Green Liquor Dregs as Sealing Layer Material to Cover Sulphidic Mine Waste Deposits

Maria Mäkitalo
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Cover Image: Green liquor dregs
Abstract

Waste rock and tailings generated by sulphide ore mining often contain large amounts of iron sulphides which oxidize when exposed to atmospheric oxygen and may generate acidity. In the absence of alkaline minerals to neutralize this acidity, elements including harmful heavy metals become mobile. Clearly, it is a high priority for mining operations to reduce the impact of mining waste on the environment. New research aimed to take advantage of industrial rest products to inhibit acid mine drainage has yielded some reason for optimism. The recycling of chemicals in sulphate pulp mills yields green liquor dregs (GLD). The fact that GLD have a low hydraulic conductivity and are alkaline opens the possibility of using it for construction of sealing layers for sulphidic mine waste.

The study consists of two parts. The aim of the first part was to characterize the GLD and evaluate their suitability for sealing layer purposes. GLD were characterized physically, mineralogically and chemically to define variations in the properties of the material and to evaluate if they can act as a potential candidate for construction of sealing layers. Compared to lime, the pure GLD appear to have a higher porosity and surface area even though both materials have comparable particle size. The shear strength may, however, be insufficient. In cover applications, where high compaction grade and low hydraulic conductivity are desirable, mixing additives to GLD is necessary to improve the material properties. Based on the characterization results, the difference between batches is fairly small both mineralogically and physically. GLD could be an alternative to traditional sealing layers made of till since it was shown to have relatively low hydraulic conductivity and high water retention potential. The small particle size and high buffer capacity makes it a better candidate than till which usually varies in size and hydraulic conductivity. There is a chemical variation of the material but the element content does not seem to be an environmental concern.

The aim of the second part of the study was to improve the performance of the GLD by blending them with other rest products. Geotechnical and geochemical investigations were performed on GLD mixed with tailings. Humidity cell tests were used to study the effect of GLD on the mobility of elements considered to be major environmental issues in the tailings. By adding tailings to GLD, the shear strength improved 2-3 times after 1 month of curing. The water retention capacity remained at a high level. Humidity cell tests revealed that a 50/50 mix of GLD and tailings has a direct effect on the metal leaching from tailings. The alkaline capacity of the pulping waste raised the pH, thereby stabilizing the tailings and reducing the leaching of Al, Cd, Cu, Ni, Co, Cr and Mn. The amount of leached elements could be directly related to the pH during the test. Elements that showed an increase of leaching as a result of the application of GLD were Mo and As. This is explained by the chemical behavior of these elements and their tendency to become mobile at high pH.

In summary, GLD have the potential to both reduce the amount of leachate generated in tailings and, due to their alkaline property, improve the leachate quality by decreasing the metal mobility. However, restrictions occur when GLD are blended with tailings containing large amounts of As and Mo since an increased leaching may be expected. Further research will focus on the aging of the material and its long-term stability.
**Sammanfattning**

Gräberg och anrikningssand som genereras från brytning av sulfidmalm innehåller ofta stora mängder järnslifter som oxideras när de utsätts för atmosfärrens syre och då kan generera syra. Tungmetaller kan bli mobiliserade av avsaknad av alkaliska mineral som kan neutralisera denna syra. Att minska miljöeffekterna från gruvavfall är en hög prioritet från gruvbolagens sida. På senare år har forskning i att använda restprodukter för att minska det sura metallhaltiga lakvatten som gruvavfall kan generera och dra nytta av reaktionsprodukternas reaktivitet givit hoppfulla resultat. Grönlutslam (GLS) är en restprodukt som uppstår när kemikalierna i sulfatmassabruken återvinns. Slammet innehåller höga halter meso och är alkaliskt samtidigt som det har en låg hydraulisk konduktivitet, vilket öppnar möjligheten att använda det för konstruktion av tätskikt för sulfidhaltigt gruvavfall.


**Sammanfattningsvis** har GLS potential att både minska mängden lakvatten som genereras från anrikningssand och tack vare dess alkaliska egenskaper förbättra kvaliteten på lakvatten genom minskad mobilitet av metaller. Försiktighetsåtgärder bör vidtas om GLS ska blandas med gruvavfall rikt på Mo och As eftersom det kan generera en ökad utlåtning av dessa metaller. Fortsatt forskning kommer att fokusera på materialets äldrande och dess stabilitet på lång sikt.
List of articles

Papers included in the thesis referred to by roman numbers:
I. Characterization of green liquor dregs for potential usage as a barrier for sulphidic mine waste.
Makitalo, M., Jia, Y., Maurice, C., Öhlander, B
Submitted manuscript

II. Improving green liquor dregs barrier properties for application on sulphidic mine waste.
Makitalo, M., Stenman, D., Ikumapayi, F., Maurice, C., Öhlander, B.
Manuscript

Additional related papers not included in the thesis:


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1. Scope of thesis
The primary objective was to evaluate the potential of using green liquor dregs (GLD) in sealing layers for sulphydic mine waste. GLD are wastes from the paper mill and no attempt is made to control their composition. Quality monitoring and material characterization are generally limited. The properties of various batches of GLD were studied to understand the effect of the variation on the barrier function for the remediation of mine waste. Improvement of GLD properties by mixing them with other materials have been carried out as well as an evaluation of the geochemical interactions between GLD and sulphydic mine waste.

2. Introduction
2.1 Mining in Sweden
Sweden has a long history of mining, over 1000 years. It has been and still is an important source of income. In the 1920ies there were almost 500 mines in production in Sweden. There are today 13 active mines. Three are iron ore mines and 10 are sulphide ore mines. Sweden produces a wide variety of commodities from gold to coal. It is Europe’s number one producer of iron (92%) and lead (32%) and is the second leading producer of zinc (26%), silver (18%) and gold (33%). Sweden is third in copper production (10%) (SGU, 2011). Shifts in the global market place are driving high demand of metals as large third-world countries like China and India modernize. Exploration in Sweden as well as in the rest of the world has seen a steady increase since 2002 (SGU, 2011).

2.2 Environmental impact of mining
It has long been known that mining may have detrimental effects on soil, water and biota. One of the major challenges is the large amount of mine waste that is generated. The total production of mine waste (tailings and waste rocks) in Sweden today is 80-100 million tons per year. Of this, a large part comes from sulphide ore mines. Over the years 700 million tons of tailings and waste rock from sulphide ores have been deposited and that number continues to increase. The impact of mining waste on the surroundings needs to be very small. This puts high demands on the management of mining operations, as well as on methods for waste disposal and remediation of waste deposits. Environmental authorities in Sweden require remediation methods that function over very long time periods without maintenance (next glaciation perspective). The Swedish Environmental Protection Agency in cooperation with the County Administrative Boards have assessed that there are 600 sites that are in need for remediation. Of these, 30 are assessed to be a major risk for health and environment and 100 presents a substantial risk. The cost for remediation of mining waste is estimated to 2-3 billion Swedish crowns (US$300-450 million). Most of this cost will fall on the Swedish government. (Swedish Environmental protection agency 091008)

3. Oxidation of sulphydic mine waste
Waste rock and tailings from sulphide ores often contain pyrite or pyrrhotite that will oxidize when exposed to atmospheric oxygen and water (Fig. 1). This generates a metal-rich acidic leachate (INAP, 2009).
When tailings containing pyrite are exposed to oxygen and water, the pyrite oxidizes to form sulfates and acidity (reaction 1) (Höglund et al., 2006). The oxidation of pyrite is summarized by the following reactions:

\[
\begin{align*}
\text{FeS}_2(s) + 7/2\text{O}_2(g) + \text{H}_2\text{O} & \rightarrow \text{Fe}^{3+}(aq) + 2\text{SO}_4^{2-}(aq) + 2\text{H}^+(aq) \quad (1) \\
4\text{Fe}^{2+}(aq) + \text{O}_2(g) + 4\text{H}^+(aq) & \rightarrow 4\text{Fe}^{3+}(aq) + 2\text{H}_2\text{O} \quad (2)
\end{align*}
\]

Hydrolysis of generated \( \text{Fe}^{3+} \) in reaction 2 may occur and ferric hydroxide is formed (reaction 3). The \( \text{Fe}^{3+} \) may also oxidize pyrite (reaction 4).

\[
\begin{align*}
\text{Fe}^{3+}(aq) + 3\text{H}_2\text{O} & \rightarrow \text{Fe(OH)}_3 + 3\text{H}^+(aq) \quad (3) \\
\text{FeS}_2(s) + 14\text{Fe}^{3+}(aq) + 8\text{H}_2\text{O} & \rightarrow 15\text{Fe}^{3+}(aq) + 2\text{SO}_4^{2-}(aq) + 16\text{H}^+(aq) \quad (4)
\end{align*}
\]

### 4. Prevention of acid rock drainage

To prevent metal leaching or acid rock drainage (ARD) there are various techniques to remediate mine waste sites. Oxygen is the most important factor for oxidation and if it can be prevented from reaching the mining waste, oxidation rates will slow down (Höglund et al., 2004). The traditional strategy to reduce ARD generation is to prevent oxygen from reaching the waste either by applying a water cover (Holmström and Öhlander, 1999) or by covering the tailings with a soil sealing layer (Lindvall et al., 1997).
Active treatment methods, such as neutralization of already formed ARD with CaCO₃ with the aim of making iron precipitate and formation of gypsum (reaction 5), are also used but they require monitoring and maintenance over a long time, which is costly and not sustainable.

\[
\text{Fe}^{3+}(aq) + 2\text{SO}_4^{2-}(aq) + \text{H}^+(aq) + 2\text{CaCO}_3(s) + 5\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_3(s) + 2\text{CaSO}_4\cdot2\text{H}_2\text{O}(s) + 2\text{CO}_2(g) \quad (5)
\]

### 4.1 Sealing layer as prevention of ARD

To prevent oxygen from reaching the tailings, a cover is applied to prevent oxidation. The cover is constituted of several layers (Fig. 5). A sealing layer with low hydraulic conductivity is applied on top of the tailings. Sometimes a drainage layer is applied on the top or/and below this layer. On top of the sealing layer there will be a ~1.5 m protective layer (in Sweden the most common material is till) and this is usually followed by a vegetation layer.
The most important quality of a material used for sealing layer purposes is that it efficiently minimizes oxygen diffusion and transport. To keep the oxygen diffusion at a low level, it is advantageous if the material is water saturated. The reason for this is that the concentration of O\textsubscript{2} in water is 30 times less than in air and the free diffusion coefficient for oxygen is 10 000 times smaller in water than in air according to Fick’s law (Mbonimpa et al., 2003). One way to assess a materials ability to hold water is to perform suction tests, also called water retention capacity tests. However, in the literature this test is not often used. Studies often focus on the materials hydraulic conductivity. Hydraulic conductivity is a factor that is closely related to the oxygen transport. Low hydraulic conductivity reduces oxygen diffusion, which slows down pyrite oxidation. The EU Landfill Directive 1999/31/EC (EU, 1999) requires a hydraulic conductivity of 1x10\textsuperscript{-9} m/s for sealing layers on municipal landfills for hazardous waste. However, this regulation does not apply for mine wastes. Although there are no requirements of a minimal hydraulic conductivity, 1x10\textsuperscript{-9} m/s is generally aimed for when creating sealing layers (Höglund et al., 2004). A high water retention capacity together with a high grade of saturation prevents air-entry, and thereby oxygen to reach the waste. This may limit oxidation of the tailings more efficiently than a material that exhibits a hydraulic conductivity of 1x10\textsuperscript{-9} m/s or lower suggesting that the focus has to be on both the ingress of precipitation into the waste to reduce seepage of leachate as well as minimizing the risk of oxygen transport (of oxygen dissolved in water), and the ability to keep moisture to avoid desiccation cracks in which water and oxygen can travel and reach the waste.

Other desirable qualities are the ability to resist change and degradation by micro-organisms. The material also has to have the strength to prevent it from sliding. Finally, it may also be advantageous if it can react with the waste and retain heavy metal ions.

In recent years, research has been performed to find a use for waste materials such as sewage sludge, fly ash and green liquor dregs to inhibit the acid mine drainage and take advantage of the materials reactive nature.

5. Green liquor dregs

5.1 Origin

Most paper mills today use the sulphate production process (Fig. 6.). The process involves treating wood chips with sodium hydroxide and sodium sulphide to disrupt the chemical bond between cellulose and lignin thereby liberating the cellulose. The major advantage with this method is that the inorganic chemicals used in the process can be recycled and reused in the recovery boiler. However, large amounts of waste material are released. Green liquor dregs (GLD) are a rest product that comes from the recycling of the chemicals. At the sulphate pulp mills it is the largest waste fraction and usually all of it is deposited in landfills. GLD are classified as a non-hazardous chemical waste by the Swedish EPA (SFS, 2001:1063). The world’s largest producers of sulphate mass are USA, Canada, China, Finland and Sweden respectively (Skogsindustrierna, 2006). In Sweden ~134 000 tons of GLD (dry matter content) are produced yearly (Arm et al., 2007).

5.2 Use of green liquor dregs

Since the landfilling of GLD is costly, reusing the material would be a great gain for the pulp and paper mill industries. They have been used in several different sanitary landfill cover applications (Pousette and Mácsik, 2000; Hargelius, 2008). Pöykö et al. (2006) showed that GLD could act as a neutralizing agent for acidic wastewater. GLD have previously been used in applications such as a stabilization agent for road construction (Toikka, 1998). In recent years, studies have been performed on how to use lime waste to reduce metal leaching from mine tailings (Herbert et al., 2007; Calace et al., 2005; Sartz, 2010). Together with the fact that GLD are alkaline and have been
shown to have a low hydraulic conductivity (Toikka, 1998), the possibility arises of using them for construction of sealing layers for sulphidic mine waste.

Fig. 6. Kraft production process

6. Material and methods

6.1 Rest products from the paper mill

GLD and bark sludge (BS) were provided by Billerud Karlsborg pulp and paper mill, situated near Kalix in Northern Sweden. The GLD were collected from containers before deposition. The sampling took place at four different occasions and ~ 30 kg were collected each time and were stored in sealed plastic containers at room temperature. The BS is the dewatered fraction released from the stem when rinsing the logs. It is a mixture of bark, sand and needles. It was collected in sealed plastic bags à 0.75 kg/bag and stored at -20°C.

6.2 Tailings

Tailings were provided by the mining company New Boliden and originate from the Kristineberg mine in Sweden. They were taken after the addition of lime at the flotation process, a method used to raise the pH to enable recovery of the valuable minerals (Bolin et al., 1991). Kristineberg mine is situated 120 km west of Skellefteå. The ore is rich in sulphur, with a reported content of 25.9% (Årebäck et al., 2005). The major minerals found are pyrite, sphalerite, chalcopyrite and galena, with trace amounts of pyrrhotite (Årebäck et al., 2005).
6.3 Experimental
A physical, mineralogical and chemical characterization of GLD has been carried out with the aim of defining variations in the properties of the material and to determine if they are a viable candidate for construction of sealing layers for sulphidic mine waste. The composition was studied with elemental analysis and XRD. The microstructure was studied with BET, particle size analysis and SEM. Surface characteristics were analyzed by electrophoretic mobility. The hydraulic conductivity of GLD and admixtures have been analyzed. Evaluation of the buffer capacity potential and how it can chemically treat tailings with high leaching potential was assessed. Leaching tests are commonly used to assess environmental effects of waste. However, standard leaching test developed for waste characterisation are not optimal for GLD because of their sticky consistency and low permeability. Humidity cell tests useful to assess GLD-treated tailings have been developed.

7. Findings
The material characterization performed on GLD revealed a small particle size throughout the material, and consequently a high porosity (Paper I). The study revealed variations of the quality of the GLD retrieved. Variations in the chemical and mineral composition of the GLD were observed and are believed to depend both on the origin of the wood and the efficiency of the GLD retrieval. Table 1 shows the mean values of the elemental content for four batches of GLD. GLD trap non-process elements (NPE), such as Mg, Si and Al originating from the wood (Lundqvist et al., 2006; Ulmgren, 1987). GLD have a high resistance to filtering. Therefore, a cloth covered with lime is used to filter the dregs since the resistance is lower for lime. When GLD is removed from the filter a slice of lime from the filter is also removed (Ek et al., 2009). This leads to various amounts of lime mixed with the green liquor, which strongly influences the final composition of the dregs. Increasing dry content is correlated to the amount of lime that is scraped off from the pre-coat. The dry content varies widely. The concentrations of NPE increase when small amounts of lime is present in the GLD and the dregs are wetter (Paper I). The surface area, the density and the porosity varied significantly between the batches studied (Paper I). No significant effect regarding hydraulic conductivity, pH and particle size compared to the natural variation observed in the replicates was noted. Further, GLD have a high neutralization potential equivalent to 750 g CaCO$_3$ per kg GLD (Paper I). GLD are therefore believed to be able to mitigate the effect of ARD, to prevent the formation of ARD, and to and stabilize the mine waste. The properties of the GLD are beneficial for the use in sealing layer applications (Table 2) but the observed variation may complicate the use on a large scale. Therefore potential negative effects of the quality variation on the intended application of the material should be addressed. There are two main limitations to the use of GLD for the remediation of mine waste:

<table>
<thead>
<tr>
<th>ELEMENT</th>
<th>SAMPLE</th>
<th>GLD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry matter</td>
<td>%</td>
<td>43± 7</td>
</tr>
<tr>
<td>Si</td>
<td>mg/kg</td>
<td>8548± 3070</td>
</tr>
<tr>
<td>Al</td>
<td>mg/kg</td>
<td>5198± 3059</td>
</tr>
<tr>
<td>Ca</td>
<td>mg/kg</td>
<td>270256± 41558</td>
</tr>
<tr>
<td>Fe</td>
<td>mg/kg</td>
<td>5424± 2318</td>
</tr>
<tr>
<td>K</td>
<td>mg/kg</td>
<td>2855± 584</td>
</tr>
<tr>
<td>Mg</td>
<td>mg/kg</td>
<td>51163± 14146</td>
</tr>
<tr>
<td>Mn</td>
<td>mg/kg</td>
<td>12360± 1532</td>
</tr>
<tr>
<td>LOI 1000°C</td>
<td>% TS</td>
<td>41± 1</td>
</tr>
<tr>
<td>As</td>
<td>mg/kg</td>
<td>0.3± 0.1</td>
</tr>
<tr>
<td>Cd</td>
<td>mg/kg</td>
<td>5.7± 1.9</td>
</tr>
<tr>
<td>Co</td>
<td>mg/kg</td>
<td>4.4± 1.0</td>
</tr>
<tr>
<td>Cr</td>
<td>mg/kg</td>
<td>98± 20</td>
</tr>
<tr>
<td>Cu</td>
<td>mg/kg</td>
<td>149± 48</td>
</tr>
<tr>
<td>Hg</td>
<td>mg/kg</td>
<td>0.040± 0.0</td>
</tr>
<tr>
<td>Ni</td>
<td>mg/kg</td>
<td>45± 11</td>
</tr>
<tr>
<td>Pb</td>
<td>mg/kg</td>
<td>3.7± 1.5</td>
</tr>
<tr>
<td>S</td>
<td>mg/kg</td>
<td>12839± 4268</td>
</tr>
<tr>
<td>Zn</td>
<td>mg/kg</td>
<td>1214± 420</td>
</tr>
<tr>
<td>CaO</td>
<td>% TS</td>
<td>37± 6</td>
</tr>
</tbody>
</table>
(1) the material needed to construct a sealing layer becomes less economical as the transport distances increases

(2) the GLD have poor mechanical properties which make them inappropriate to use in slopes. To improve the mechanical properties, GLD have to be mixed with a structure material.

Table 2. Properties of GLD. The number given after the property indicates the number of batches used for the calculation of the average.

<table>
<thead>
<tr>
<th>Properties</th>
<th>GLD</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>10.4 ± 0.5</td>
</tr>
<tr>
<td>Surface area (m²/g)</td>
<td>18 ± 4</td>
</tr>
<tr>
<td>Bulk density (g/cm³)</td>
<td>0.56 ± 0.16</td>
</tr>
<tr>
<td>Compact density (g/cm³)</td>
<td>2.57 ± 0.00</td>
</tr>
<tr>
<td>Porosity [%]</td>
<td>78 ± 6</td>
</tr>
<tr>
<td>Hydraulic conductivity (m/s)</td>
<td>1x10⁻⁶ ± 7x10⁻⁷</td>
</tr>
<tr>
<td>Dry matter content [%]</td>
<td>43 ± 7</td>
</tr>
<tr>
<td>Particle size, d₅₀ (µm)</td>
<td>11.9 ± 3.9</td>
</tr>
<tr>
<td>Buffer capacity to maintain a pH&gt;6 (mmol H⁺/g)</td>
<td>18.5 ± 1.0</td>
</tr>
<tr>
<td>Zetapotential (mV)</td>
<td>Neg. over the entire pH range</td>
</tr>
</tbody>
</table>

GLD may be mixed with tailings to improve the mechanical properties (Paper II). Mixing GLD and tailings is one way to reduce GLD consumption per square meter of sealing layer (GLD is “diluted” with tailings), and consequently makes it more economical. The results of the mineralogical and chemical characterization of the GLD also revealed that the particles have a negative surface charge at pH above 2 (zeta potential), i.e. they are able to bind cations present in the ARD (Paper I). However, the mix of GLD and tailings showed an increased hydraulic conductivity (Paper II). This may not be a problem since the hydraulic conductivity is relatively low and suction tests showed that the capillarity forces in GLD bind water strongly to the particles preventing it from drying (Paper I & II). GLD blended with tailings showed only a small negative effect on the water retention capacity compared to GLD alone (Fig. 7) (Paper I & II).

![Fig. 7. Water retention capacity of two batches of GLD and GLD mixed with tailings and bark sludge. Two types of silt are also shown as a reference (Bussière et al., 2003). The area between the dashed lines represents the water retention capacity of five sealing layers made of clayey till reported by Höglund et al. (2004).](image-url)
However, the capacity to retain water is still very large compared to other materials used as sealing layers. Compared to clayey till, the most common material in sealing layers in covers on mine waste in Sweden (Högland et al., 2004), the water retention is 4-5 times higher in the GLD at similar under-pressure. The high water content in GLD and GLD mixed with tailings and the strength of the water bounding are major advantages for the use in sealing layers. This means that the material may stay saturated even at times of drought when used in a sealing layer application. This would effectively prevent oxygen to reach the waste, thereby slowing down the oxidation of the under-laying mine waste. GLD are therefore believed to be an excellent barrier material in the sealing layer. The mixed material would be able to bind metal ions and neutralize ARD (due to its neutralization potential). The alkalinity of the GLD showed to have a direct effect of the stabilization of most elements when blended with tailings. SEM images on GLD mixed with tailings show coating on mineral surfaces (Fig. 8.) It is possible that GLD may enhance the precipitation of secondary minerals such as Fe-oxyhydroxides, resulting in coatings on the reactive pyrite surfaces, thereby making the surfaces less susceptible for oxidation (Perez-Lopez et al., 2007; Huminicki and Rimstidt, 2009).

![GLD, Tailings, GLD + Tailings, Coating on mineral surface](image)

Fig. 8. SEM pictures of GLD, tailings and a GLD/tailings mix. Coating was occasionally visible on the tailings mineral surfaces. Mixing GLD and tailings increased coating on mineral surfaces.
8. Conclusions

GLD could be an alternative to traditional sealing layers made of till since the material proved to have relatively low hydraulic conductivity and a high water retention potential. The small particle size and high buffer capacity makes it a better candidate than till, which usually varies in size and hydraulic conductivity. There is a chemical variation of the material, but element content does not seem to be an environmental concern. However, potential negative effects of the quality variation on the intended application of the material should be addressed. Adding stabilizing materials to the GLD is necessary to increase the shear strength.

Tailings may be added to GLD to improve the shear strength of the material. The alkalinity of the GLD showed to have a direct effect of the stabilization of most elements when blended with tailings. As long as the GLD can buffer the acidity formed by the sulphidic tailings, the metals are expected to be stable. Only when the buffering capacity is consumed do the metals become mobile. By choosing a proportion where GLD can neutralize the acid generating potential of the tailings, it is not likely that the buffering capacity will be exhausted. Due to its water binding capacity it may also reduce mineral oxidation in the underlying waste. Restriction of using the application with tailings rich in As and Mo may need to be considered due to the increase of leaching of these elements at high pH.

9. Future perspectives

1) Experiments of GLD blended with tailings and fly ash as stabilizing materials are being pursued as a potential way to improve the mechanical properties. Humidity cell tests will evaluate the ability to bind metal ions and neutralize ARD.

2) Aged GLD originating from Iggesund pulp and paper board, Sweden were collected at a landfill. The GLD had been deposited since 1998 in an organized pattern making it possible to collect GLD with a spectrum of different ages. Aged GLD were also sampled at Rönnkärverken, Sweden, where it was placed as a sealing layer on top of oxidized tailings for five years (applied in 2006). The tailings are pyrite-rich and originate from Boliden’s copper and gold mining in the Skellefte district. Samples have been collected at the site and investigation of the chemical interactions between GLD and the tailings are being pursued. Solid samples have been taken in profiles through the deposit. Mineralogy, chemical composition, and leachability of metals will be analyzed. Precipitates of secondary minerals such as Fe hydroxides will be studied in detail. Infiltrating water will be sampled in lysimeters, placed in depth profiles.

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11. References


Arm, M., Lindeberg, J., Helgesson, H., 2007. Sammanställning av material och användningsområden. Underlag i Naturvårdsverkets regeringsuppdrag "Återvinning av avfall i anläggningsarbeten" (In Swedish)


Huminicki D.M.C., Rimstidt, J.D., 2009. Iron oxyhydroxide coating of pyrite for acid mine drainage control. Applied Geochemistry 24, 1626–1634


SGU, 2011. Bergverksstatistik (In Swedish)

Skogsindustrierna, 2006. Skogsindustrin- En faktasamling (In Sweden)

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Characterization of green liquor dregs for potential usage as a barrier for sulphidic mine waste

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Abstract
A physical, mineralogical and chemical characterization of green liquor dregs, a rest product from the sulphate paper mills, has been carried out with the aim of defining variations in the properties of the material and to be able to evaluate whether they are a potential candidate for construction of sealing layers for sulphidic mine waste. The difference between batches is fairly small both mineralogically and physically. Green liquor dregs could be an alternative to traditional sealing layers since the material proved to have relatively low hydraulic conductivity and high water retention potential. However, the strength of the green liquor dregs is insufficient for engineering applications suggesting that addition of stabilizing materials may be necessary.
1. Introduction

Mining generates large amounts of wastes consisting mainly of waste rock (rocks with low mineralization that are removed in order to access the ore) and tailings (ground material left over after processing the ore). In Sweden alone >30 mt of waste rock and >30 mt of tailings are generated from sulphide ore mining each year, and the amount is steadily increasing. Over the years ~700 mt of sulphide ore waste have been deposited at various sites (Högglund et al., 2004). Waste rock and tailings generated by the exploitation of sulphide ore often contain large amounts of metal sulphides (often the Fe sulphide pyrite) which oxidize when exposed to atmospheric oxygen. Pyrite oxidation generates acidity. In the absence of alkaline minerals to neutralize this acidity, elements such as heavy metals are mobile. When water reaches the waste it creates a favorable environment for acidophilic bacteria catalyzing the oxidation reaction (Banks et al., 1997). It also transports the metal-rich acidic leachate that is formed, called acid rock drainage (ARD), which may be harmful to human health as well as to animals and plant species.

The traditional strategy to reduce ARD generation is to prevent oxygen from reaching the waste in order to slow down oxidation either by applying a water cover (Holmström and Öhlander, 1999) or by covering the tailings with a soil sealing layer (Lindvall et al., 1997). Active treatment methods, such as neutralization of already formed AMD, are also used but they require monitoring and maintenance over a long time, which is costly and not sustainable. It is important that the material used for sealing layer purposes efficiently minimizes oxygen diffusion and transport as well as the ingress of precipitation into the waste to reduce seepage of leachate. The ability to keep moisture is a desirable quality, to avoid desiccation cracks in which water and oxygen can travel and reach the waste. An ability to resist change and degradation are other important qualities. To avoid high maintenance costs the material should be durable and not be prone to degradation by micro-organisms. If the material used as a sealing layer is placed directly on top of the waste it can be advantageous if it can react with the waste and retain heavy metal ions. Finally, the material has to have the strength to prevent it from sliding. A sealing layer with a high level of water saturation reduces the amount of oxygen transported through to the waste. To understand the diffusion of oxygen through different materials, Fick’s laws of diffusion are often used. In the model the mass flux of oxygen depends on an effective diffusion coefficient of the media, \( D_e \), \( D_e \) is a function of pore size and the free diffusion coefficient among other things. The free diffusion coefficient for oxygen is 10 000 times smaller in water than in air. This, together with the fact that the concentration of \( O_2 \) in water is 30 times less than in air, explains why oxygen transport is slow in saturated materials or through a water cover (Mbbonimpa et al., 2003). Using a material with low hydraulic conductivity minimizes water passing through the cover, and also minimizes the risk of oxygen transport and acid leachate production. To function as an effective barrier against water infiltration, sealing layers for mine waste require a hydraulic conductivity of \( 10^{-7} \text{ m/s} \) (Högglund et al., 2004).

In Sweden, sealing layer construction is commonly based on clayey till (Högglund et al., 2004). In recent years, studies have been performed on how to use lime waste to reduce metal leaching from mine tailings (Herbert et al., 2007; Calace et al., 2005). A material containing a large amount of lime is green liquor dregs (GLD). GLD make up the largest waste fraction retrieved in the chemical recovery cycle at the sulphate pulp and paper mills. Almost all of the GLD produced in Sweden, ~240 000 tonnes, are being landfilled each year. GLD consist of calcium carbonate, \( \text{Na}_2\text{CO}_3 \), \( \text{Na}_2\text{S} \) and insoluble solids (Pöyköi et al., 2006; Martins et al., 2007). However, the quality of the GLD is not constant. In the process, a pre-coat lime filter is used to prevent clogging when the dregs are extracted. The lime content varies depending on how much lime is scraped off from the filter. However, GLD are alkaline independent of the amount of lime they contain. They are classified as
a non-hazardous chemical waste by the Swedish EPA (SFS, 2001:1063). Together with the fact that they are alkaline and have been shown to have a low hydraulic conductivity (Toikka, 1998), the possibility arises of using them for construction of sealing layers for sulphidic mine waste.

We hypothesize that GLD can potentially decrease the leaching of metals in sulphidic mine waste if water seeps through, not only due to the sealing effect, but also because they have the ability to raise the pH in the waste due to the calcium carbonate content and their alkaline nature. Since landfilling of GLD is costly, reusing the material would be a great gain for the pulp and paper mill industries as well as for the mining industry. Although GLD have been used in several different sanitary landfill cover applications (Pousette and Mácsik, 2000; Hargelius, 2008), there have been no studies that show any extensive characterization of the material. In the present investigation green liquor dregs were characterized physically, mineralogically and chemically to define variations in the properties of the material and to be able to evaluate whether they are a potential candidate for construction of sealing layers. The primary objective was to, by a laboratory investigation, examine the material’s capacity to hinder water and reduce oxygen from passing through the material. The aim was also to study GLD’s ability to interact with the mine waste, such as by binding metal ions and raising pH. Finally, the mechanical strength of the material has been studied to assess how it withstands the loads from a protective layer and forces acting on the material.

2. Material and methods

2.1 Material
Sample collection:
GLD were kindly provided by the Billerud Karlsborg sulphate pulp and paper mill in northern Sweden. The sulphate production process is the most common process at paper mill production plants (compared with sulphide pulp). Fresh GLD were scraped from a lime filter and collected from containers before the GLD were deposited. The sampling took place on four different occasions and ~ 30 kg were collected each time and stored in sealed cans at room temperature. The four batches are referred to as A, B, C and D in this article.

2.2 Methods
Dry matter content and paste pH
Dry matter content and paste pH were analyzed in duplicates for all four batches of GLD. Dry matter content, was determined by drying the sample in an oven at 105°C for 24 hours according to Swedish standard SS 028113-1 (SIS, 1981).
GLD was analyzed at the Billerud Karsborg pulp and paper mill on 178 occasions over one year. Ca concentrations were analyzed at the mill for 14 of the samples.

Paste pH was analyzed by mixing a 5 g sample with 10 ml of deionized water according to Weber et al. (2006). The pH was measured with a pH meter (Metrohm Ltd, 704 pH Meter, Herisau, Switzerland).

Particle size
Laser diffraction analysis was conducted using a laser-based CILAS Granulometer 1064 (CILAS, Orléans, France) to obtain the particle size distribution. The sample was suspended in distilled water and dispersed with an ultrasonicator before analysis. The particle size distribution was calculated using the CILAS software (de Boer et al., 1987). Particle size was analyzed in duplicates for all four batches of GLD.
**Zeta potential measurements**

To determine the surface properties of the particles, the pH effect on the electrophoretic mobility was analyzed with a ZetaPhoremeter IV (ZetaCOMPACT, CAD instrumentation, Les Essarts le Roi, France) with attached charge-couple device (CCD) video camera. The analysis was done after suspending the GLD in 1mM KNO₃ and adjusting the pH with either HNO₃ or KOH to values between 2 and 12. The analysis was performed when the solution had maintained the desired pH for 30 min. The results were analyzed with a zeta4 software which calculates the zetapotential based on the particle mobility with the Smoluchowski equation (Xu et al., 2003; Pallier et al., 2010). The determination of the isoelectric point gives insight into the stability of the particles (Hunter, 1981). The analysis was done in triplicates on GLD batch B.

**Total element composition**

The amount of 31 different elements was determined for all four batches of GLD with duplicate samples. The modified EPA method 200.7 (ICP-AES) and 200.8 (ICP-MS) (US EPA, 1991) were used and performed by an accredited laboratory (ALS Scandinavia, Luleå, Sweden). The samples were dried at 50°C and digested with HNO₃ and analyzed for As, Cd, Co, Cu, Hg, Ni, Pb, S and Zn. All other elements were analyzed after fusion with LiBO₂ and then dissolution in HNO₃.

**Density measurement**

A multivolume helium pycnometer (Pycnometer 1305, Micromeritics, Norcross, GA, USA) was used to determine the density of GLD batch B. The analysis was done in triplicates. A sample with known weight was placed in a 35 cm³ chamber and was pressurized with He. The pressure was recorded. The helium gas expands, which results in a drop in pressure. The volume and density of the sample can be calculated from the two pressure readings. To determine the volume of the sample the Ideal Gas Law (PV=nRT) was applied. The bulk density and compact density were also calculated on GLD samples (batches B and D) that were used for water retention capacity experiments.

**Surface area**

The surface area was analyzed for all four batches of GLD and performed in duplicates. The samples were dried with a freeze dryer system (Freezone 4.5, Labconco Corp., Kansas City, MO, USA). To determine the surface area the samples were degassed with a DeSorb 2300A instrument (Micromeritics, Norcross, GA, USA) and analyzed with a FlowSorb instrument (Micromeritics, Norcross, GA, USA) according to the method described previously by Peterson and Slamovich (1999). The surface area was calculated from the adsorption and desorption of nitrogen on the particle surfaces.

**Hydraulic conductivity**

Constant Rate of Strain (CRS) tests were done on GLD batches B and D according to SIS (1991). Cylinders that measured 15 cm and had a diameter of 7 cm were filled with GLD. The samples were set under a 30 kPa load for 28 days resembling a 1.5 m top cover. The cylinders were placed in an oedometer and an increase of induced stress was applied on the samples. Drainage was only allowed from the top. The hydraulic conductivity was calculated based on the deformation and the pore pressure from the lower surface.

**Water retention capacity**

The water retention capacity (WRC) was measured on GLD batches B and D in duplicates. The samples were packed into cylinders and saturated from below. The cylinders were placed on a ceramic plate and pressurized from below using a pressure plate apparatus (Soilmoisture Corp.,
USA). The following tensions were applied: 0.1; 0.5; 0.8; 1; 2.5 and 5.0 m water column (mwc). 50 and 150 mwc were determined on separate bulk samples. The volume of the loose samples was calculated using the bulk density. The bulk density was determined from the weight of the dried samples (105°C for 24 h) divided by the cylinder volume.

Mineralogical characterization

X-ray diffraction analysis (XRD) was performed on both wet and dried pulverized material with a Siemens D5000 diffractometer using CuKα radiation generated at 40kV and 40 mA. The scanning range was measured in Bragg-Brentano geometry from 5° to 90°. XRD analysis gives an insight in the mineralogical composition of the GLD.

SEM

Scanning electron microscopy (SEM) studies were carried out on GLD batch A using an FEI Magellan 400 XHR Scanning Electron Microscope. A cylinder that measured 15 cm and had a diameter of 7 cm was filled with GLD. The sample was set under a 30 kPa load for 85 days resembling a 1.5 m top cover. Thereafter, it was removed from the cylinder and left to air dry. There was no coating of the sample prior to analysis. The instrument was equipped with an INCA Energy 450 system with X-MAX80 EDS detector. It was run at 10kV. The detectors used were TLD (through-lens detector) and ETD (Everhart-Thornley detector) as a secondary electron detector.

Porosity

The total porosity was calculated for GLD batches B and D according to the equation: Total porosity = (Particle density – Bulk density) / Particle density. Density was determined from the water retention capacity (see above).

Buffering capacity

The buffering capacity was determined for GLD batches A, B, C, and D with the batch titration method. The procedure was modified from the method described previously by Wyatt (1984). 0.75 g of dried GLD was placed in 50 ml plastic containers and mixed with 0, 0.5, 1, 1.5...to 16 ml of 1M HCl. Water was added to get a final volume of 20 ml. The samples were placed on an orbital shaker (IKA KS 260 basic, IKA-Werke GmbH & Co., Staufen, Germany) and agitated for 24 h to reach equilibrium. The pH was measured with a pH meter (Metrohm Ltd, 704 pH Meter, Herisau, Switzerland).

Batch leaching

A leaching test was performed on GLD in triplicates originating from Billerud Karlsborg sulphate pulp and paper mill. The procedure was modified from the Swedish standard SS-EN 12457-4 (SIS, 2003). Deionized water was added at L/S 10. The samples were agitated once a day for 6 days and centrifuged to collect the supernatant. The eluates were filtered with a 45μm nylon membrane and analyzed by an accredited laboratory (ALS Scandinavia, Luleå, Sweden) according to a previously described method.

Shear strength

Replicate samples of GLD were packed into15 cm cylinders with a diameter of 7 cm and cured at 5°C (soil temperature in field conditions) under a load of 20 kPa, which is equal to a 1 m top cover. The samples were tested for uniaxial compressive strengths after a curing time of 1 month. The deformation rate was set at 1.5 %/min.
3. Results

Dry matter content

The dry matter content of the GLD was measured on 178 occasions over one year at the paper mill factory Billerud Karlsborg. The average dry content was 46± 7 %. The 5th and the 90th percentiles were 35% and 54% respectively. The dry matter weight for 14 of the samples is correlated to measured concentrations of Ca. The correlation coefficient was calculated as 0.75. GLD used for characterization experiments were collected on four different occasions. Dry matter content for batches A, B, C and D was 51 %, 47 %, 36% and 33 % respectively.

Particle size

Figure 1 shows the particle size distribution for GLD batches A, B, C and D. The d90 (90 mass-% of the particles has a smaller diameter) of the four batches of GLD was 26.4±0.5 μm. D50: The median particle diameter, d50 was 11.9±3.9 μm and the d10 was 1.9±0.5 μm. For particle sizes <1 μm, the distribution curve is uncertain due to instrument limitations. Particle size distribution for clayey till used for construction of sealing layers at the Kristineberg mining area in northern Sweden is also shown for comparison (Mattson, 1992).

![Figure 1. Particle size distribution curves for clayey till used for construction of sealing layers (Mattson, 1992) and GLD batches A, B, C and D.](image)

Zeta potential

The zeta-potential for GLD batch B is negative over the entire pH range. In the presence of cations these could adsorb to the surface of the GLD particles. The isoelectric point (the pH where the net electric charge of the particles is 0) was not attained.

Total element composition and batch leaching

Table 1 shows the total element composition of different batches of GLD. The amounts of trace elements are low. GLD contains high amounts of Ca. The Ca comes from the lime that is added in the process. The table also illustrates the leaching behavior of important contaminants and comparison with the regulatory levels (European Council, 2002). The majority of the contaminants were below the level of inert waste. Hg, Pb and S had a higher value than the limit but none of them exceeded the limit for non-hazardous waste.
Table 1. Metal concentrations in GLD batches A, B, C and D expressed on a dry matter basis. Results are means of duplicate samples. R² = coefficient of determination for multiple regression of dry substance. Results of GLD leaching experiments at L/S 10 and comparison with regulatory concentration limits for inert and non-hazardous waste at the same L/S quote (European Council, 2002). N/A indicates no data available.

<table>
<thead>
<tr>
<th>ELEMENT</th>
<th>SAMPLE</th>
<th>BATCH</th>
<th>R²</th>
<th>GLD Leaching limit values at landfills for inert waste</th>
<th>Leaching limit values at landfills for non-hazardous waste</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>A</td>
<td>B</td>
<td>C</td>
</tr>
<tr>
<td>Dry matter</td>
<td>%</td>
<td></td>
<td>52±0</td>
<td>48±0</td>
<td>38±0</td>
</tr>
<tr>
<td>Ni</td>
<td>mg/kg</td>
<td></td>
<td>4090±42</td>
<td>6740±355</td>
<td>10110±35</td>
</tr>
<tr>
<td>Al</td>
<td>mg/kg</td>
<td></td>
<td>27100±14</td>
<td>29930±134</td>
<td>52300±75</td>
</tr>
<tr>
<td>Ca</td>
<td>mg/kg</td>
<td></td>
<td>317000±0</td>
<td>296500±2121</td>
<td>249500±3536</td>
</tr>
<tr>
<td>Fe</td>
<td>mg/kg</td>
<td></td>
<td>3180±14</td>
<td>3950±834</td>
<td>6110±580</td>
</tr>
<tr>
<td>K</td>
<td>mg/kg</td>
<td></td>
<td>1940±99</td>
<td>2940±42</td>
<td>3035±35</td>
</tr>
<tr>
<td>Mg</td>
<td>mg/kg</td>
<td></td>
<td>38050±355</td>
<td>43650±374</td>
<td>50100±707</td>
</tr>
<tr>
<td>Mn</td>
<td>mg/kg</td>
<td></td>
<td>8390±57</td>
<td>10850±71</td>
<td>12800±171</td>
</tr>
<tr>
<td>P</td>
<td>mg/kg</td>
<td></td>
<td>4015±21</td>
<td>5600±14</td>
<td>1260±14</td>
</tr>
<tr>
<td>Ti</td>
<td>mg/kg</td>
<td></td>
<td>86±3</td>
<td>84±15</td>
<td>90±1</td>
</tr>
<tr>
<td>LOI 1000°C</td>
<td>%</td>
<td>TS</td>
<td>41±0</td>
<td>41±0</td>
<td>43±0</td>
</tr>
<tr>
<td>As</td>
<td>mg/kg</td>
<td></td>
<td>0.3±0.1</td>
<td>0.2±0.1</td>
<td>0.4±0.0</td>
</tr>
<tr>
<td>Ba</td>
<td>mg/kg</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Cd</td>
<td>mg/kg</td>
<td></td>
<td>3.4±0.1</td>
<td>3.7±0.2</td>
<td>4.9±0.1</td>
</tr>
<tr>
<td>Co</td>
<td>mg/kg</td>
<td></td>
<td>3.2±0.2</td>
<td>3.8±0.2</td>
<td>4.8±0.1</td>
</tr>
<tr>
<td>Cr</td>
<td>mg/kg</td>
<td></td>
<td>76±6</td>
<td>94±1</td>
<td>95±4</td>
</tr>
<tr>
<td>Cu</td>
<td>mg/kg</td>
<td></td>
<td>105±6</td>
<td>110±3</td>
<td>169±14</td>
</tr>
<tr>
<td>Hg</td>
<td>mg/kg</td>
<td></td>
<td>0.04±0.0</td>
<td>0.04±0.0</td>
<td>0.04±0.0</td>
</tr>
<tr>
<td>Ni</td>
<td>mg/kg</td>
<td></td>
<td>3.6±2</td>
<td>3.0±5</td>
<td>46±8</td>
</tr>
<tr>
<td>Pb</td>
<td>mg/kg</td>
<td></td>
<td>2.4±0.2</td>
<td>2.9±0.1</td>
<td>3.3±0.0</td>
</tr>
<tr>
<td>S</td>
<td>mg/kg</td>
<td></td>
<td>8330±636</td>
<td>9825±955</td>
<td>13350±212</td>
</tr>
<tr>
<td>Sn</td>
<td>mg/kg</td>
<td></td>
<td>0.2±0.0</td>
<td>0.1±0.0</td>
<td>0.3±0.0</td>
</tr>
<tr>
<td>Sr</td>
<td>mg/kg</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Zn</td>
<td>mg/kg</td>
<td></td>
<td>753±45</td>
<td>1090±42</td>
<td>1215±21</td>
</tr>
<tr>
<td>CaO</td>
<td>%</td>
<td>Dry matter</td>
<td>44±0</td>
<td>41±0</td>
<td>35±1</td>
</tr>
</tbody>
</table>

Buffering capacity

The acid titration curves for GLD batches A, B, C and D are presented in Figure 2. Results are means of duplicate samples. The acid neutralizing capacity is very similar for the four batches of GLD. There is a large buffering capacity at pH 8.
**XRD**
The diffractograms showed that GLD are composed of calcite (CaCO₃). Brucite (Mg(OH)₂), which is a common form of Mg in ash, could also be detected.

**Surface area, pH, hydraulic conductivity, bulk density, compact density and porosity**
Parameters such as surface area, pH, porosity, hydraulic conductivity, compact density and bulk density were determined to assess how much the batches of GLD varied. The results are summarized in table 2.

**Table 2.** Surface area, pH, hydraulic conductivity, bulk density, compact density and porosity of GLD batches A, B, C and D. The analyses were performed with duplicate samples, except the hydraulic conductivity and pH, which were done in triplicates. N/A indicates no data available.

<table>
<thead>
<tr>
<th>GLD-batch</th>
<th>Surface area (m²/g)</th>
<th>pH</th>
<th>Hydraulic conductivity (CRS method) (m/s)</th>
<th>Bulk density (g/cm³)</th>
<th>Compact density-calculated (g/cm³)</th>
<th>Compact density (by pycnometer) (g/cm³)</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>12.1±0.1</td>
<td>11.0±0.1</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>B</td>
<td>16.8±0.1</td>
<td>10.0±0.0</td>
<td>1x10⁻⁴ ±7 x10⁻⁴</td>
<td>0.67±0.00</td>
<td>2.60±0.00</td>
<td>2.57±0.00</td>
<td>73.2±0.4</td>
</tr>
<tr>
<td>C</td>
<td>21.4±0.0</td>
<td>10.6±0.1</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>D</td>
<td>20.4±0.2</td>
<td>10.1±0.0</td>
<td>1x10⁻⁴ ±7 x10⁻⁴</td>
<td>0.44±0.00</td>
<td>2.47±0.00</td>
<td>N/A</td>
<td>82.2±0.1</td>
</tr>
</tbody>
</table>
Water retention capacity

The WRC curves for batches B and D of GLD are presented in Figure 3. Compared with five sealing layers made of clayey till reported by Höglund et al. (2004) the WRC is significantly higher for GLD. WRC is a hydraulic property affecting the transport of fluids in the material.

![Figure 3](image)

**Figure 3.** Water retention characteristics of GLD batches B and D. The result for two types of silt is also shown as a reference (Bussière et al., 2003). The area between the dashed lines represents the water retention capacity of five sealing layers made of clayey till reported by Höglund et al. (2004).

SEM

Two different structures were noted from the SEM results. GLD consisted mainly of small (<0.5 \( \mu \text{m} \)) flat crystals (Fig 4a). Some larger crystals could also be seen (up to 2 \( \mu \text{m} \)). Because of their flat structure the crystals are tightly packed. Areas where the crystals were intergrown and formed a dense mass could also be detected (Fig. 4b).

![Figure 4](image)

**Figure 4.** SEM images of GLD. 4a: GLD crystals 4b: Intergrown GLD crystals
Shear strength

The shear strength of GLD was assessed at 11.8±1.6 kPa after one month curing time. Comparing the GLD with common materials used as sealing layers such as Ca-bentonite, Na-bentonite and clayey till showed that the undrained shear strength was 4 times lower than the Ca-bentonite and clayey till sealing layers (SGI, 2007). It was also shown to be 6 times lower than a sealing layer made of Na-bentonite (SGI, 2007).

4. Discussion

GLD are wastes for the mill and no attempt is made to control their composition. Quality monitoring and material characterization are generally limited with one exception – regular dry content measurements. To be accepted for the remediation of mine waste, the effect of various material compositions on the desired function should be understood to identify possible limitations. GLD comprise one of the streams out of the pulping process to reduce the concentration of non-process elements (NPEs), such as Mg, Si and Al originating from the wood (Lundqvist et al., 2006; Ulmgren, 1987). The GLD retrieving process, using a pre-coat lime filter, leads to various amounts of lime mixed with the green liquor, which strongly influences the final composition of the dregs.

The dry content of GLD monitored at the mill ranges between 29 and 72%, commonly within the range 36 and 54%. Increasing dry content is a consequence of larger amounts of lime scraped off from the filter coating. When a small amount of lime is scraped from the filter, the concentration of NPE increases relatively and the dregs are wetter. The comparison of the composition of the four batches indicates a clear negative correlation between the NPE and the dry content of the retrieved GLD. The dryer GLD batches contain higher proportions of lime (i.e., Ca) and generally lower content of all the other elements.

The observed variation in the chemical and mineral composition of the GLD is believed to depend both on the origin of the wood and the efficiency of the GLD retrieval. The paper mill has no active quality control of the GLD and the study revealed variations of the quality of the GLD retrieved. The variation between batches had no significant effect regarding the hydraulic conductivity, pH and particle size of the studied materials compared to the natural variation observed in the replicates. However, the surface area, the density and the porosity varied significantly between the batches. The observed variation may complicate the use of the rest product on a large scale. Therefore potential negative effects of the quality variation on the intended application of the material should be addressed.

An important factor when looking at the properties of sealing layers used for mine waste is the ability to act as a barrier for oxygen transport. Pore size and saturation are factors that affect the effective diffusion coefficient, \( D_e \), which in turn affects the oxygen flux through the material. The porosity, or void space between the particles of the material, forms channels where oxygen can travel. \( D_e \) increases with increasing pore size and quantity (Mbonimpa et al., 2003) and the oxygen penetration decreases when the particles are irregularly shaped compared to a more regular structure (Erickson and Tyler, 2001). Decreasing particle size is correlated to increasing total porosity (Mbonimpa et al., 2003). The SEM analysis showed that green liquor dregs crystals are small, flat and stacked in a way that forms a dense mass. As the porosity of GLD is high, >70%, the oxygen diffusion may occur if the material dries and is not saturated. However, the results indicate that the water content of the material is high, meaning that the voids are water-filled, decreasing the oxygen flux. The material may stay saturated or close to saturation even in dryer periods because of its high ability to retain water, assuring low oxygen diffusion.
Of great importance when constructing sealing layer is choosing a material that decreases water infiltration and consequently slows down leaching. No single soil parameter determines its hydraulic conductivity, but decreasing the particle size of a material is correlated to decreasing its hydraulic conductivity (e.g., Sivapullaiah et al., 2000, Benson and Trast, 1995). The hydraulic conductivity is negatively correlated to porosity in the case of fine-grained material (Marion et al., 1992; Kollermann and Gorelick, 1995) and the specific surface area (Benson and Trast, 1995; Vuković and Soro, 1992). A high porosity enables water to enter the material, but the large surface area also enhances chemical interactions binding water to particles, thereby limiting water transport, enabling a high grade of saturation. Our results showed that GLD have adequate characteristics, such as a small particle size of d50~12μm, high porosity and average surface area of 18m²/g to limit the water flow through the material. The tests confirmed a low hydraulic conductivity, between 1x10⁻⁸ and 7x10⁻⁹ m/s. However it does not reach the recommended minimum hydraulic conductivity of 1x10⁻⁶ m/s to limit the transport of water to the waste sufficiently to prevent the formation of an acid leachate.

Hydraulic conductivity is a factor that is closely related to the oxygen transport. Low hydraulic conductivity reduces oxygen diffusion, which slows down pyrite oxidation. Research has shown that oxygen diffusion decreases significantly as the degree of saturation increases above 85% (O’Kane, 1995). GLD has very high water retention potential, much higher compared to other cover materials (Fig. 4) such as till (Höglund et al., 2004) and desulphurized tailings (Sjoberg et al., 2001). The WRC is similar to sulphidic tailings that had a finer particle size than desulphurized tailings (Sjoberg et al., 2001). GLD showed a small particle size distribution, but the particle size is larger compared to clay minerals such as kaolinites and montmorillonite, which show particle sizes of <1 μm (Arnott, 1965). Comparing the particle size distribution of GLD with sealing layers made of till in the Kristineberg area of Sweden (Mattson, 1992) shows that GLD particles are significantly smaller. Although the particle size falls into the range of silt, the water retention capacity is more comparable to clayey materials than silty materials, especially at high under-presures. The high WRC reduces the oxygen flux through the material maintaining saturated or close to saturated conditions. The risk of shrinkage and cracking due to desiccation is reduced, which is otherwise a common problem in clay and may have a significant impact on the sealing layer performance. The material’s high capacity to hold water is believed to be due to the crystalline structure together with the ionic charge of the particles. The crystalline structure of GLD shows some similarities with that of bentonite, which suggests that water may be held tightly by electrostatic attraction between the parallel flakes in a similar way (Weaver, 1946; Sébaïbi et al., 2003).

Ideally, the material used as a sealing layer should not only decrease oxygen penetration but also simultaneously function as a chemically reactive barrier retaining heavy metal ions originating from the mine waste. The material itself should not be hazardous or able to transform into hazardous substances. A major concern when using rest products is assessing their potential negative impact on the environment they are used in. Both unwanted alteration of the material, altering its function, and bi-effect on surrounding mine waste caused by GLD leachate, for example, are potential issues to be addressed. The results indicate that GLD are chemically stable in the sense that they resist degradation since they contain little organic material that may decompose over time. The material also lacks elements that are likely to interact and transform into harmful substances (e.g. conversion of inorganic mercury to hazardous methylmercury by sulphate processing bacteria) or oxidize easily, thereby changing its initial structure and properties. The results show that the zeta potentials are similar to those of kaolin and montmorillonite at lower pH, but that the clay minerals show a larger negative charge at high pH (Kosmulski and Dahlsten, 2006). However, the GLD have a negative zeta potential at all pH levels and that the isoelectric point does not exist, which is not the case with kaolin. This indicates that the GLD particles are relatively stable and resist the
formation of aggregates (Hunter, 1981). It is therefore expected, together with the high WRC, that crack formation due to aggregation, providing a pathway for water and oxygen, would be limited. The function can be maintained independent of the pH.

The chemical characterization showed that Ca expressed as CaO stands for 30-40% of the GLD. The XRD analysis indicated the presence of calcite, which is in agreement with Martins et al. (2007), while no other buffering minerals were detected. However, most of the minerals are believed to occur in amorphous form, not detectable by XRD. The proportion of CaCO$_3$ and CaO was not established. The higher content of Ca in batches A and B (Table 1) explains the higher acid buffering capacity observed compared to the two other batches. The XRD analysis showed that the material also contains small amounts of Brucite, resulting from the substitution of Ca by Mg (Martins et al., 2007).

The buffering capacity of GLD is high, which is consistent with its large reservoir of lime. To maintain the pH>6, the average neutralization capacity was 18.5 mmol H$^+$/g dry weight for the four batches of GLD. The net neutralization potential was determined as -437 kg CaCO$_3$/ton for tailings with high sulphur (16%) content originating from the Kristineberg mine in Sweden (results not shown). In this extreme case, in a GLD/tailings blend 472 kg of GLD is required to neutralize the acid produced from 1 ton of tailings. The high buffering capacity indicates that GLD could act as an alkaline barrier. GLD’s neutralization capacity is not expected to run out when used as a sealing layer since the dissolution of buffering compounds such as CaO, Ca(OH)$_2$, and CaCO$_3$ is slow due to the low hydraulic conductivity. This is in agreement with Pöykiö et al. (2006), who showed that GLD could act as a neutralizing agent for acidic wastewater. Leaching experiments showed that the amount of elements leached was below the leaching limits for non-hazardous waste regulated by the European Union (European Council, 2002), making it a good candidate for sealing layer application. In addition, previously performed leaching experiments have shown that the addition of 10% green liquor dregs to tailings reduced leaching of metals such as Cu, Co, Cd and Ni (Maurice et al., 2009). This is most likely due to the fact that GLD increases the pH, immobilizing metal ions by precipitation of secondary minerals and absorption to mineral surfaces (Coston et al., 1995; Kooner, 1993). It is also possible that the GLD particles are binding metal cations due to their negative zeta potential and large surface area, preventing the leaching of metals from the mine waste further or at lower pH than expected.

Characterizing the GLD gives insight into how the material properties vary and enables the establishment of possible application fields. The material exhibits several favorable properties for sealing layer application such as a high water retention capacity ensuring that the layer stays saturated, making it an effective oxygen barrier. The high pH and the large buffering capacity may chemically treat the tailings, making metals co-precipitate. The small variations observed between batches are not expected to lead to low quality materials if used for barrier applications. Using GLD instead of traditional till ensures that the sealing layer has a small particle size throughout the material. A homogenous sealing layer is important to achieve uniform water saturation. There are several advantages to using GLD over virgin material such as till for construction of sealing layers. Opening quarries is not only costly but also has a significant environmental impact. A shortage of cover material close to the mines is often an issue in northern Sweden and Finland. This solution would solve two waste problems at the same time, and till quarrying would decrease. However, because the quality of GLD varies, there is a risk that not all of the GLD produced would have the appropriate characteristics for use in sealing layer applications, although they could still be used in other fields. Based on the results, GLD with low hydraulic conductivity would be most suitable to use for construction of sealing layers. GLD have previously been used in applications such as a stabilization agent for road construction (Toikka, 1998).
Although the material has been shown to have several desirable properties to function as a sealing layer, some practical issues have to be addressed before it can be used in this way. The material is very sticky, which makes it difficult to handle on a large scale. Results show that the strength of the GLD is insufficient for engineering applications. It is important that the material exhibit good compressive strength so it can support the weight of a protective layer but also exhibit plasticity to resist cracking that can be caused by differential settlements in the landfill. If GLD are applied as a sealing layer in a slope there is a risk of sliding due to the low shear strength and the high water content. Improving the mechanical properties is therefore necessary. Mixing GLD with mineral admixtures (e.g. fly ash) could potentially reduce the stickiness, increase the strength and reduce the hydraulic conductivity. The material may also be frost sensitive, which is a common problem with silty soils. This would cause damage to the material (frost heave) when used at shallow depths in cold regions.

5. Conclusions

Compared to lime, the pure GLD appear to have a higher porosity and surface area even though both materials have comparable particle size. In cover applications, where high compaction grade and low hydraulic conductivity are wanted, mixing of additives to GLD may improve the material properties.

Based on the characterization results, the difference between batches is fairly small both mineralogically and physically. GLD could be an alternative to traditional sealing layers made of till since the material proved to have relatively low hydraulic conductivity and a high water retention potential. The small particle size and high buffer capacity makes it a better candidate than till, which usually varies in size and hydraulic conductivity. There is a chemical variation of the material, but element content does not seem to be an environmental concern. More research is needed to further evaluate the chemical behavior and the function of the material. Adding stabilizing materials to the GLD is necessary to reduce the stickiness, increase the shear strength and lower the hydraulic conductivity.

6. Future work

Further research is being pursued to improve the barrier properties, by increasing the shear strength and reducing hydraulic conductivity by adding other materials to the GLD. Leaching tests useful to assess GLD-treated tailings are being developed. The remediation of mine waste should be efficient in a long-term perspective. Therefore, the effect of aging on GLD properties should be studied.

7. Acknowledgments

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8. References


Kooner, Z. S., 1993. Comparative study of adsorption behavior of copper, lead and zinc onto goethite in aqueous systems. Environ. Geol. 21, 242–250


Improving green liquor dregs barrier properties for application on sulphidic mine waste

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Abstract

Green liquor dregs, a rest product from the sulphate paper mills, have been blended with tailings with the aim of improving the properties to function as a candidate for construction of sealing layers for sulphidic mine waste. Geotechnical and geochemical investigations including humidity cell tests were performed on green liquor dregs mixed with tailings. By adding tailings to green liquor dregs, the shear strength improved and the water retention capacity remained at a high level. Green liquor dregs showed to also have the potential to, due to their alkaline property, improve the leachate quality by decreasing the metal mobility in the tailings. However, restrictions occur when the dregs are blended with tailings containing large amounts of As and Mo since an increased leaching of these elements may be expected.
1. Introduction

Mining produces mainly two types of wastes; waste rock and tailings. Waste rock is the material of coarser size that is removed to access the ore while tailings are finely ground material retrieved after processing the ore. Mine waste from sulphide ores are often chemically reactive due to that it often contains iron sulphides such as pyrite and pyrrhotite. When pyrite or pyrrhotite is exposed to atmospheric oxygen they oxidize which generates acidity (Höglund et al., 2004). If no alkaline material is present to neutralize this acidity, heavy metals can become mobile and are transported with water that enters the waste. This leachate is called acid mine drainage (AMD) and is one of the greatest concerns when dealing with sulphidic, pyrite rich mine waste. AMD may cause severe environmental pollution so finding methods to prevent the formation of AMD is a necessity. A traditional prevention method is to cover the waste with soil (often till) that is expected to be water saturated. The aim is to limit the oxygen diffusion since oxygen diffuses 10 000 times slower in water compared to air. Water can only contain 1/30 amount of O₂ compared with the same volume air (Mbonimpa et al., 2003). The usage of till in sealing layers is often costly due to the opening of quarries and finding till of suitable quality close to the mine is not always possible.

Sustainable methods reducing the risk of AMD formation without risking the economical premises of the mining industry are needed. A relatively new engineering technology is to use industrial waste (e.g. sewage sludge, fly ash, green liquor dregs) in sealing layers taking advantage of the materials reactive nature in the prevention of AMD.

Green liquor dregs (GLD) are the largest waste fraction retrieved in the chemical recovery cycle at the sulphate pulp and paper mills and has been characterized previously. The material showed to have qualities such as low hydraulic conductivity, high water retention capacity and high pH which are favorable for usage in sealing layers (Makitalo et al., submitted). However, the study revealed that adding stabilizing materials to the GLD is necessary to reduce the stickiness and increase the shear strength to be able to use it as a candidate for sealing layer purposes. We hypothesize that GLD may decrease the leaching of metals in sulphidic mine waste not only due to the sealing effect, but also because they have the ability to raise the pH in the waste due to the calcium carbonate content and their alkaline nature. Maurice et al. (2010) showed that addition of only 10% GLD to tailings reduced metal leaching, especially of copper. Because of their sticky consistency it is a challenge to mix the GLD with other materials. Since mixing the materials well is crucial, Hargelius (2008) found that adding a small amount of organic matter made the material less sticky and easier to mix. It may also improve the stability of the material and decrease the hydraulic conductivity.

Mixing tailings to GLD may improve the shear strength of the mixture. Addition of tailings would reduce the water content and improve the conditions to generate a better physical strength. Chtaini et al. (2001) incorporated alkaline paper mill waste (1/3 sludge and 2/3 tailings) and studied the effect on the production of AMD. Monitoring results showed that mixing mine residues with alkaline paper mill waste allowed an efficient control of AMD by reducing the diffusion of oxygen. The paper mill waste cover generated an alkaline front which resulted in metal precipitation as hydroxides (Bellaloui et al., 1999).

To be economically feasible, the GLD has to be used efficiently. Mixing GLD and tailings is one way to reduce GLD consumption per square meter of sealing layer (GLD is “diluted” with tailings), and consequently to improve the economic viability.

One risk with using highly alkaline materials as sealing layers is that they create an anoxic environment which allows for the potential formation of thiosalts. Thiosalts such as thiosulphate are
intermediate products when sulphide minerals oxidize and form sulphate under high pH (Kuyucak, 2006). When thiosulphate oxidize to form sulphate it generates sulphuric acid. High amounts of thiosalts such as thiosulphate may therefore pose a risk of acidification and subsequently leaching of metals.

In the present investigation tailings and bark sludge (BS) were characterized to document the properties of the materials to be able to evaluate if a mix of them together with GLD can function for construction of sealing layers. The primary objective was to add tailings and BS to GLD and find an admixture that has improved shear strength compared to GLD alone but also inhibits water and oxygen conduction. The effectiveness of GLD ability to control acid generation and metal leaching from sulphidic tailings was assessed along with the potential of generating thiosulphates.

2. Material and methods

2.1 Material

Sample description:
Tailings (T) originating from the Kristineberg mine, Sweden were kindly provided by the mining company Boliden Mineral AB. The tailings originating from this mine are known to contain pyrite, pyrrhotite, sphalerite, chalcopyrite, galena and covellite (Holmström et al., 2001). T were taken from the process after addition of lime to the water. GLD and BS were provided by Billerud Karlsborg pulp and paper mill. The GLD came from the process and were collected from containers before deposition. The sampling took place at three different occasions and ~ 30 kg were collected each time and stored in sealed plastic containers at room temperature. The three batches are named A, B and C. The BS is the dewatered fraction released from the stem when rinsing the logs. It is a mixture of bark, soil and needles. It was collected and stored in sealed plastic bags at 0.75 kg/bag, which were stored at -20°C. All materials used are considered waste.

2.2 Methods

Total element composition
A total of 31 different elements were determined for the tailings and 21 different elements were determined for bark sludge, all with duplicate samples. An accredited laboratory (ALS Scandinavia, Luleå, Sweden) performed the analyses by using the modified EPA method 200.7 (ICP-AES) and 200.8 (ICP-MS) (U.S. Environmental Protection Agency, 1991).

The samples were dried at 50°C, digested with HNO₃ and analyzed for As, Cd, Co, Cu, Hg, Ni, Pb, S and Zn. All other elements were analyzed after merging them with LiBO₂ and separating them into fragments in HNO₃.

Acid-base accounting
To examine the tailings acid producing potential (AP) and neutralizing potential (NP) the method of acid-base accounting developed by Sobek et al. (1978) was used. The NP was determined in triplicates by adding 0.1 M of HCl to the sample followed by incubation at 95°C for 30 min. Deionized water was added and the sample was boiled for 1 min. After cooling to room temperature the sample was back-titrated with 0.1M NaOH to determine the amount of consumed HCl.

The AP was calculated from the amount of total sulphur in the sample with equation 1 and the net neutralization potential (NNP) was calculated according to equation 2 (Sobek et al., 1978). Total sulphur was analyzed with a Leco Sulfur Analyzer.
\[ \text{AP} = 31.25 \times \% S \quad (1) \]
\[ \text{NNP} = \text{NP} - \text{AP} \quad (2) \]

**Water retention capacity**

The water retention capacity (WRC) was measured in duplicates. The sample was a blend of 64% GLD, 32% tailings and 4% BS. Percentages are given in dry matter content. Cylinders filled with the blend were placed on ceramic plates, were saturated and pressurized from below with tensions 0.1, 2.5 and 10.0 m water column (mwc) using a pressure plate apparatus (Soilmoisture Corp., USA). 25 mwc, 50 mwc and 150 mwc were applied on separate bulk samples. The bulk volume was determined using the bulk density that was determined from the weight of the dried samples (105°C for 24 h) divided by the cylinder volume.

**Weathering cell**

A modified weathering cell method similar to the ones described by Hakkou et al., (2008) and Cruz et al., (2001) was used. The method was preferred because it is faster to perform and has been found to be a valid alternative to traditional humidity cell tests (Villeneuve et al., 2003). Three samples with a total of 67 g (dry weight) of material were placed in 250ml centrifuge flasks in duplicates. The materials were tailings, batch A GLD and a blend of 50% batch A GLD and 50% tailings. Leaching cycles were performed twice a week by leaching the sample with 50 ml deionized water on day 1 and 4, exposing the samples to atmospheric air all other days. When adding water, the sample was mixed with a spoon to ensure that the material was in contact with the water. After 3 h in contact with the material the flasks were centrifuged at 4000 rpm for 10 min with a Becton Dickinson centrifuge and the leachate was recovered by decantation. The leachate was filtered with a 0.45μm nylon membrane filter.

54 leaching cycles were performed in total. At cycle 39, 41, 43, 48, 49 and 50, HCl was added to the GLD/tailings blend and GLD samples to consume the remaining NP and stimulate/enhance the formation of acid mine drainage. Acid was added to the sample Tail 1 at cycle 39 and 41, only. The leachates were analyzed for conductivity and pH using a WTW GmbH Multi-340i meter with a WTW SenTix 41 electrode for pH measurements. Metal analysis was performed by ALS Scandinavia, Sweden. Sulphates were measured at its absorbance at 450 nm with a UV-VIS spectrophotometer (Beckman Coulter AB, Bromma, Sweden, DU® 730 life science) and thiosulphate analysis was performed by iodometric titration.

**Hydraulic conductivity- CRS tests**

Constant Rate of Strain (CRS) tests were performed according to SIS (1991). The samples analyzed were GLD mixed with various amounts of BS and tailings. The experiment was performed with replicates. Cylinders that measured 15x7 cm were filled with the blends and pressurized with a 30 kPa load from the top of the sample during 28 days resembling a 1.5 m top cover. An increase of induced stress was applied to the samples in an oedometer allowing drainage only from the top. Based on the deformation and pore pressure, the hydraulic conductivity could be determined.

**Surface area**

The surface area was analyzed on tailings in triplicates with a FlowSorb instrument (Micromeritics, Norcross, GA, USA) as previously described by Peterson and Slamovich (1999).

**Dry matter content and paste pH**

Dry matter content and paste pH were analyzed in duplicates for tailings and BS. The dry matter content was performed according to Swedish standard SS 028113-1 (SIS, 1981).
Paste pH was determined with a method previously described by Weber et al (2006) where 5 g sample was mixed with 10 ml of deionized water followed by 5 min incubation in room temperature. pH was measured with a pH-meter (Metrohm Ltd, 704 pH Meter, Herisau, Switzerland).

**Particle size**

To obtain the particle size of tailings, laser diffraction analysis was conducted using a laser-based CILAS Granulometer 1064 (CILAS, Orléans, France) according to a method previously described (Makitalo et al., submitted). The analysis was performed in duplicate.

**Density measurement**

Density measurements were performed with a multivolume helium pycnometer (Pycnometer 1305, Micromeritics, Nercross, GA, USA) as previously described (Makitalo et al., submitted). The analysis was done in triplicate.

**Shear strength**

Three samples were analyzed for shear strengths; 100% GLD, blends of 60% GLD and 40% T and blends of 30% GLD and 70% T. 15 cm cylinders with a diameter of 7 cm were filled with the mixtures. The samples were cured at 5°C (soil temperature in field conditions) under a load of 20 kPa which is equal to 1 m top cover. The samples were tested for uniaxial compressive strengths after a curing time of 1 month. The deformation rate was set at 1.5 %/min.

### 3. Results

**Hydraulic conductivity**

Table 1 shows the hydraulic conductivity of GLD amended with tailings and BS. Both runs performed on sample 1-3 were done with a batch C of GLD with 34% dry matter content. The first run on sample 4-7 was done with a batch B of GLD having a dry matter content of 47% while run 2 was done with a batch A with 52% dry matter content. For each run, the order of packing the material into cylinders and running experiments was randomized. The hydraulic conductivity varies between 1E-08 and 2E-09 m/s. The 50/50 GLD/ tailings blend generated the lowest hydraulic conductivity, however a large variation was observed between runs.

<table>
<thead>
<tr>
<th>RUN</th>
<th>GLD (%)</th>
<th>Tailings (%)</th>
<th>BS</th>
<th>Hydraulic conductivity (m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>50</td>
<td>50</td>
<td>-</td>
<td>Run 1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>7E-09 2E-09</td>
</tr>
<tr>
<td>2</td>
<td>33</td>
<td>66</td>
<td>-</td>
<td>Run 2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2E-08 2E-08</td>
</tr>
<tr>
<td>3</td>
<td>25</td>
<td>75</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1E-08 1E-08</td>
</tr>
<tr>
<td>4</td>
<td>76</td>
<td>19</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1E-08 5E-09</td>
</tr>
<tr>
<td>5</td>
<td>64</td>
<td>32</td>
<td>4</td>
<td></td>
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<td></td>
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</tr>
<tr>
<td>6</td>
<td>73</td>
<td>18</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1E-08 4E-09</td>
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<tr>
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<td>62</td>
<td>31</td>
<td>8</td>
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</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1E-08 1E-08</td>
</tr>
</tbody>
</table>
Total element composition

Table 2 shows the total element composition of GLD, tailings and BS. GLD contain high amounts of Ca, Mg and S. Ca and Mg are elements that are removed and precipitated in the GLD in the process (Ullmgren, 1987). Ca is also expected to originate from the lime filter used to filter the dregs. S is accumulated in the dregs due to the use of the sulphate production process, the process used at the paper mill production plant. The large amount of S in the tailing comes from sulphide minerals. The tailings showed to be rich in elements that are often a problem in AMD (e.g. Cu, Zn, Cr, Al).

<table>
<thead>
<tr>
<th>ELEMENT</th>
<th>SAMPLE</th>
<th>GLD Batch A</th>
<th>BS</th>
<th>Tailings</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry matter</td>
<td>%</td>
<td>52± 0</td>
<td>35± 0</td>
<td>66.4</td>
</tr>
<tr>
<td>Si</td>
<td>mg/kg</td>
<td>4990± 42</td>
<td>N/A</td>
<td>15000</td>
</tr>
<tr>
<td>Al</td>
<td>mg/kg</td>
<td>2710± 14</td>
<td>971± 41</td>
<td>5100</td>
</tr>
<tr>
<td>Ca</td>
<td>mg/kg</td>
<td>317000± 0</td>
<td>8300± 1301</td>
<td>12400</td>
</tr>
<tr>
<td>Fe</td>
<td>mg/kg</td>
<td>3180± 14</td>
<td>1565± 219</td>
<td>16100</td>
</tr>
<tr>
<td>K</td>
<td>mg/kg</td>
<td>1980± 99</td>
<td>747± 35</td>
<td>9400</td>
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<tr>
<td>Mg</td>
<td>mg/kg</td>
<td>38050± 353</td>
<td>816± 66</td>
<td>37700</td>
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<tr>
<td>Mn</td>
<td>mg/kg</td>
<td>8390± 57</td>
<td>265± 33</td>
<td>876</td>
</tr>
<tr>
<td>P</td>
<td>mg/kg</td>
<td>4015± 21</td>
<td>336± 13</td>
<td>361</td>
</tr>
<tr>
<td>Ti</td>
<td>mg/kg</td>
<td>86± 3</td>
<td>77± 12</td>
<td>1780</td>
</tr>
<tr>
<td>LOI 1000°C</td>
<td>% Dry matter</td>
<td>41± 0</td>
<td>N/A</td>
<td>12</td>
</tr>
<tr>
<td>As</td>
<td>mg/kg</td>
<td>0.3± 0.1</td>
<td>&lt;10</td>
<td>146</td>
</tr>
<tr>
<td>Cd</td>
<td>mg/kg</td>
<td>3.6± 0.1</td>
<td>&lt;3</td>
<td>5.5</td>
</tr>
<tr>
<td>Co</td>
<td>mg/kg</td>
<td>3.2± 0.2</td>
<td>&lt;3</td>
<td>89.8</td>
</tr>
<tr>
<td>Cr</td>
<td>mg/kg</td>
<td>76± 6</td>
<td>4± 0</td>
<td>855</td>
</tr>
<tr>
<td>Cu</td>
<td>mg/kg</td>
<td>105± 6</td>
<td>5± 0</td>
<td>1390</td>
</tr>
<tr>
<td>Hg</td>
<td>mg/kg</td>
<td>0.04± 0.0</td>
<td>N/A</td>
<td>0.78</td>
</tr>
<tr>
<td>Ni</td>
<td>mg/kg</td>
<td>30± 2</td>
<td>&lt;3</td>
<td>47.5</td>
</tr>
<tr>
<td>Pb</td>
<td>mg/kg</td>
<td>2.4± 0.2</td>
<td>&lt;10</td>
<td>1170</td>
</tr>
<tr>
<td>S</td>
<td>mg/kg</td>
<td>8330± 636</td>
<td>438± 6</td>
<td>15300</td>
</tr>
<tr>
<td>Sn</td>
<td>mg/kg</td>
<td>0.2± 0.0</td>
<td>N/A</td>
<td>281</td>
</tr>
<tr>
<td>Zn</td>
<td>mg/kg</td>
<td>733± 45</td>
<td>58± 6</td>
<td>5380</td>
</tr>
<tr>
<td>CaO</td>
<td>% Dry matter</td>
<td>44± 0</td>
<td>N/A</td>
<td>1.74</td>
</tr>
</tbody>
</table>

Weathering cell

The pH was high for all samples in the start of the experiment. Acid was added to GLD and GLD/tailings blend at cycle 39, 41, 43, 48, 49 and 50, while acid was added to the sample Tail 1 at cycle 39 and 41. Figure 1 shows the water quality of the leachate vs. time.
Figure 1. (A) Development of pH in the leachates (B) Development of the conductivity in the leachates (C) Sulphate concentrations (D) Thiosulphate concentrations in leachate (E) S concentrations in leachate (F) Fe concentrations in leachate (G) Ca concentrations in leachate (H) Mg concentrations in leachate (I) Mn concentrations in leachate (J) Cu concentrations in leachate (K) Ni concentrations in leachate (L) Co concentrations in leachate (M) Zn concentrations in leachate (N) Hg concentrations in leachate (O) Pb concentrations in leachate (P) As concentrations in leachate (Q) Mo concentrations in leachate (R) Al concentrations in leachate (S) Na concentrations in leachate.
ABA
The net neutralization potential was calculated based on the NP and AP values. NNP= NP-AP. A negative NNP shows that the waste is potentially acid generating (prEN 15875:2008). The tailings were identified as strongly acid producing based on the NNP value from the ABA test. The NNP was determined to -437 kg CaCO3/ton.

Water retention capacity
The WRC curves for GLD with amendments are presented in Figure 2. The admixture consists of 64% GLD, 32% tailings (T) and 4% BS. GLD without amendments are shown as a reference (Makitalo et al., submitted). An average of 12% decrease in WRC is noted for the blend compared to GLD alone.

Figure 2. Water retention characteristics of GLD blended with tailings and bark sludge. The result for GLD without amendments is shown as a reference (Makitalo et al., submitted).

Particle size
Figure 3 shows the particle size distribution for tailings. The d90 (90% finer than this size) was 102.2±10.8 μm. The median particle diameter, d50 was 36.5±3.4 μm and the d10 (10% finer than this size) was 3.7±0.3 μm. Particle size distribution curves for GLD (Makitalo et al., submitted) and clayey till (Mattson, 1992) are shown for comparison. The clayey till originates from a sealing layer constructed for mine waste in the Kristineberg mining area in Northern Sweden.

Figure 3. Particle size distribution curve for tailings. Clayey till used for sealing layer for mine waste (Mattson, 1992) and GLD (Makitalo et al., submitted) are also shown.
Shear strength

The shear strength for GLD and GLD amended with tailings is shown in Table 3. Compared to GLD an increase of shear stress was observed when GLD was blended with tailings. Water ratio and dry density are also shown.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tailings/GLD (%)</th>
<th>T$_s$ (kPa) 30 d curing</th>
<th>Classification (kPa)</th>
<th>Water ratio (%)</th>
<th>$\rho_t$ (t/m$^3$)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0/100/0</td>
<td>11.8±2.2</td>
<td>Very low (10-20)</td>
<td>117</td>
<td>0.64</td>
</tr>
<tr>
<td>2</td>
<td>70/30/0</td>
<td>15.7±4.3</td>
<td>Very low (10-20)</td>
<td>49</td>
<td>1.27</td>
</tr>
<tr>
<td>3</td>
<td>40/60/0</td>
<td>19.0±13.4</td>
<td>Very low (10-20)</td>
<td>78</td>
<td>0.90</td>
</tr>
</tbody>
</table>

*Measurements before curing.

Table 3. Shear strength after 30 days of curing.

Surface area, paste pH and density

Surface area, pH, and compact density were determined for the tailings. pH was performed in triplicates and the other parameters were measured in duplicates. The surface area was 4.0±0.1 m$^2$/g, pH was 10.0±0.2 and compact density was 3.52± 0.00 g/cm$^3$. The high pH is due to the fact that lime was added to the tailings at the process.

4. Discussion

Hydraulic properties

The addition of amendments to the GLD could not further decrease the hydraulic conductivity. On the contrary, the amendments appear to increase the hydraulic conductivity up to one order of magnitude. However, the variation between the replicates was large and the results of the hydraulic conductivity could not be confirmed to be significant. The variation of chemical composition between different batches of the materials is believed to be an important factor that affects the hydraulic conductivity. Sample 1-3 was run with the same batch and showed less variation than sample 4-7 that was run with two different batches of GLD. Since GLD is a waste it is difficult to obtain a homogenous product. Hydraulic conductivity is a property that may vary. However, hydraulic conductivity is only one hydraulic properties of the soil. When designing a sealing layer, the water retention properties should also be considered since one of the most important factors limiting oxygen diffusion is the material’s ability to stay saturated. GLD and GLD blended with tailings show a very high water retention capacity that is expected to limit the oxygen reaching the waste. This is a factor that has shown very small variations (Makitalo et al., submitted). This means that even though the hydraulic conductivity was approximately one order of magnitude higher than the hydraulic conductivity that is generally aimed for when creating sealing layers (Höglund et al., 2004), the high water retention capacity together with the high grade of saturation prevents air-entry, and thereby oxygen to reach the waste. This may limit oxidation of the tailings more efficiently than a material that exhibits a hydraulic conductivity of 1x10$^{-9}$ m/s or lower. The pathway of oxygen through a saturated sealing layer is largely the oxygen that is dissolved in water and comes through by percolation. Since the dissolution of oxygen in water is 10 000 times lower than in air, the oxygen concentration that reaches the waste is low making the oxidation of the sulfidic mine waste slow.
GLD has a high water retention capacity compared to materials with similar particle size such as clayey/sandy silt (Makitalo et al., submitted). The reason of the GLD’s high water retention capacity may lie in its structure. GLD consist of flat parallel crystals. It is possible that water molecules exist in between the flakes and are retained by electrostatic attraction in a way similar to bentonite which shows a similar structure (Weaver, 1946; Sébaïbi et al., 2003). A small decrease of the water retention capacity was observed with blends of GLD/tailings/BS. The decrease may be due to the smaller surface area of the particles of the tailings limiting the binding of water.

Shear strength

GLD amended with tailings showed higher shear strength compared to GLD alone. GLD amended with 40% tailings showed the highest shear strength but showed a large variation between duplicates (9.5 kPa compared to 28.4 kPa). The large variation was due to cracks in one of the samples that resulted in the lower shear strength. It is unclear if the reason of the crack was due to blend of the materials or coincidence. This should be investigated further. Shear strength between 20-40 kPa is classified as low, based on the Undrained Shear Strength classification definition (BS EN ISO 14688-2:2004, 5.3). Such shear strength levels may be acceptable in horizontal applications such as on top of heaps or tailings deposits. However on a slope, the risk for landslide is obvious. In such a case addition of binder such as fly ash may be required to increase the shear strength. Fly ash possesses self-hardening properties and mixing it with other materials such as cement has shown to improve shear strength.

Geochemistry

The initial pH of the tailings was high (pH ~10) in the humidity cell test. This was due to the fact that lime is added to tailings at the process, a method used to raise the pH to enable recovery of the valuable minerals (Bolin et al., 1991). The results showed that the tailings contained 15% sulfur and the ABA results indicated that the tailings were potentially acid producing which was confirmed by the generation of acid leachate after 33 cycles, indicating that the carbonates in the sample Tailings 2 had been consumed. For the replicate sample of tailings this process required longer time. Acid (of the total amount of 0.021 mol) was added to Tailings 1 at cycle 39 and 43 as an attempt to speed up the process by consuming the remaining carbonates. This attempt was successful and the two tailings replicates behaved similarly as the pH decreased and stabilized just below pH 4. The electrical conductivity increased indicating an increased weathering rate. Sánchez España et al. (2005) showed that there is a clear correlation between the electrical conductivity and total dissolved solids and sulphate meaning that increased electrical conductivity can be an indication of AMD.

Consuming all the carbonates in the GLD and the GLD/tailings blend without acid addition was expected to require a long time since it previously has been shown that GLD’s buffering capacity is large (18.5 mmol H+/g dry weight to maintain the pH>6) (Makitalo et al., submitted). Based on the NNP of the tailings and the buffering capacity of the GLD, 479 kg GLD/ tone of tailings (i.e. a blend of 30% GLD and 70% tailings) is required to maintain a pH >6. Since a 50/50 blend was used, the carbonates were expected to buffer any acidity formed by the tailings. A total of six acid additions were performed at cycle 39, 41, 43, 48, 49 and 50 to consume the carbonates present in GLD to decrease the pH enabling evaluation of when the buffer capacity ceases. The pH dropped instantly when the acid was added but raise during the following cycle. The carbonate dissolution was too slow to be complete. A total amount of 1.34 mol HCl was added to the GLD (0.02 mol/g) and 0.71 mol to the GLD/tailings blend (0.01 mol/g).
Based on the mobility of metals it is likely that the environment of GLD/tailings blend is dysoxic during the first 35 cycles of the experiments. The material’s ability to hold water prevents it from drying. Even after centrifugation, large amounts of water (25% of the added H₂O in the first few cycles) remains in the material, preventing oxygen from entering. Based on the fact that oxygen thus only enters through the transport of water (i.e. the water saturation degree of the sealing layer is 1.0) and the expected infiltration/year is 300 mm which is normal for the area (1xE-8 m/s), the oxygen flux is ~0.1 mol/m²/year. The depletion of pyrite in a 30 cm thick 30/70GLD/tailings sealing layer would take approximately 11,000 years. If the neutralization potential would cease for some reason (the construction is applied in a wrong way or acid originating from another source contribute to additional acidity), the metals show a different behavior which can be seen in the diagrams i.e. at the point of the acid addition.

Reactions taking place during buffering
Fe leaching is very low for the GLD/tailings blend as well as from all other samples until the acid addition. The tailings originating from Kristineberg mine contains high amounts of pyrite. It is therefore likely that large amounts of Fe in the tailings are bound as FeS₂ and possibly FeS as well. Iron dissolution was close to zero until cycle 35 for T2 and cycle 39 for T1 when acid was added. However, the absence of dissolved Fe, does not indicate the absence of pyrite oxidation as free Fe is directly adsorbed or precipitated as metal oxides/hydroxides. Ca, Mg and Mn occur in carbonates and are likely the products of neutralization reactions in tailings. The dissolution and leaching of these elements is caused by pyrite oxidation. In the first 30 cycles of the experiment, the leaching concentrations are low which support that oxidation of pyrite is absent or very slow. The GLD/tailings blend and GLD alone showed high levels of sulphate leaching from the start of the humidity cell experiment while the initial sulphate concentration of the tailings leachate were low. For the blend and the tailings alone, the sulphate concentration fluctuated with time while for the GLD the leaching decreased with time and was almost absent at cycle 15.

The thiosulphate concentration at the start of the humidity cell tests was high in all samples which is most likely due to the alkaline and anoxic environment. The formation of thiosulphates is a substantial risk when dealing with materials exposed to reduced environment and high pH. Thiosulphate in the GLD is, however, expected to originate from the paper process, where sodium hydrosulphide in the weak black liquor is oxidized to sodium thiosulphate. This highest leaching concentration of thiosulphate was found in the samples containing GLD. For all samples, the thiosulphate leaching was decreasing with time. The conversion from thiosulphate to sulphate is complex with intermediate sulphur species formed that may explain why no clear negative correlation between thiosulphate and sulphate was noted. However, it can be concluded that generation of acid due to the oxidation of thiosulphate does not seem to be an issue for this application since pH can be maintained at a high level.

Our study shows similar leaching behavior of the GLD/tailings blend for Cd, Cu, Ni, Co, Cr, Zn and Hg except for the first few cycles of the experiment. These elements originate mainly from the sulphide minerals in the tailings (Table 2). The leaching of these metals with the exception of Cr, Hg and Zn increased in the first few cycles with the GLD/tailings blend compared to GLD and tailings alone. The leaching is expected to be largely pH dependent. At high pH and low Eh, these metals are in the form of soluble metal oxide ions. Since the pH was >11 for the GLD/tailings blend in the first leaching cycle Zn is expected to be soluble as ZnO₂⁻. A small increase of metal leaching (e.g. Ni, Zn, Cu) is noted at cycle 5 which can be explained by the liberation of metals adsorbed to mineral surfaces due to the constant disturbance of the sample due to the repeated wetting, stirring and centrifugation. It is possible that this lag phase varies depending of the metal and how hard it binds to mineral surfaces. This may explains the fluctuating leaching behavior during the first few cycles.
During cycle ~5-35 the metals were retained and a decreased leaching was observed for the GLD/tailings blend. This is explained by the decrease of the pH. When pH is alkaline, below ~11-12, Cd, Cu, Ni, Co, Cr and Zn were retained as sulphides or oxides/hydroxides. Adsorption may be another mechanism. Several studies show that surfaces of sulfide minerals have a strong affinity to adsorb dissolved metals (Jean and Bancroft, 1986; Wang et al., 1989; Müller et al., 2002). Carlsson (2000) showed that As, Cd, Co, Cu, Mn, Ni, Pb and Zn are adsorbed to mineral surfaces for tailings originating from Kristineberg. Zn is expected to be stable as ZnS and Cr as Cr₂O₃, while elemental Hg is dominating at this pH. This can be confirmed by the decrease of the amount of these metals in the leachate when pH decreased to <11 in the GLD and GLD/Tailings. As an example, the GLD/Tailings blend shows a 50-90% reduction of leached Zn compared with Tailings and GLD alone until cycle 28. At cycle 35, when Tailings 1 showed a drop of pH and increased leaching of Zn the effect became larger. The leaching of Zn in tailings/GLD blend was 2 μg/l while a level of 48 000 μg/l was observed for Tailings 1. Ni show similar leaching behavior and is expected to be precipitated as Ni(OH)₂ between pH 8-12.

Al is mobile in the GLD/tailings mix due to the high pH. When pH decreases the Al is expected to precipitate as Al(OH)₃.

The leaching of Pb is inhibited by the GLD application when pH is above 6. In mildly alkaline and reducing conditions Pb tends to precipitate as carbonates if carbonates are available or as sulphides in a strongly reducing environment (Brennan et al. 1996). Only at the start of the experiment, the release of Pb was induced which may be due to the highly alkaline environment caused by the GLD/tailings blend.

Mo and As were elements that showed an increase of leaching as a result of the application of GLD. The largest increase occurred in the first few cycles. This is explained by the chemical behavior of As and its tendency to become mobile at high pH. Under anaerobic conditions, the mobility of As increases. This supports that oxygen penetration was limited in the Tailings/GLD blend before acid was added and the carbonates started to be consumed. The largest concentrations were generated at cycle one (2500 μgL⁻¹) and two (450 μgL⁻¹).

Mo shows similar behavior as As. The result shows that Mo is mobile in the tailings at the higher pH. For GLD/tailings blend when the pH is high, the Mo concentrations increased by a factor up to 10.

GLD have the potential to both reduce the amount of leachate generated in tailings and due to their alkaline property, improve the leachate quality by decreasing the metal mobility. The application is expected to last at least 11 000 years if it is blended properly. However, the increased leaching of As and Mo may cause environmental problems if the tailings used as an amendment for GLD contain large amounts of these elements. Restrictions may apply in this case.

**Reactions taking place after buffering ceased**

After the buffer capacity ceases and the pH is reduced to values <6, trace elements such as Cd, Cu, Ni, Co, Cr, Zn and Hg become mobile. This can be seen in the diagrams after cycle ~35 when acid is added. Acid addition represents the worst-case scenario of what happens when the buffering capacity have ceased. In nature, the acid would be produced from the natural oxidation of pyrite. In this experiment, Tailings 2 showed an increased leaching of sulphate in cycle 33, after a 6 month long break, an indication of sulphide weathering. The oxidation of pyrite may have needed time to get started or that the tailings had dried which enable oxygen to enter. For the other samples there were no signs of oxidation. Although the tailings are rich in FeS₂ and possibly FeS, the iron leached
after the artificial acidification is not likely to originate from pyrite since it is acid-insoluble because of its molecular structure (Luther, 1987; Rohwerder et al., 2003). Also, when comparing the Fe concentration with S concentrations it is unlikely that the metals are derived only from the sulphide minerals since small amounts of S was found. The molar ratio of Fe:S at the time of the first acid addition at cycle 39 was 22:1. This suggests that the Fe is originating from iron oxo/hydroxides since common secondary precipitates are ferricydrite, jarosite, schwertmannite, lepidocrocite and goethite (Gleisner and Herbert, 2002; Jönsson, 2003). The large negatively charged surface area of the secondary precipitates enable adsorption of metal cations that are released during the acidification when pH increases.

Part of the iron and sulphur may also originate from oxidation of other sulphide minerals since arsenopyrite, chalcopyrite, covellite, galena, pyrrhotite and sphalerite have been reported in tailings from Kristineberg (Holmström et al., 2001). The molecular structures of these sulfdie minerals are different from pyrite and these minerals can be dissolved by nonoxidative proton attack (Schippers and Sand, 1999; Rohwerder et al., 2003) at anoxic and dysoxic conditions releasing ferrous iron (e.g. from chalcopyrite and pyrrhotite). As shown in Fig. 1F, the concentration of leached iron is largest from the GLD/tailings blend. This is explained by that 24 ml HCl was added to the GLD/tail blend while only 1 ml of HCl was added to Tail 1. The leaching from the GLD/tail blend compared to the tailings alone is close to 24 times which confirms the fact that more H⁺ is available in the GLD/tail blend enabling dissolution of more iron oxides and hydroxides. This is only noted at the first acid addition. After this worst-case scenario the iron occuring as hydroxides are almost depleted.

The acidification caused by acid addition, causes the dissolution and leaching Ca, Mg, and Mn minerals. A more likely and natural scenario is that the leaching of the elements is occurring at a slow pace, at the same rate as the pyrite oxidation. When the carbonate minerals have been consumed, the leaching of these elements is expected to cease.

When acid was added at cycle 39, Cd, Ni, Co, Cr, Zn, Pb and Hg showed increased concentrations in the tailing/GLD blend compared to GLD and tailings alone. The difference is believed to be an effect of the larger amount of acid added to the blend than to the tailings. The acid addition to the GLD/tailings blend caused the pH to decrease to values below pH 8 which suggests that the CaCO₃ were consumed. GLD is expected to have lost its ability to act as an alkaline barrier. However, at cycle 41 only Ni, Co and Mn showed an increased leaching. For all the other sulphide associated elements the leaching decreased and at cycle 54 only Ni and Mn showed increased leaching behavior for the blend compared to tailings alone.

The observed leaching of Al, K and Na is most likely due to the effect of silicate dissolution since silicates contain aluminum (eg alumino-silicate), potassium (eg k-feltspars) and sodium (eg albite). When the samples are acidified and the pH reaches levels < pH 4, Al dissolves since Al hydroxids buffer between pH 3.8-4.8.

A decrease of As was observed at cycles 39-54. The lower pH may have contributed to the stabilization of As. When acid was added to GLD/Tailings blend to lower the pH, the leaching of As for the GLD application decreased with 30%. When sulphidic tailings oxidize, amorphous Fe(OH)₃ and goethite can be formed which can adsorb As.

When the oxidation produce a lower pH, Mo concentrations in the leachate is expected to decrease as can be seen in diagram (1R). Mo is most likely trapped as ferrimolybdite (Fe₅(MoO₄)₃ · H₂O)
at low pH. The mobility of Mo is greatly restricted during weathering due to low pH. However, if pH raises and is above the stability field of ferrimolybdite, Mo is released again (LeAnderson et al 1987).

It can be concluded that after the buffer capacity have ceased (> 11000 years), the GLD application will lose its ability to stabilize metals (expect As and Mo) derived from the tailings.

5. Conclusions

Tailings may be added to GLD to improve the shear strengths of the material. However, the blend showed an increased hydraulic conductivity and a small negative effect on the water retention capacity compared to GLD alone. However, the capacity to retain water is still very large compared to other materials used as sealing layers (eg clayey till). This means that the material may stay saturated even at time of drought when used in a sealing layer application. This would effectively prevent oxygen to reach the waste, thereby slowing down the oxidation of the under-laying mine waste. The alkalinity of the GLD showed to have a direct effect of the stabilization of most elements when blended with tailings. As long as the GLD can buffer the acidity formed by the sulphidic tailings the metals are expected to be stable. When the buffering capacity is consumed the metals become mobile. Based on the hydraulic conductivity and the fact that oxygen mainly can enter dissolved in water and not through the air due to the saturated layer, the oxygen diffusion is very low. The depletion of pyrite in the material used in our experiment, is expected to take 11 000 years. Restriction of using the application with tailings rich in As and Mo may be considered due to the increase of leaching of these elements.

6. Acknowledgements

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7. References


BS EN ISO 14688-2:2004, 5.3


Müller, B., Axelsson, M. D., Öhlander, B., 2002. Adsorption of trace elements on pyrite surfaces in sulfidic mine tailings from Kristineberg (Sweden) a few years after remediation.

prEN 15875:2008 Characterization of waste - Static test for determination of acid potential of acidic waste.


