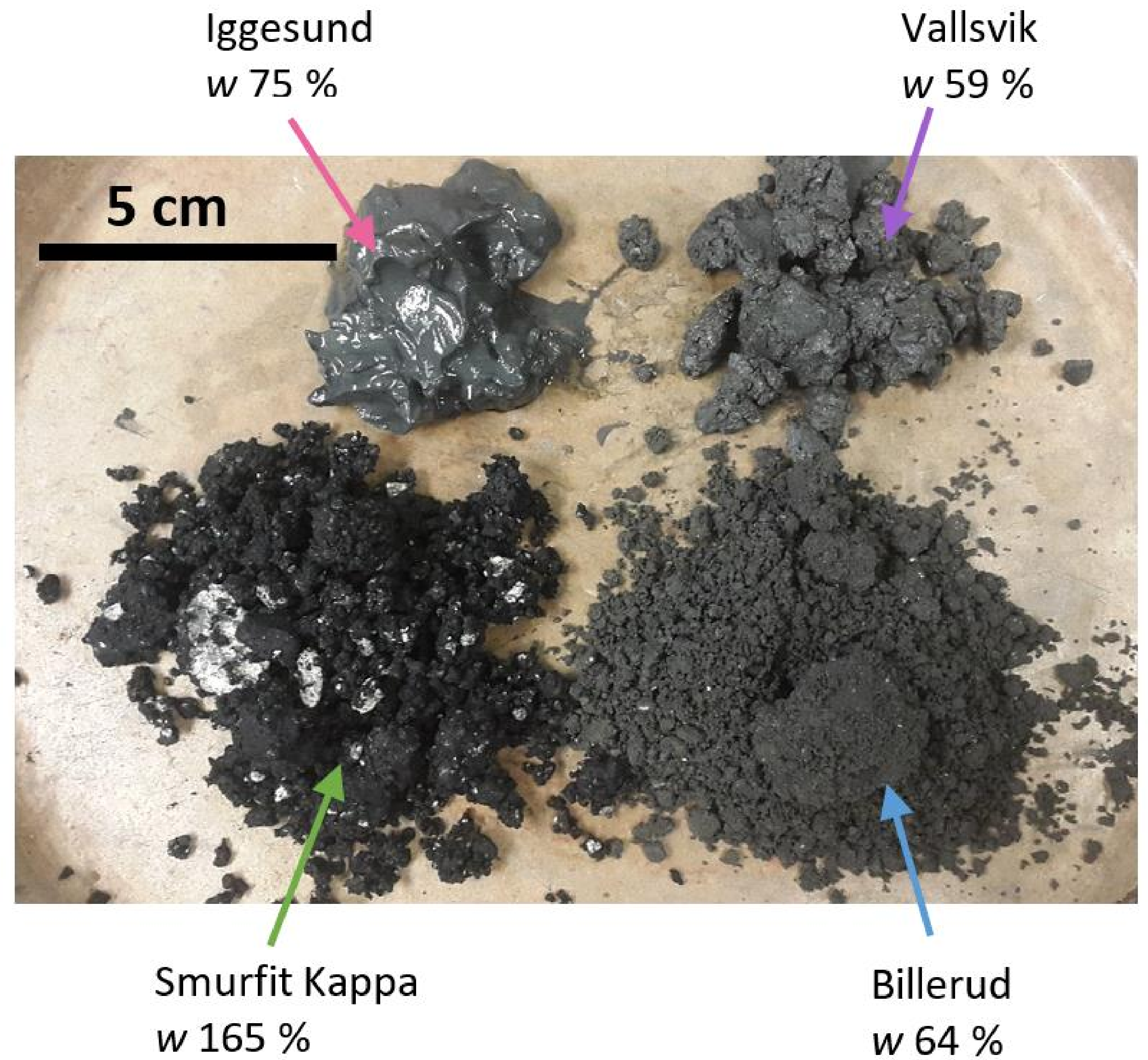


Figure 1. Green liquor dregs sampled from four paper mills: Iggesund (I), Vallsvik (V), Smurfit Kappa (SK), and Billerud (B). The GLD samples had different water contents (indicated in the figure), colours and textures.

## 2.2. Specific gravity and particle size distribution

Specific gravity of the materials was determined by gas and water pycnometers according to ASTM standard D5550 and D854. Material water contents were determined according to ASTM standard D2216, by drying a minimum of 20 g sample at 105°C for a minimum of 16 hours. Particle size distribution (PSD) curves were determined at Lulea Technical University laboratories by a combination of sieving and laser diffraction (Cilas 1064, CILAS). PSD of GLD B and SK, and of the till were also measured using a combination of sieving and hydrometer test (ASTM D422).

Characterisation of water and solid content showed that the sample from Smurfit Kappa (SK) was distinctly different from the three other GLD samples (Table 1). SK had a lower solid content (38%) and higher water content (165%) compared to the other three materials that were similar in terms of solid contents (57–63%) and water content (59–75%; Table 1).

Specific gravity of till was approximately 2.67 but varied between 2.43 and 2.63 for the four GLD samples (Table 1).

Three of the GLD samples (B, I and V) had similar grain size distribution curves with a $d_{10}$ around 4 µm, and a $d_{60}$ between 24 and 30 µm. GLD SK was slightly different from the others and contained a larger coarse fraction with $d_{10}$ = 7 µm, and $d_{60}$ = 97 µm. The PSD of the till and the field blend were similar, especially for the fine fraction. The till had the composition of a silty sand with a clay content of approximately 3%.

The particle size distributions curves showed the presence of two distinct fractions in the GLD, i.e. a finer fraction (clay and silt), and a coarser fraction (which can constitute almost half the sample in the case of SK)(Figure 2). The coarser fraction partly consisted of larger GLD grains, possibly agglomerates or mesa fragments (no chemical analysis was performed), and partly of lithogenic grains (sand of quartz and feldspar minerals). The mineral fraction likely came from the handling process. Sand is for example often used during the transport of dregs to ease loading.

The texture of the GLDs (Figure 1) did not seem to be related to either their water content or PSD (Figure 2).

Table 1. Geotechnical properties of GLD Smurfit Kappa (SK), Billerud (B), Iggesund (I) and Vallsvik (V), till and field blend. $D_x$: diameter corresponding to x% passing; $\rho_s$: specific gravity; pycn.: pycnometer.

| | **Green Liquor Dregs (GLD)** | | | | | |
|---|---|---|---|---|---|---|
| | **Smurfit Kappa (SK)** | **Billerud (B)** | **Iggesund (I)** | **Vallsvik (V)** | **Till** | **Field blend** |
| Clay, ≤ 2 µm (%) | 3.1 | 5.8 | 6.4 | 6.4 | 3.0 | 2.6 |
| Silt, 2 – 63 µm (%) | 53.4 | 70.9 | 73.9 | 67.4 | 31.9 | 31.3 |
| Sand, 63 – 200 µm (%) | 43.5 | 23.3 | 19.7 | 26.2 | 65.2 | 66.0 |
| $D_{10}$ (µm) | 7 | 4 | 4 | 4 | 10 | 10 |
| $D_{30}$ (µm) | 17 | 12 | 13 | 13 | 53 | 52 |
| $D_{60}$ (µm) | 97 | 25 | 24 | 30 | 160 | 265 |
| Solid content (%) | 38 | 61 | 57 | 63 | 99.7 | 89 |
| Initial water content (%) | 165 | 64 | 75 | 59 | <0.3 | 13 |
| $\rho_s$ (g cm$^{-3}$) – gas pycn. | 2.43 | 2.63 | 2.63 ± 0.02 | 2.61 | - | - |
| $\rho_s$ (g cm$^{-3}$) – water pycn. | 2.50 ± 0.30 | 2.64 ± 0.22 | - | - | 2.67 ± 0.08 | - |

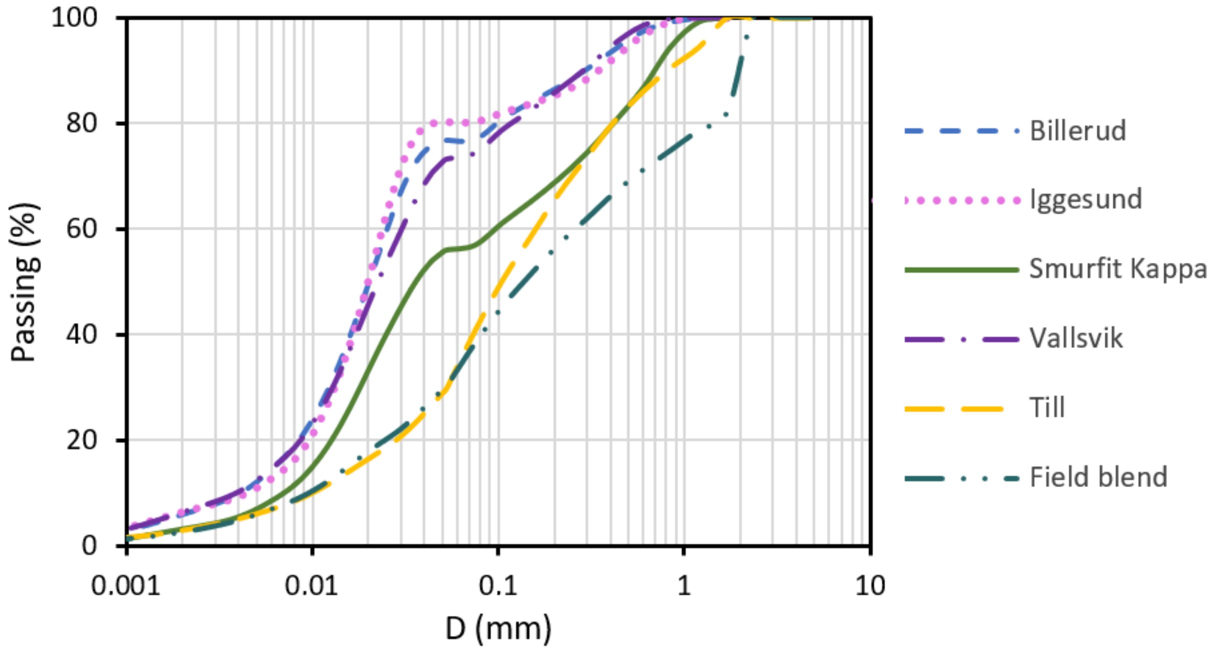


Figure 2. Particle size distribution curves of GLD Smurfit Kappa (SK), Billerud (B), Iggesund (I) and Vallsvik (V), till and field blend. Different methods were used to determine sample PSDs (see text for details). Till and field blend were sieved to a maximum particle size of 2 mm.

## 2.3. Oxygen diffusion tests

### *2.3.1. Principle*

Oxygen diffusion tests were developed and largely used by Yanful (1993), Aubertin et al. (1995), and Mbonimpa et al. (2003), to evaluate oxygen diffusion through tailings and various materials, especially for cover systems. The protocol used in this study follows the approach initially proposed by Yanful (1993) and modified by Aubertin et al. (1995, 2000), and Aachib et al. (2004). In this test, a specimen (around 3 cm high and 8.5 cm in diameter) is packed in a test cell (Figure 3). Empty volumes (reservoirs) are left above and below the material and the column is sealed with lids. At the beginning of the test, an oxygen gradient is imposed across the material: the bottom reservoir is flushed with nitrogen gas (100% $N_2$, i.e. 0% $O_2$) and the top reservoir is flushed with air (around 20,9% $O_2$). The cell is then hermetically closed, and the diffusion test is started. Oxygen sensors are placed in each reservoir and continuously measure the oxygen concentration. Changes in concentration occur as an effect of oxygen diffusing through the specimen. The test is finished when equilibrium is reached in the cell. In some tests however, the diffusion is so slow that oxygen concentrations do not reach equilibrium after several days. In this study, the duration of the tests varied from less than an hour to more than two weeks. Based on the measurements of oxygen concentration over time, the effective oxygen diffusion coefficient can be estimated using inversed numerical simulations.

*2.3.2. Specimen preparation*

The till was first wetted to the target water content and then mixed manually with GLD. GLD additions (between 2.5 and 7.5%) were expressed in dry weights to compare blends in terms of solid content (GLD have different initial water contents). The mixing was performed by hand for three minutes to achieve a uniform blend, after which the material was left in an airtight bag for at least 12 h to let the moisture homogenise. The material was then placed and packed in one layer, using a metal compactor, directly in the diffusion cell made of PVC. Diffusion cells were 8.5 cm in diameters and around 12 cm in height, but the sample itself was around 2 to 3 cm thick, leaving enough space to keep air reservoirs above and below the specimen (Figure 3). Depending on the specimen, compaction could become more difficult when water content increased, so for high degree of saturations, compaction was achieved at lower water content and additional water was added on top of the specimen. In these cases, the cell was closed and left at rest for another 12 h to let the moisture content homogenise in the sample. Sample dimensions and water content, together with top and bottom reservoir volumes, were measured at the beginning and at the end of each test. In total, 81 specimens were prepared and tested. Porosity was usually comprised between 0.25 and 0.35, with a few more (pure till) and less (pure GLD) dense samples.

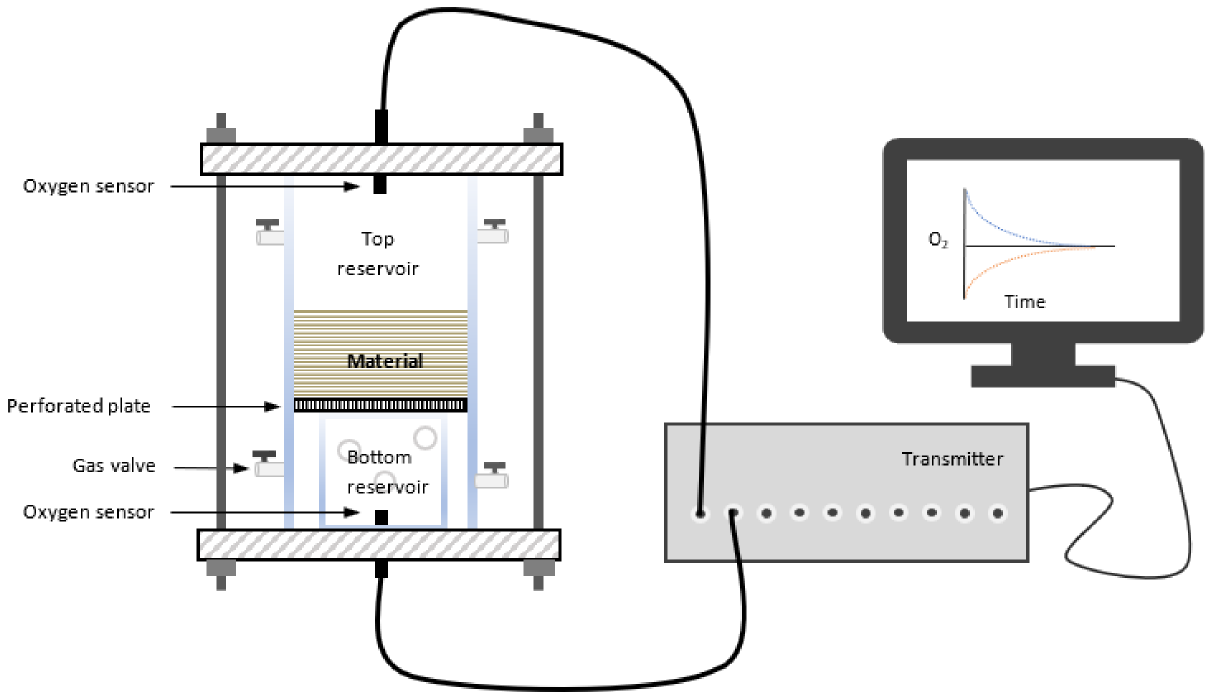


Figure 3. Diffusion test setup and instrumentation (after Aachib et al., 2004).

### *2.3.3. Instrumentation*

Oxygen concentrations in the top and bottom reservoirs were monitored using fiber-optic oxygen sensors (dipping probes PSt3, PreSens) made of 2 mm polymer optical fibre with a polished distal tip coated in an oxygen sensitive foil. These sensors have a measurement range of 0-100% atmospheric $O_2$ with a detection limit of 0.03%. Reported accuracy of the sensors is ±0.4% $O_2$ at 20.9% $O_2$, and ±0.05% $O_2$ at 0.2% $O_2$ (PreSens, 2016). Each sensor was calibrated individually following the protocol suggested by the manufacturer. The sensors were connected to an Oxy-10 transmitter recording the measurements every 2 seconds (Figure 1).

### *2.3.4. Test interpretation*

Oxygen concentration measurements were interpreted using numerical simulations carried out with Vadose/W (Geoslope, 2016). Vadose/W is a 2D finite element code (now replaced by Seep/W) which can assess the unsaturated behaviour of materials, including oxygen diffusion and consumption. The experiments were modelled using the porosity and degree of saturation of each specimen and experiment. A few tests showed a degree of saturation slightly above 100% (probably because of uncertainties in porosity estimation) and $S_r = 100\%$ was assumed in the interpretation. Boundary conditions represented temperature during the test (T = constant = 24°C), atmospheric oxygen concentrations in the top reservoir, no oxygen in the bottom reservoir. An iterative curve fitting procedure was set to minimise the root mean squared error (RMSE) between the observed data and simulated values to obtain the best fitting model. RMSE was calculated using the following equation:

$$\mathrm{RMSE} = \sqrt{\frac{1}{N}\sum_{i=1}^{N}(P_i - O_i)^2} \tag{5}$$

where $O_i$ is the experimental oxygen concentration, $P_i$ the simulated oxygen concentration with Vadose/W and N the number of values compared.

Once the best fit had been adjusted, the corresponding parameter $D_e$ was determined.

## 2.4. Drying tests

The effect of drying was evaluated for till, pure GLD SK, field blend and different till-GLD SK blends (with 2.5, 5 and 7.5 % of SK). Specimens were prepared at a high degree of saturation ($S_r$ > 85%) and an initial diffusion test was performed before the cell was opened and the specimen exposed to drying. Two approaches were used for drying, either a 3 h exposure with a fan (high evaporation) or 2 h without fan (moderate evaporation). After drying, the cells were sealed again and left at rest for 12 h (to let the moisture content homogenise in the sample) before a new diffusion test was carried out. The new degree of saturation was estimated by weight, and assuming a constant sample volume. The procedure was repeated 2 to 4 times for each test.

## 3. Results

### 3.1. Effective oxygen diffusion coefficient in till-GLD mixes

Laboratory results showed that the diffusion coefficient tended to decrease significantly with increasing degree of saturations, from around $3\times10^{-6}$ $m^2$ $s^{-1}$ for dry materials, to values as low as $1\times10^{-11}$ $m^2$ $s^{-1}$ for materials close to saturation (Figure 4). The slope of the curve was steeper for degrees of saturation exceeding 80%. These results had a strong impact on the duration of the tests: for the driest specimens, the oxygen concentration in both reservoirs could reach an equilibrium within a few minutes, while the tests ran for over 15 days for the highest degrees of saturation without any significant diffusion. Some results show degrees of saturation exceeding 100% at the beginning of the tests, which can be explained by measurements errors on the specimen volume or the water content during the setup or dismantling of the diffusion cells.

The general trend of the curves is relatively similar for the different specimens, independently of the nature or quantity of GLD added. The measured diffusion coefficients and the variation of $D_e$ with the degree of saturation were all in the same range of results (Figure 4).

Measured diffusion coefficients were compared to predicted values calculated with the MMS model (equation 3). In general, the model was close to the measured values, especially for degrees of saturation smaller than 80%. For higher degrees of saturation, the difference could however reach several orders of magnitude (not taking into account the possible error on $S_r$). The general trends, including the steeper slope for higher degrees of saturation, were nevertheless well reproduced by the model, and over 75% of the measured diffusion coefficients were within one order of magnitude of the predicted values. Results showed no particular trend in terms of overestimation or underestimation, and measured values were indifferently on both sides of the predicted curves, yet a majority of predicted values were slightly underestimated.

Measurement repeatability was verified by comparing results from different cells and specimen size but using the same material (till) prepared at the same water content (w = 7%) and packed at approximately the same porosity (n = 24-28%, i.e. $S_r$ = 36-46%). Measured diffusion coefficients were close, with an average of $8\times10^{-7} \pm 1\times10^{-7}$ $m^2$ $s^{-1}$ (Figure 4A – orange triangles). These results were also within the range of results predicted by the MMS model.

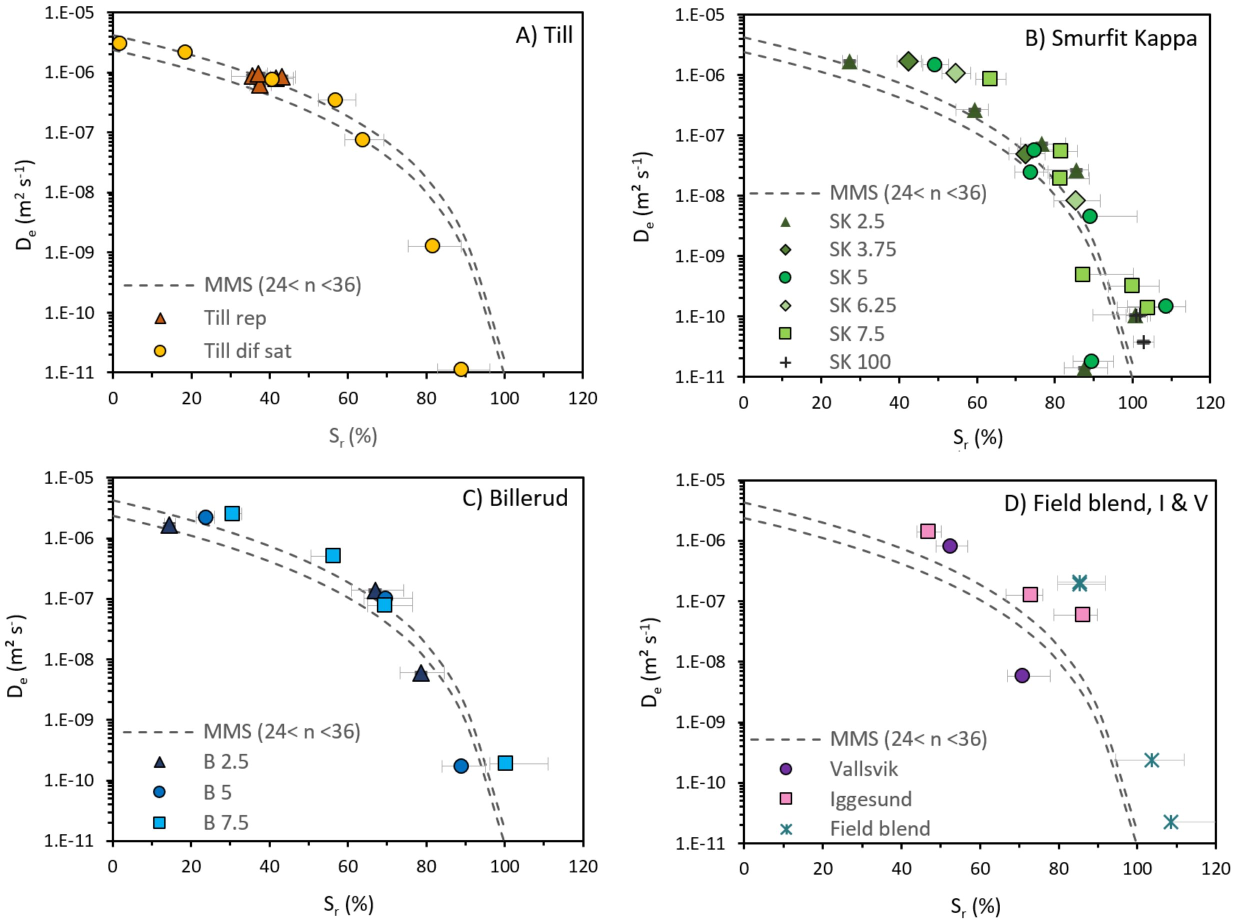


Figure 4. Measured diffusion coefficient $D_e$ as a function of the degree of saturation for the different tested materials: A) Till, B) Smurfit Kappa (SK), C) Billerud (B) and D) Field blend, Vallsvik (V) and Iggesund (I). Results are indicated for the different mixing ratios and compared with the MMS predictive model calculated for the minimum and maximum porosity of the tests (dashed lines). Error bars are also shown.

### 3.2. Drying tests

The effect of drying and wetting cycles on the diffusion coefficient was tested on till-SK blends, pure till, pure SK, and on the field blend (Figure 5). Results showed similar trend for all samples: a sharp increase of $D_e$ after the first or second drying phase, and then a somewhat more limited increase for the subsequent drying cycles. Despite uncertainties in the estimation of $S_r$ (which could explain values exceeding 100% sometimes) the increase of $D_e$ following drying seemed significantly more important than predicted by MMS model. For example, the degree of saturation of the Field blend after two drying cycles was approximately 88%; the measured effective diffusion coefficient was around $2\times10^{-7}$ $m^2$ $s^{-1}$, while MMS model predicted rather a value around $6\times10^{-9}$ $m^2$ $s^{-1}$ (Figure 5). Measured values seemed to get closer to predicted values after a few additional drying cycles, when the degree of saturation became smaller than about 70 to 80%.

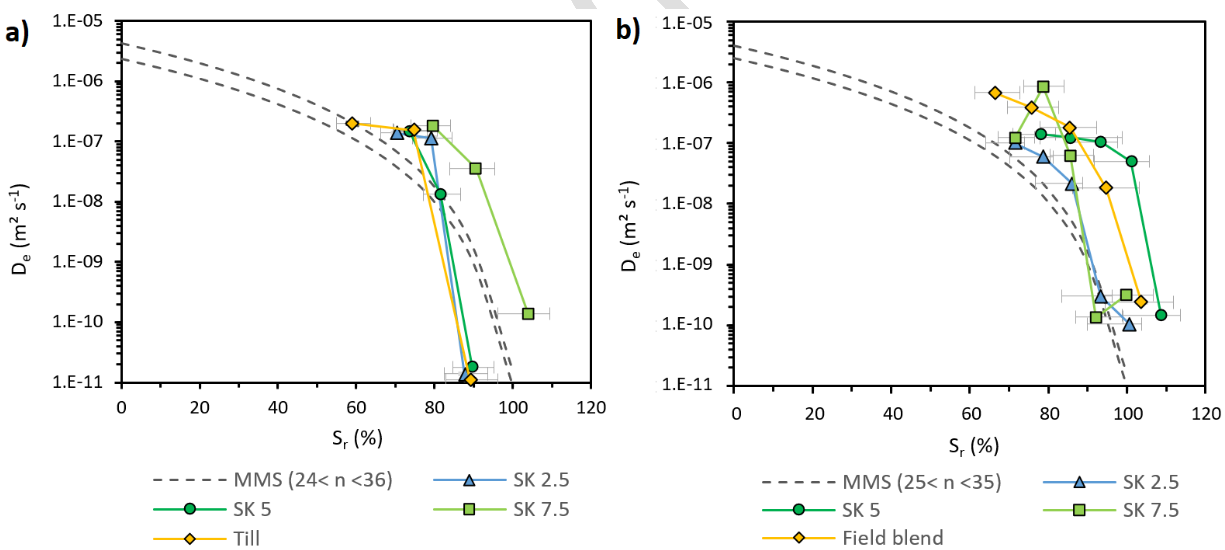


Figure 5. Measured diffusion coefficient $D_e$ during drying tests (decreasing degree of saturation); a) high evaporation and b) moderate evaporation (see section 2.4 for details). Each point corresponds to a drying phase. MMS predictive model calculated for minimum and maximum porosity is shown (dashed lines).

# 4. Interpretation and discussion

## 4.1. Effect of GLD mixing on diffusion

The effective oxygen diffusion coefficient $D_e$ of till and GLD mixes followed the same general trend as for natural soil: it decreased with increasing degrees of saturation, first relatively slowly for low degree of saturation, and then more abruptly when $S_r$ exceeded around 80%. The range of values measured (between $3\times10^{-6}$ and $1\times10^{-11}$ $m^{2}$ $^{s-1}$) was typical for partly saturated soils, tailing and other fine-grained porous materials (e.g. Aachib et al., 2004). Generally, the natural water content of the GLD was not enough to reach sufficiently high degrees of saturation in the blend (i.e. $S_r \geq 85\%$), and water addition would be required in the field after compaction so the sealing layer can efficiently control oxygen diffusion. It is expected that a few seasons may be required for the sealing layer to reach a maximum degree of saturation (as observed for moisture retaining layers in covers with capillary barrier effects or CCBE; Bussière et al., 2009).

The addition of more and wetter GLD in the blend contributed to increase the final degree of saturation of the mix, but also resulted in lower compaction (results not shown here, see Virolainen, 2018). In general, GLD addition tends to increase bulk porosity without any significant increase of the degree of saturation (Sirén et al., 2016; Nigéus, 2018). This could have implications for the long-term performance of till-GLD covers as increased porosity could make them more sensitive to drying (reduced water retention properties), frost action, and root penetration.

## 4.2. Predictive model

The MMS predictive model was able to predict the effective diffusion coefficient of most tests with reasonable accuracy (i.e. within one order of magnitude of the measured value, and often less;

Figure 6). There was a slight tendency of the model to predict lower values than measured. This could be an effect related to the uncertainty of $S_r$ or some differences between measured and effective $S_r$ (also see discussion regarding mixing below). Diffusion tests for high degrees of saturation are also more difficult to interpret because of a significantly lower oxygen concentration decrease, resulting in greater uncertainties (Aachib et al., 2004; Toussaint, 2016). Overall, MMS model seems reasonably reliable to predict the effective diffusion coefficient of till-GLD mixes, independently of the amount or nature of GLD added. The model however tended to underestimate the diffusion coefficient in the case of drying and wetting cycles, possibly because of some form of hysteresis (see section 4.3).

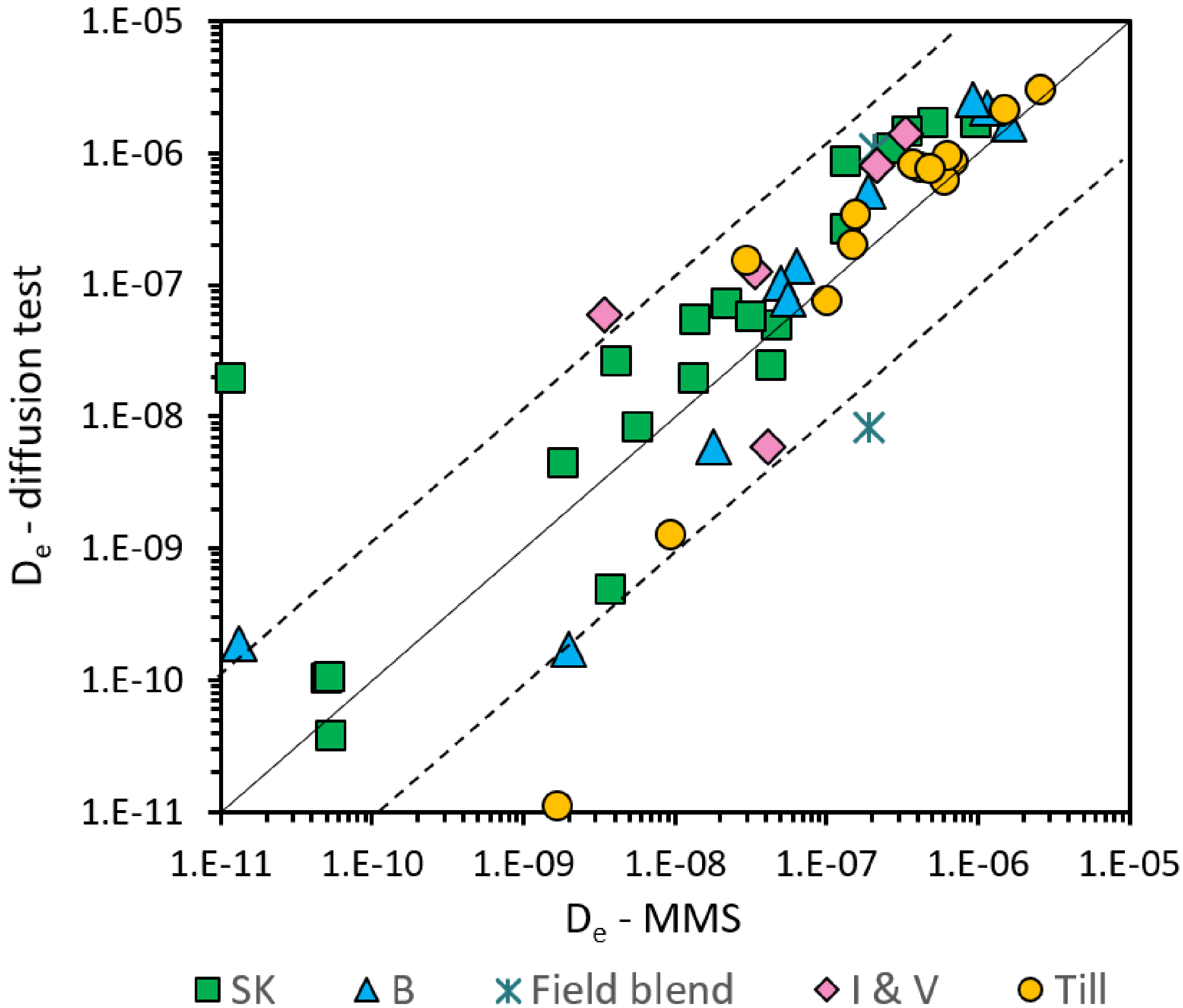


Figure 6. Comparison of measured effective oxygen diffusion coefficient $D_e$ and predicted values calculated with MMS model (ref; see text for details). All the test results are presented for till, Smurfit Kappa (SK), Billerud (B), Iggesund (I), Vallsvik (V) and field blend. Dashed lines indicate the range within one order of magnitude from the 1:1 solid line.



**4.3. Effect of drying**

Drying tests showed a rapid increase of the diffusion coefficient with short (2 or 3 h) exposures to the atmosphere for all nine tested materials. Within four hours of drying, $D_e$ generally increased by at least two orders of magnitude and the measured value was significantly higher than predicted with MMS model. Also, the same trend was observed for all specimens, independently of the amount of GLD added to the till. This result differed from previous studies which showed a relatively good capacity of GLD to retain water at relatively high suctions (Hamberg and Maurice, 2013; Mäkitalo et al., 2014) and also till-GLD blends (Mäkitalo et al., 2015a; Nigéus, 2018). It is expected that most of the water loss originate from the till which is more prone to desaturation. Moreover, it was observed on several samples that the rather small quantity of mixed GLD (from 2.5 to 7.5%) was not spread evenly in all the till pores. However, the total water loss in the samples during the drying tests was greater than the till initial water content or the added water, which indicates that water must have been lost from the GLD as well.

Pure GLD was also tested in diffusion cells and some specimens were subjected to drying (results not presented here). Pure GLD effective diffusion coefficient at saturation was smaller than $4\times10^{-11}$ $m^2\ s^{-1}$ (equilibrium was not reached after 7 days of test). However, after one cycle of drying, the diffusion occurred in only a few minutes. Shrinkage had most probably created preferential flow paths between the specimen and the sides of cell. Even though this is very dependant of the specimen size (thickness and diameter) and the test conditions, GLD appears to be very sensitive to shrinkage. In a field application, such boundary effects would not occur, but desiccation cracks may appear at the surface.

Shrinkage and rapid desaturation seemed therefore to significantly reduce the performance of till-GLD mixes. These materials should therefore not be subjected to drying as they could lose their ability to act as diffusion barriers. More tests, preferably on larger sample sizes and in field conditions, also with different types of GLD, should be performed to confirm these observations.

The effect of rewetting should also be studied as the addition of water could contribute to swelling and possible to the sealing of voids.

### 4.4. Considerations regarding cover design using till-GLD blends

Very low effective diffusion coefficients were measured in this study. For example, the diffusion coefficient of the field blend (which is representative of the mixing achievable in the field site) was smaller than $2\times10^{-11}$ $m^2$ $s^{-1}$ when almost saturated, and hardly any diffusion occurred over 15 days even though the specimen was only 2.4 cm thick. In other words, a till GLD mix should be able to efficiently control oxygen diffusion to reactive mine waste, as long as it remains close to saturation and is not exposed to evaporation (section 4.3).

Previous numerical simulations showed that protection layers made of coarse till was efficient to control evaporation and protect sealing layer from drying, even during extremely dry conditions (Höglund and Herbert, 2004). Other results showed however, that slightly finer tills were not efficient enough to prevent the exposition of sealing layer to evaporation during the summer (Collin, 1998). The design of the protection layer can therefore be critical to ensure the long-term performance of sealing layers made of till-GLD mixes. The design of the protective cover should enhance infiltration to rapidly increase the degree of saturation of the sealing layer and act as efficient protection against evaporation, drainage, erosion, freeze-thaw action, and root penetration.

### 4.5. Experimental challenges

The results obtained in this study, yet promising, would need to be confirmed by other tests, on other materials, and for larger scales (e.g. Demers et al., 2009). Some uncertainties remain, essentially because of experimental errors. The largest uncertainty related to the diffusion tests was the determination of the degree of saturation, related itself to the determination of the sample volume. A relatively small error in the height measurement (±0.5 mm) could result in significant variations in the determination of $S_r$ (approximately ±10%). This sensibility, which has even more effect on materials with a high degree of saturation (because of the great variations of $D_e$) was also noted by Toussaint (2016) and is difficult to correct with the current design of the experiment.

The determination of specific gravities for GLD was also rather uncertain, because of the peculiar nature of the material. Specific gravities determined in this study by gas pycnometer were comparable to other values reported in the literature (Mäkitalo et al., 2014; Nigéus, 2018). Water pycnometer results, however, were similar, but the standard deviation of those tests did not meet quality assurance as specified in the standard. Two methods were also used for the determination of GLD particle size distribution. The hydrometer test seemed, however, less suitable for GLD and tended to overestimate largely the fraction of the finest particles (below 15-20 μm) as the salt content in the water increased. This was possibly a result of some dissolution of dregs altering the density of the solution used during the tests.

Blending of till and GLD can also be complex. GLD tend to form small clumps in the till, because of high water content and a certain "stickiness". This could be seen both in the laboratory blends that were mixed by hand and in the field blend that had been machine mixed (Nigéus et al., 2018). Both methods result in small agglomerates of the GLD being evenly distributed in the material, but not in every pore. Thus, when adding GLD to till, the calculated degree of saturation might be relatively high, but the water will be concentrated to the GLD agglomerates, and the effective $S_r$ will be lower than the calculated $S_r$. Consequently, the till between agglomerates can remain drier and allows for faster diffusion. This phenomenon did not have a significant effect on the results as observed above, but it could influence the water retention capacity of the material and explain why the diffusion increased so sharply upon drying. This would need however to be studied more extensively. It is also recommended to make the distinction between the bulk degree of saturation (measured as a whole) and the effective degree of saturation (which influences the diffusion of oxygen). This was not possible in these tests, but could require the use of scanning techniques (e.g. Salba et al., 2014). Scale effect and impact of higher compaction energy in the field (especially on porosity) should also be studied by carrying out additional tests, including the sampling and testing of undisturbed specimens.

## 5. Conclusion

This project evaluated the effective oxygen diffusion coefficient in blends of till and GLD, that could potentially be used as sealing layer material. Results from the diffusion tests show a significant variation of $D_e$ with the degree of saturation and a generally good prediction by the MMS model. The model was slightly less precise for high degrees of saturation ($S_r > 80\%$). All blends (2.5-7.5%) were able to reach low $D_e$, provided enough water was added to reach higher degrees of saturation. The type and properties of the GLD didn't seem to have a significant influence on the effective oxygen diffusion coefficient.

Results also indicated that the till-GLD blends were highly sensitive to evaporation and should not be exposed to drying. Therefore, in the case a till-GLD blend is used as sealing layer, it is critical that the protective layer enhance water infiltration while efficiently preventing evaporation.

However, both GLD and till are highly variable materials and tests performed in this study should not be directly extrapolated to other materials and conditions. The results still provide a first attempt at evaluating the variability of the effective oxygen diffusion through these material blends and at validating the precision of the MMS predictive model for blends. Further studies evaluating the oxygen diffusion through till-GLD layers should include tests on larger and thicker samples and use tills containing larger particle sizes to better represent field blends. Studies should also focus on investigating drying of the blends with and without protection covers in natural field conditions.

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