Green liquor dregs in mine waste remediation, from laboratory investigations to field application

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Abstract

The oxidation of sulphides in mine wastes is a possible threat to the environment as it has potential to generate acid rock drainage (ARD). A way to reduce ARD formation is to apply a soil cover to reduce oxygen fluxes and water infiltration to the underlying reactive wastes. A typical mine waste cover in Sweden consists of a compacted sealing layer of a fine grained till overlaid by a non-compacted protection layer. However, a fine grained till with low enough hydraulic conductivity (HC) can be difficult to find in the vicinity of the mine and it might be necessary to mix it with a fine grained material. In this study a mixture of till and a residue from pulp and paper production, Green Liquor Dregs (GLD) was studied in laboratory and in a pilot cell study. The objective of the laboratory study was to investigate if an addition of GLD will improve the HC of tills with different clay contents. The results show that HC of the different tills studied decreases with addition of 5-10 w. % of GLD, except from the clayey till that already had a low HC without addition of GLD. In the pilot scale study a cell was constructed to investigate the feasibility to compact a sealing layer of a fine grained till and 10 w. % of GLD. The pilot scale study shows that it can be difficult to reach a high compaction degree in the field. However, it does not necessarily mean that the HC of the sealing layer will increase. In fact the laboratory study shows the opposite trend, a decrease in HC with a decrease in dry density for tills with low clay content. The main conclusion of the study is that addition of GLD can be an alternative option to improve the properties of a local till that alone does not meet the requirements for HC.

Key words: Mine closure, green liquor dregs, sealing layer, mine waste, acid rock drainage

Introduction

The oxidation of sulphides in mine wastes and the production of acid rock drainage (ARD) is a major long-term threat to the environment as sulphides may become mobile with access to oxygen with metal leaching as a result (Nordström et al. 2015; Saria et al. 2006). One method to reduce sulphide oxidation is to apply a dry cover on top of the mine waste deposit (Höglund et al. 2004). A dry cover in Sweden usually consists of a sealing layer placed on top of the mine waste and above this, a protective layer. The sealing layer is typically made of a fine-grained local till and its purpose is to mitigate oxidation of sulphides by reducing infiltrating water and oxygen to reach the mine waste (Höglund et al. 2004). The presence of a fine grained material is known to decrease the hydraulic conductivity (HC; Benson et al. 1994; Benson and Trast 1995; Leroueil et al. 2002). To further lower HC the sealing layer should be compacted to a high density (Leroueil et al. 2002; Watabe et al. 2000). Connected with compaction is the molding water content which is also known to affect the HC. The lowest HC can be reached 1-2 % wet of the line of optimum water content (Benson and Trast 1995). The optimum water content is the water content where the highest dry density can be reached in the material.

When a fine-grained till with a low enough HC is not present nearby the mine, other materials that can replace the till needs to be used. Previous studies have shown that a residue from pulp and paper production, Green Liquor Dregs (GLD), has potential to be used as a sealing layer (Mäkitalo et al. 2014; Mäkitalo et al. 2015a; Mäkitalo et al. 2015b; Mäkitalo et al. 2016; Ragnvaldsson et al. 2014) i.e. it is fine grained (d100 < 63µm), commonly has a HC in the range of 1E-08 and 1E-09 m/s and a high WRC capacity. Other characteristics of GLD are high pH (10-11), relatively high porosity (73 - 82 %),
a bulk density of 0.44-0.67 g/m$^3$, a compact density of 2.47 to 2.60 g/cm$^3$ (Mäkitalo et al. 2014). GLD consist of up to 75 % of CaCO$_3$, which generates from the retrieving process where a pre-coat lime mud filter (mixture of CaCO$_3$, CaO and Ca(OH)$_2$) is used leading to various amounts of lime mud mixed with the green liquor (Mäkitalo et al. 2014). However, to solely use GLD in the sealing layer is not reasonable neither from economical or a geotechnical point of view. In a geotechnical perspective GLD is not suitable due to its stickiness, low shear strength and high water content (Mäkitalo et al. 2014). Recent field studies have shown that a mixtures between till and GLD exhibit potential to be used in a sealing layer on top of mine waste (Mácsik and Maurice 2015; Mäkitalo et al. 2015b). However, the properties of the till and its effect on the HC of the mixture have not yet been studied.

In this study 5 to 20 w. % of GLD were mixed with three sieved (<20 mm) tills with different contents of fines and clays to investigate how the fine grained material in the tills affect the HC and compaction properties of the mixtures. The tills consisted of two fine grained (~35 % <63 µm) tills with different clay content (2.6 and 4.3 % <2 µm respectively) and one sandy till (~14 % <63 µm). The compaction properties and hydraulic conductivity of the different mixtures were investigated.

To assess feasibility, a pilot scale study consisting of a dry coverage with a sealing layer made of a mixture between a fine grained till (~30 % < 63 µm) and 10 w. % GLD from four different paper mills was conducted.

The objective of the laboratory study was to (i) investigate if an addition of GLD will decrease the hydraulic conductivity of tills with different fines- and clay contents. The objective of the pilot scale study was to investigate (ii) which dry densities could be reached in a sealing layer of till and 10 w. % GLD from different paper mills.

**Methods**

*Materials for the laboratory study*

Three tills with different particle size distributions were used in the laboratory study. Till 1, a fine grained till (34 % < 63µm; 2.6 % < 2µm) was collected at a till carrier in Boden, northern Sweden. Till 2, a sandy till (14 % <63µm) was collected from another till carrier outside of Boden and till 3, also a fine grained till but with a higher clay content compared to till 1 (35 %<63µm; 4.3 %<2µm) was collected in Luleå, northern Sweden. The materials were collected in plastic buckets with lids.

The GLD used in the laboratory study came from the Smurfit Kappa paper mill in Piteå, northern Sweden. The GLD was collected in sealed plastic containers to preserve the water content of the material.

The total solid contents (TS) of the materials were determined with the SIS standard SS-EN 14346:2007.

The tills were sieved to below 20 mm and air dried to lower the water content. They were then mixed with 5, 10, 15 and 20 wt. % of GLD. The weight percent was calculated towards a dry till and a natural moist GLD. The mixing was carried out by hand with a small shovel until the mixture was homogenised. Till 3 was used naturally moist (TS 90.8 ±0.8 %, n = 6) when analysing hydraulic conductivity.

*Particle size distribution*

The till was washed and dry sieved according to SS-EN 933-1:2012 to obtain the weight percentage of fines in the material. The sieve used was a mechanical Retsch AS 200 sieve with amplitude 2.2 mm/“g”. The sizes of the sieves were 12.5, 10, 8, 5, 4, 2, 1, 0.5, 0.25, 0.125 and 0.063 mm.

Particle size distributions for the fines were done by laser diffraction analysis on triplicate samples of each material using a CILAS Granulometer 1064 (CILAS, Orléans, France). The particle size distribution was calculated using the CILAS software.
Proctor compaction

Proctor compaction was carried out according to standard SS-EN 13286-2:2010. For the proctor compaction experiments the till was air dried at least 24 hours prior to mixing with GLD. The GLD was naturally moist for till 1 and 2, but air dried for till 3.

Hydraulic conductivity

HC measurements were conducted on a moist till (TS 91±1 %, n=24) with 5, 10, 15 and 20 wt. % addition of GLD. The constant head-method was used in air tight cylinders with a volume of 943 cm$^3$. The walls of the cylinders were sealed with a thin layer of bentonite. The mixtures inside the cylinder were compacted with proctor compaction in five equally thick layers with a falling weight of 4.54 kg, falling 45 cm 25 times on each layer. Dry density and water content of the samples were calculated from the “left over mixture” when compacting the samples. The values are therefore only an estimation of the values in the actual sample. Water was lead to the bottom of the cylinder with a hydraulic gradient of 8.3 for till 1 and 2, 12.5 cm for till 3. The water passing through the cylinder was collected in a plastic bottle, sealed from the top to prohibit evaporation. The plastic bottle was weighed regularly and the time was noted to measure the velocity of the water passing through the sample. HC was calculated using Darcy’s law.

Pilot cell construction

In August 2014 a 400 m$^2$ cell was constructed in Boden, northern Sweden as part of a pilot-scale study. The pilot cell consisted of 0.2 m foundation of till, 0.5 m sealing layer and 1.5 m protection layer (Figure 1). The sealing layer consisted of a mixture between till and 10 w. % GLD from different paper mills and were compacted with different number of passes with an excavator-mounted compactor. The TS of the different GLD ranged from 43 to 56 %, with the GLD from Metsä Board paper mill being wettest and the GLD from Domsjö being driest (Table 1). The protection layer consisted of a fine grained till (~30 % < 63 µm). Density was measured on the surface of the sealing layer by water volumetry and with a Troxler nuclear density gauge at a depth of 50 and 250 mm. Material was also compacted in the laboratory with the proctor compaction method.

![Figure 1](image_url)

**Figure 1** The pilot cell at Boden, northern Sweden which consist of six different cells with a 0.5 m sealing layer and a 1.5 m thick protection layer on top of that. The sealing layer consist of till and 10 w. % of GLD from different paper mills. The protection layer consist of a fine grained till.

**Table 1** Overview of the selected materials, the thickness of the sealing layers, the number of passes with an excavator-mounted compactor and total solids (TS) of GLD from different paper mills.

<table>
<thead>
<tr>
<th>GLD (Paper mill)</th>
<th>Cell 1</th>
<th>Cell 2</th>
<th>Cell 3</th>
<th>Cell 4</th>
<th>Cell 5</th>
<th>Cell 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Smurfit Kappa TS= 46±3 %</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.25 GLD/Till</td>
</tr>
<tr>
<td>SCA Obbola TS= 49±3 %</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.25 Till</td>
</tr>
<tr>
<td>Domjö TS= 56±3 %</td>
<td>6 and 9</td>
<td>6</td>
<td>6</td>
<td>6</td>
<td>3</td>
<td>6</td>
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</table>

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<tr>
<th>Thickness of sealing layer (m)</th>
<th>0.25 GLD/Till</th>
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<tbody>
<tr>
<td>Compaction (nr of passes)</td>
<td>0.25 Till</td>
</tr>
</tbody>
</table>
Results

Laboratory study

The particle size distribution of the tills shows that the GLD has 100 % of fines (<63µm), of which ~10 % is in the clay fraction (<2µm; Mäkitalo et al. 2014). Till 1 is a fine grained till and consists of around 34 % fines of which 2.6 % is in the clay fraction. Till 2 is a sandy till and consist of around 14 % fines of which only 0.7 % is in the clay fraction. Till 3 is a clayey till and has the same percentage of fines as till 1, but a higher percentage of these are in the clay fraction, 4.3 % compared to 2.6 % in till 1 (Table 2).

The performed proctor tests shows that the highest dry density was reached with the pure till; 2.1 g/cm³ in the fine grained till (till 1) and 2.0 g/cm³ in the sandy till (till 2). The maximum dry density decreases with increasing addition of GLD in the mixture; from 2.1 to 1.9 g/cm³ in the fine grained till, 2.0 to 1.9 g/cm³ in the sandy till and down from 2.6 to 2.5 g/cm³ in the clayey till (Figure 1 and Table 2).

The optimal water content after compaction increased from 8-16 % with increasing amount of GLD added to the till (Figure 2).

In the fine grained till (till 1) the HC first decreased from 3E-08 to 2E-08 m/s with 5 w. % addition of GLD to then increase up to c. 7E-08 m/s with 10 w. % or higher addition of GLD in the mixtures (Figure 3). In the sandy till (till 2) the HC decreased when adding up to 20 w. % of GLD (from 7E-8 to 4E-8 m/s), with the lowest values (2E-8 m/s) with 5 to 10 w. % of GLD in the mixture. The HC in the clayey till (till 3) increased from 3E-10 to 5E-09 m/s when adding up to 20 w. % of GLD (Figure 3). The dry density after compaction of the HC samples decreased with increasing addition of GLD to the till; from 2.01 ± 0.05 to 1.87 ± 0.03 g/cm³ in the sandy till and down from 2.12 to 1.67 g/cm³ in the clayey till when adding up to 20 w. % of GLD (Table 2). The molding water content of the HC samples increased with increasing percentage of GLD added, from 9 to 21 % for adding up to 20 w. % of GLD. The increase in water content was greater for the clayey till compared to the fine grained- and sandy till (Table 2). The water contents of the mixtures were greater than the optimal water contents which were determined by proctor compaction (Figure 2 and Table 2). The molding water content of the samples tested for HC are for pure till 0-2 % wet of the optimum molding water content, 2-5 % wet of optimum for 5 w. % addition of GLD, 3-5 % wet of optimum for 10 w. % addition of GLD and 5-7 % wet of the optimum molding water content for 15 w. % of GLD addition.

Table 2

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Hydraulic conductivity (HC), compaction properties, fines/clay content and total solids (TS) of the materials used in this study. The dry density and molding water content of the samples tested for HC are an estimation from the soil left over after compaction.</th>
</tr>
</thead>
<tbody>
<tr>
<td>w. % GLD</td>
<td>Hydraulic conductivity (HC)</td>
</tr>
<tr>
<td></td>
<td>Average HC (m/s)</td>
</tr>
<tr>
<td>Till 1 (Fine grained till)</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>5</td>
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<td></td>
<td>10</td>
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<td></td>
<td>15</td>
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<td></td>
<td>20</td>
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<tr>
<td>Till 2 (Sandy till)</td>
<td>0</td>
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<td></td>
<td>5</td>
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<td>10</td>
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<td></td>
<td>15</td>
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<td></td>
<td>20</td>
</tr>
<tr>
<td>Till 3 (Clayey till)</td>
<td>0</td>
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<tr>
<td></td>
<td>5</td>
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<tr>
<td></td>
<td>10</td>
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<tr>
<td></td>
<td>15</td>
</tr>
<tr>
<td>GLD</td>
<td>1E-08±7E-09*</td>
</tr>
</tbody>
</table>

*(Mäkitalo et al 2014)
Pilot cell study

Dry density is an indicator of the compactness of a material at a given volume. Based on the proctor compaction test performed on the different mixtures, a dry density of 1.8 g/cm³ was set as a limit for a high degree of compaction. Density measurements of the sealing layer of the pilot cell shows that the dry density was above the required at a depth of 250 mm when using Troxler apparatus for all cells (Figure 4). Proctor compaction tests shows similar results as the Troxler. At the surface, the till alone reaches the required 1.8 g/cm³, but the till and GLD mixtures does not reach up to this value. However, the compaction is expected to have increased after the application of the protection layer. The dry density at 50 mm depth is lowest in the cells with GLD from Metsä Board paper mill (cell 4-6), the GLD that had the highest water content (Table 1).
Discussion

The proctor compaction curve in Figure 2 shows that the maximum dry density decreases as more GLD is added to the sieved till (<20 mm). This is likely due to the properties of the GLD, i.e. its high water content, porosity and flow stress. The high porosity and water content of the GLD leads to liquefaction when intensive compaction energy is applied and water is released which makes the material difficult to compact (Mäkitalo et al. 2015b). The proctor compaction curves also show that the maximum dry density increases with higher clay content in the tills, which is expected (Figure 2).

The dry density for the clayey till (till 3) is higher than for the fine grained till (till 1), even if the content of fines are similar (Table 2), which shows that a higher clay content is important to reach a higher dry density.

Only the mixture that consisted of a clayey till (till 3) had a HC below 1E-08 m/s (Figure 3), which is a required minimum for a sealing layer on top of mine waste in northern Sweden. The HC in this mixture also reached below 1E-09 with up to 5 w. % of GLD added, which is recommended by (Höglund et al. 2004) for a sealing layer on top of mine waste. A decrease of the HC was expected with an addition of GLD as the fine grained material in the mixtures increased (Benson et al. 1994; Benson and Trast 1995; Leroueil et al. 2002). A high amount of clay minerals generally corresponds to a decrease in the size of microscale pores which controls the flow in soil compacted wet of the line of optimums, which leads to a low hydraulic conductivity (Benson and Trast 1995). A decrease in HC is seen for the fine grained and sandy tills (till 1 and 2) with addition of GLD up to a w. % of 5-10 (Figure 3). The lack of decrease in HC with increasing amount of GLD for the clayey till (till 3) is likely due to that the clay particles in the till alone fill up the micropores leaving no place for the GLD. The addition of GLD is therefore only deteriorating the compaction degree of the mixture due to an increase in water content, which leads to a lower HC. The same mechanism is believed to be the reason to the increase in HC when more than 5 w. % and 10 w. % of GLD is added for the fine grained and the sandy till respectively. Composition of the soil has shown to be an important factor that can control the hydraulic conductivity of a soil, especially for compaction wet of the line of optimum water content where flow is controlled by the size, shape and connectivity of microscale pores (Benson et al. 1994). The reason for the much lower HC in till 3 compared to till 1 (Figure 3) is likely the higher clay content of till 3 (4.3 compared to 2.6 %), as the percentage of fines is similar in the two different tills (Table 2). A study conducted by (Benson et al. 1994) showed a strong relationship between clay content and hydraulic conductivity and a weak relationship between fines and hydraulic conductivity when studying clay. However, in contradiction to this (Benson and Trast 1995) also saw a weak relationship between fines and hydraulic conductivity in their study of different clays, but no relationship between clay content and hydraulic conductivity was found. The increase in HC in the clayey till (till 3) with an addition of GLD, and in the fine grained and the sandy till (till 1 and 2) with an addition of GLD above 5 and 10 w. % respectively is likely also due to the compaction properties of the mixtures. In addition to the clay content HC has also shown to be highly dependent on the
degree of compaction, with decreasing HC with increasing degree of compaction (Benson et al. 1994; Leroueil et al. 2002; Watabe et al. 2000). However, low HC values cannot be reached if the material is unable to be compacted due to excessively high water content which is the case when adding more than 10 w. % of GLD (Figure 2 and Figure 3). A study conducted by (Benson and Trast 1995) on thirteen compacted clays shows that HC is sensitive to molding water content, where the lowest HC was reached at molding water content of 1-2 % wet of the line of optimums. The molding water content of the samples tested for HC are for pure till 0-2 % wet of the optimum molding water content, 2-5 % wet of the optimum for 5 w. % addition of GLD, 3-5 % wet of optimum for 10 w. % addition of GLD and for 15 w. % of GLD addition the water content is 5-7 % wet of the optimum molding water content (Figure 3 and Table 2). Around 10 w. % of GLD seems to be a threshold and with increasing amount of GLD above that the water content increases beyond the 1-2 % wet of optimum that according to (Benson and Trast 1995) generates the lowest HC. The properties of the GLD discussed in the beginning of this chapter are likely also contributing to the materials difficulties to be compacted.

The unexpectedly low decreases or no decrease in HC when adding GLD to the tills might be due to the method of compaction used, i.e. standard proctor compaction. Studies conducted by Mäkitalo et al. 2015b shows that mixing time and mixing effort increases the water content and porosity of the till-GLD mixtures used in that study. A result from this may be an increase in HC. A standard proctor compactor may not be the best choice when working with GLD. In future HC samples compacted with a lighter weight and a shorter falling height should be studied and compared to the results from this study.

Comparing the results from the laboratory studies and the materials compacted in the pilot cell shows that the dry density reached in laboratory is difficult to reach in the field (Figure 2 and Figure 4). The lower dry density in cell 4-6, with GLD from Metsä Board is likely due to that this GLD had the highest water content of the GLD’s used in the pilot cell (Table 1). However, as shown in the results from the hydraulic conductivity (Table 2) a decrease in dry density does not mean that the hydraulic conductivity will automatically increase. For the tills with low clay content (till 1 and 2) the HC decreases even if the dry density decreases when adding GLD to the till.

**Conclusions**

The HC of the different tills improves with addition of 5-10 w. % of GLD, except from the till that had a higher clay content and already a low HC without addition of GLD. The decrease in the tills with lower clay content was however not enough to reach below the required 1E-08 m/s. The decrease of HC in a till with an addition of GLD is limited by the decreasing compaction properties with an increase of GLD in the mixtures, mainly due to the higher water content of the GLD. The laboratory study further concludes that the percentage of fines in the till decreases the HC and increases the compaction properties of the till, but the clay content seems to play a major role in determining compaction properties and HC.

The pilot cell study concludes that it might be difficult to compact a sealing layer made of a till and 10 w. % of GLD in field to a high compaction degree. However, it does not necessary mean that the hydraulic conductivity of the sealing layer will increase. The laboratory study shows the opposite trend, a decrease in HC with a decrease in dry density for tills with low clay content.

The main conclusion of the study is that addition of GLD can be an alternative option to improve the properties of a local till that alone does not meet the requirements for HC. Using of GLD in a remediation of a mine is beneficial for both the mining company and the industry providing the industrial residue. However, the properties of the till are important to consider. For tills with a high HC, the improvement with an addition of GLD may not be enough to meet the requirements and for tills with a high original content of clay, addition of GLD is only detrimental. It is therefore crucial to characterize the materials that are to be used in a sealing layer before applying them. Long term effects of the material in a sealing layer needs further studies. Future studies will therefore include further evaluation of the pilot-scale study and a field study will be conducted on a waste rock dump covered with a sealing layer of a till/GLD mixture.
Acknowledgements

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