

Article

## Characterization of Green Liquor Dregs, Potentially Useful for Prevention of the Formation of Acid Rock Drainage

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**Abstract:** Using alternative materials such as residual products from other industries to mitigate the negative effects of acid rock drainage would simultaneously solve two environmental problems. The main residual product still landfilled by sulphate paper mills is the alkaline material green liquor dregs (GLD). A physical, mineralogical and chemical characterization of four batches of GLD was carried out to evaluate the potential to use it as a sealing layer in the construction of dry covers on sulphide-bearing mine waste. GLD has relatively low hydraulic conductivity ( $10^{-8}$  to  $10^{-9}$  m/s), a high water retention capacity (WRC) and small particle size. Whilst the chemical and mineralogical composition varied between the different batches, these variations were not reflected in properties such as hydraulic conductivity and WRC. Due to relatively low trace element concentrations, leaching of contaminants from the GLD is not a concern for the environment. However, GLD is a sticky material, difficult to apply on mine waste deposits and the shear strength is insufficient for engineering applications. Therefore, improving the mechanical properties is necessary. In addition, GLD has a high buffering capacity indicating that it could act as an alkaline barrier. Once engineering technicalities have been overcome, the long-term effectiveness of GLD should be studied, especially the effect of aging and how the sealing layer would be engineered in respect to topography and climatic conditions.

**Keywords:** green liquor dregs; acid rock drainage; sulphidic mine waste; sealing layer

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## 1. Introduction

The major potential long-term environmental effect of mining is the formation of acid rock drainage (ARD) in sulphide-bearing mine waste, which can last for hundreds of years in a specific deposit [1,2]. The traditional strategy to reduce ARD generation is to prevent oxygen from reaching the waste to decelerate oxidation. This can be achieved by applying a dry cover or a water cover [1,2]. A composite dry cover usually consists of a protective layer and a sealing layer. The function of the protective layer is to protect the integrity of the sealing layer (e.g., root penetration, freezing/thawing, erosion) [3]. The sealing layer material in a dry cover should have the ability to minimize oxygen diffusion and reduce water percolation into the waste. Using a material with low hydraulic conductivity minimizes water percolation, oxygen transport and the risk of ARD formation. A high degree of water saturation is important to reduce the oxygen diffusion and to avoid desiccation cracks through which water and oxygen may reach the waste. The oxygen diffusion rate is  $10^4$  times lower in water than in air. This, together with the fact that the  $O_2$  concentration in water is  $\sim 20,000$  times lower than in air, explains why oxygen transport is so strongly reduced in saturated sealing layers or through a water cover [1,2]. Moreover, a sealing layer material must have mechanical strength to ensure slope and surface stability. To avoid high maintenance costs the material should be durable and not be prone to degradation. The composite cover is usually constructed by using natural soils, in glaciated terrains often till.

Using alternative materials such as industrial waste to mitigate the negative effects of ARD would solve two environmental problems at the same time. However, there is an urgent need for detailed research on the function of alternative materials before they can be used on an industrial scale. In particular, reliable predictions of the long-term efficiency are important [2].

Pulp and paper mills generate large amounts of waste such as fiber sludge, mesa lime (ML), green liquor dregs (GLD) and fly ash (FA). The alkaline waste materials ML, GLD and FA have properties suggesting that they could be useful for remediation of reactive mine waste [4–8] or neutralization of ARD [9–12]. Most paper mills use the sulphate production process where wood chips are treated with sodium hydroxide and sodium sulphide to liberate the cellulose. The method enables the inorganic chemical to be recycled and reused. However, large amounts of waste are released where GLD makes up the largest fraction retrieved in the chemical recovery cycle. Reuse and recycling of the GLD is limited and most of the GLD produced in Sweden,  $\sim 240,000$  t per year, is still landfilled, mainly at the pulp and paper mills own deposits. Even though the waste is not currently subjected to a tax for landfilling, the pulp and paper mills are facing disposal problems. GLD comprises one of the streams out of the pulping process to reduce the concentration of non-process elements (NPE), such as Mg, Si and Al originating from the wood [13]. The GLD retrieving process, using a pre-coat lime mud filter (the pre-coat is a mixture of  $CaCO_3$ ,  $CaO$  and  $Ca(OH)_2$ ), leads to various amounts of lime mud mixed with the green liquor, which strongly influences the final composition of the dregs. GLD is classified as a non-hazardous chemical waste by the Swedish EPA [14]. It has a high content of calcite, is alkaline and has been shown to have a low hydraulic conductivity [15]. This opens up the possibility of using it for construction of sealing layers in covers on sulphidic mine waste.

Since landfilling is costly, reusing the material would be beneficial for both the pulp and paper mills and the mining industry. Although GLD has been used in several sanitary landfill cover applications [16,17], no extensive characterization of the material has been performed. The objectives

of the present study were, on the basis of laboratory investigations, (i) to characterize the GLD physically, mineralogically and chemically to define variations in the material properties and (ii) to evaluate the feasibility of using GLD in sealing layers.

## 2. Materials and Methods

### 2.1. Materials

GLD were obtained from the Billerud Karlsborg sulphate pulp and paper mill in northern Sweden. The sampling took place on four occasions and ~30 kg were collected each time and stored in sealed cans, to prevent the samples from drying, at room temperature. The four batches are referred to as A, B, C and D herein.

### 2.2. Methods

#### 2.2.1. Mineralogical Characterization

X-ray diffraction analysis (XRD) was performed with a Siemens D5000 diffractometer (Siemens, Munich, Germany) using CuK $\alpha$  radiation generated at 40 kV and 40 mA. The scanning range was measured in Bragg-Brentano geometry from 5° to 90°.

#### 2.2.2. Chemical Characterization

Concentrations of 31 elements were determined for all four batches of GLD with duplicate samples. The modified EPA method 200.7 (ICP-AES) and 200.8 (ICP-SMS) [18] were used and performed by an accredited laboratory (ALS Scandinavia, Luleå, Sweden). Dry matter content, was determined drying the sample at 105 °C for 24 h according to Swedish standard SS 028113-1 [19]. Ca concentrations were analyzed using ICP-OES (Varian Vista MPX, Varian, Palo Alto, CA, USA) at the Billerud paper mill for 14 samples of GLD.

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 by Wyatt [20]. 0.75 g of dried GLD was placed in 50 mL plastic containers and mixed with 0–16 mL of 1 M HCl with 0.5 mL increments. Water was added to obtain 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).

A leaching test was performed in triplicate of GLD. The procedure was modified from the Swedish standard SS-EN 12457-4 [21]. 70 g dry mass of GLD was added to 700 mL of high purity Milli-QTM water (Millipore, Bedford, MA, USA) with pH 7 (taking the water content of the sample into consideration) to achieve a liquid-to-solid (L/S) ratio of 10 mL/g. The samples were agitated once a day for 6 days and centrifuged to collect the supernatant. The eluates were filtered with a 45  $\mu$ m nylon membrane and analyzed by an accredited laboratory (ALS Scandinavia, Luleå, Sweden) according to the previously described method. The L/S ratio was selected to simulate the long-term leaching. Assuming we have a 0.3 m cover with a weight of 400 kg/m<sup>2</sup> and the infiltration through the saturated

cover is 50 L/m<sup>2</sup> per year gives a L/S of 0.125 L/kg per year. This means that it is expected to take 80 years to achieve L/S 10 in the field by percolation through a traditional cover [22].

### 2.2.3. Physical Characterization

Dry matter content was analyzed at the Billerud paper mill on 178 samples over one year. Paste pH was analyzed in duplicate with a pH meter (Metrohm Ltd., 704 pH Meter, Herisau, Switzerland) for all four batches of GLD according to Weber *et al.* [23].

Laser diffraction analysis was conducted on duplicate samples for all four batches of GLD using a CILAS Granulometer 1064 (CILAS, Orléans, France) to obtain the particle size distribution, which was calculated using the CILAS software.

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 GLD batch B ( $n = 3$ ) in 1 mM KNO<sub>3</sub> and adjusting the pH with either HNO<sub>3</sub> or KOH to values between 2 and 12. The analysis was performed when the solution maintained the desired pH for 30 min. The results were analyzed with the zeta4 software (Parker Hannifin Corporation, Rohnert Park, CA, USA).

The surface area was analyzed in duplicate for all four batches of GLD. 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 analyzed with a DeSorb 2300A/FlowSorb instrument (Micromeritics, Norcross, GA, USA).

Constant Rate of Strain (CRS) tests were performed on GLD batches B and D according to a standard procedure [24]. Cylinders measuring 15 cm × 7 cm diameter were filled with GLD. The samples were set under a 30 kPa load for 28 days resembling a 1.5 m protective 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.

The water retention capacity (WRC) was measured on GLD batches B and D in duplicate. 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., Goleta, CA, USA). The applied tensions were: 0.1, 0.5, 0.8, 1.0, 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, which was determined from the weight of the dried samples (105 °C for 24 h) divided by the cylinder volume. 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 WRC.

A multivolume helium pycnometer (Pycnometer 1305, Micromeritics, Norcross, GA, USA) was used to determine the density of GLD batch B ( $n = 3$ ). The bulk density and compact density were calculated for GLD samples from batches B and D.

Surface and crystal structures were studied on GLD batch A using an FEI Magellan 400 XHR Scanning Electron Microscope.

Replicate samples of GLD were packed into cylinders measuring 15 cm × 7 cm diameter and cured for one month at 5 °C (soil temperature in field conditions) under a load of 20 kPa, equivalent to a 1 m top cover. The samples were tested for uniaxial compressive strengths. The deformation rate was set at 1.5%/min.

### 3. Results

Dry matter content of the GLD was measured on 178 occasions over one year at the Billerud Karlsborg paper mill. Average dry content was 46% ± 7% with 5th and 90th percentiles of 35% and 54%, respectively. For 14 of the samples, concentrations of Ca were measured at Billerud. Dry matter content and Ca concentration were correlated with a correlation coefficient of 0.75.

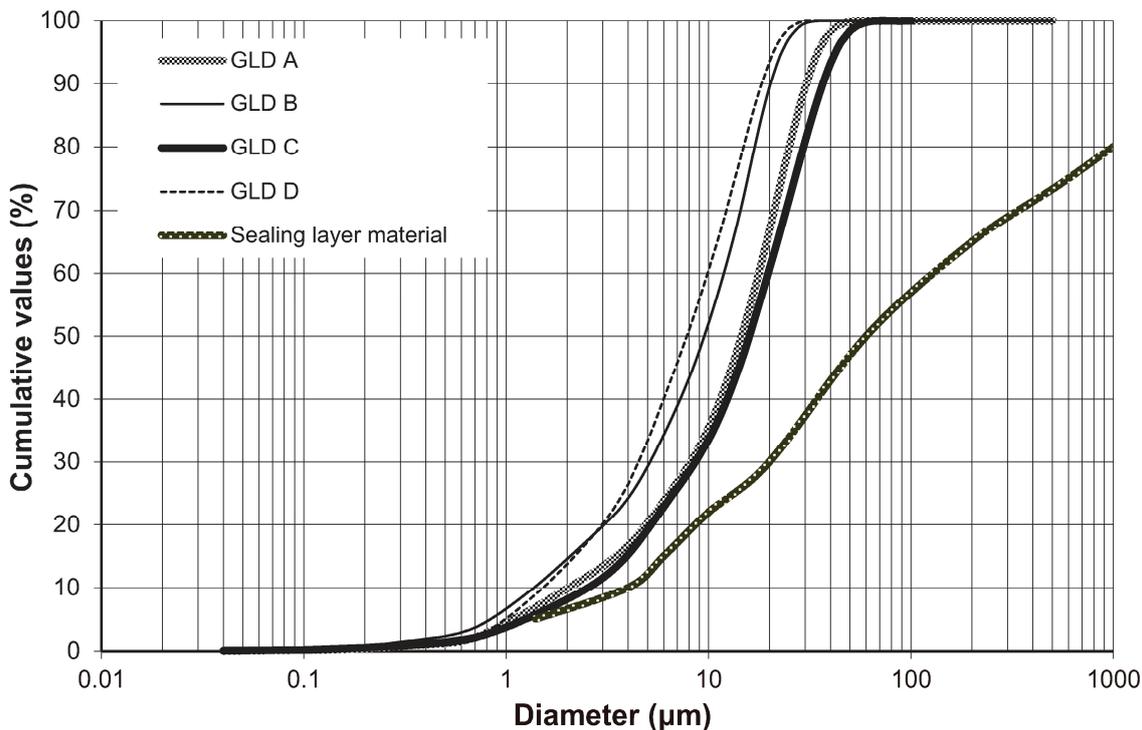
The XRD analyses showed that the crystalline phase of the GLD mainly is composed of calcite (CaCO<sub>3</sub>). Brucite (Mg(OH)<sub>2</sub>), a common form of Mg in ash, could also be detected. However, the detection limit is ~2% of sample and amorphous phases or poorly crystalline solids cannot be detected with the XRD. Particle size distribution according to laser diffraction analysis is shown in Figure 1. GLD appears to be a relatively fine-grained material with average d10, d50 and d90 values for the four batches of 1.9 ± 0.5 μm, 11.9 ± 3.9 and 26.4 ± 0.5 μm, respectively. The scanning electron microscope (SEM) measurements detected calcite crystals.

Table 1 shows the chemical composition of the different batches of GLD. Since calcite is the dominant mineral, the Ca concentration is high. Lime mud added in the process is the Ca source. The concentration of Mg is high, supporting the presence of brucite. Concentrations of Mn, Si, Al, K and P are also relatively high, indicating the presence of amorphous phases not detected by XRD. In the context of mine waste applications it is worth mentioning that the S content is high, ranging from 8330 to 18,650 mg/kg. Zn is the only trace metal that has a relatively high concentration, ranging from 733 to 1820 mg/kg. Table 2 shows the leached concentrations of elements, which are compared with the regulatory levels of important contaminants [25]. Most of the contaminants were below the level of leachates from inert waste. Of the trace metals, Hg and Pb exceeded this limit but not the limit for non-hazardous waste. K was readily leached where 97% was released. The average S concentration was 7990 mg/kg, which corresponds to a sulphate concentration of 23,970 mg/kg if it is assumed that S occurs as sulphate and corresponds to ~86% of the total sulphate in GLD. This is slightly higher than the leaching limit for non-hazardous waste. It should be mentioned that the leaching experiments performed when obtaining regulation limits were pursued using a one-step (one day) leaching test, whilst the leaching test used for GLD was performed with the batch leaching method that was ongoing for 6 days to simulate the long-term effect of leaching.

The zeta (ζ) potential for GLD batch B is negative over the entire pH range. Thus, cations 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.

In Table 3, the results of the measurements of surface area, paste pH, porosity, hydraulic conductivity, compact density and bulk density are summarized. There are differences between the batches, but not so large that they change the character of the material. Paste pH is high (10.0 to 11.0), the hydraulic conductivity rather low (10<sup>-8</sup> to 10<sup>-9</sup> m/s), porosity relatively high (73.2% to 82.2%), bulk density ranges between 0.44 and 0.67 g/m<sup>3</sup> and compact density ranges from 2.47 to 2.60 g/cm<sup>3</sup>.

**Figure 1.** Particle size distribution of green liquor dregs (GLD) batches A, B, C and D. For comparison, data for typical sealing layers consisting of clayey till is included [1].



**Table 1.** Metal concentrations in GLD duplicate batches A–D expressed on a dry matter basis.

Element	Unit	Sample batch							
		A1	A2	B1	B2	C1	C2	D1	D2
Dry matter (DM)	%	51.4	51.6	47.8	47.2	37.9	38.0	35.7	35.5
Si	mg/kg	4,960	5,020	6,630	6,850	9,720	10,500	12,300	12,400
Al	mg/kg	2,700	2,720	2,900	3,090	5,280	5,180	9,820	9,890
Ca	mg/kg	317,000	317,000	295,000	296,500	252,000	247,000	219,000	217,000
Fe	mg/kg	3,190	3,170	4,540	3,360	5,700	6,520	9,650	7,260
K	mg/kg	1,910	2,050	2,910	2,970	3,010	3,060	3,360	3,570
Mg	mg/kg	37,800	38,300	43,400	43,900	50,600	49,600	72,400	73,300
Mn	mg/kg	8,350	8,430	10,800	10,900	12,900	12,700	17,300	17,500
P	mg/kg	4,000	4,030	3,590	3,610	1,270	1,250	922	911
LOI 1000 °C	% DM	41.3	41.4	40.7	40.8	43.1	43.1	39.9	40.0
As	mg/kg	0.305	0.225	0.327	0.172	0.332	0.383	0.474	0.431
Cd	mg/kg	3.54	3.69	5.80	5.53	4.98	4.87	8.29	8.65
Co	mg/kg	3.34	3.04	3.96	3.67	4.83	4.72	5.63	5.77
Cr	mg/kg	71.9	80.2	93.2	94.3	92.0	97.7	126	127
Cu	mg/kg	101	109	112	108	179	159	224	202
Hg	mg/kg	0.04	0.04	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04
Ni	mg/kg	29.3	31.6	53.6	46.7	51.7	40.7	60.8	49.5
Pb	mg/kg	2.27	2.56	2.86	2.96	3.28	3.26	5.88	6.13
S	mg/kg	7,880	8,780	10,500	9,150	13,500	13,200	18,600	18,700
Zn	mg/kg	701	764	1,120	1,060	1,230	1,200	1,840	1,800
CaO	% DM	44.3	44.3	41.0	41.0	35.3	34.6	30.6	30.4

**Table 2.** Leaching of GLD (average of triplicate) with standard deviations at L/S 10 compared with regulatory limits for inert and non-hazardous leached with the same L/S ratio [25]. N/A = no data available.

Element	GLD L/S 10 (mg/kg)	Leaching limit values at landfills for inert waste (mg/kg)	Leaching limit values at landfills for non-hazardous waste (mg/kg)	Relative mass released from GLD (%)
Si	3.03 ± 0.00	N/A	N/A	0.01
Al	0.34 ± 0.19	N/A	N/A	0.01
Ca	29.4 ± 18.0	N/A	N/A	0.01
Fe	0.23 ± 0.00	N/A	N/A	0.01
K	1433 ± 12	N/A	N/A	97.0
Mg	8.3 ± 3.0	N/A	N/A	0.09
Mn	0.97 ± 0.76	N/A	N/A	0.01
P	3.07 ± 0.37	N/A	N/A	0.08
As	0.002 ± 0.002	0.5	2	0.32
Cd	0.0003 ± 0.0000	0.04	1	0.01
Co	0.0006 ± 0.0000	N/A	N/A	0.01
Cr	0.44 ± 0.07	0.5	10	0.7
Cu	0.045 ± 0.015	2	50	0.04
Hg	0.22 ± 0.00	0.01	0.2	0.08
Ni	7.01 ± 3.00	0.4	10	0.02
Pb	1.89 ± 0.00	0.5	10	0.06
S	7,990 ± 104	Sulphate: 1,000	Sulphate: 20,000	85.6
Zn	0.088 ± 0.051	4	10	0.01

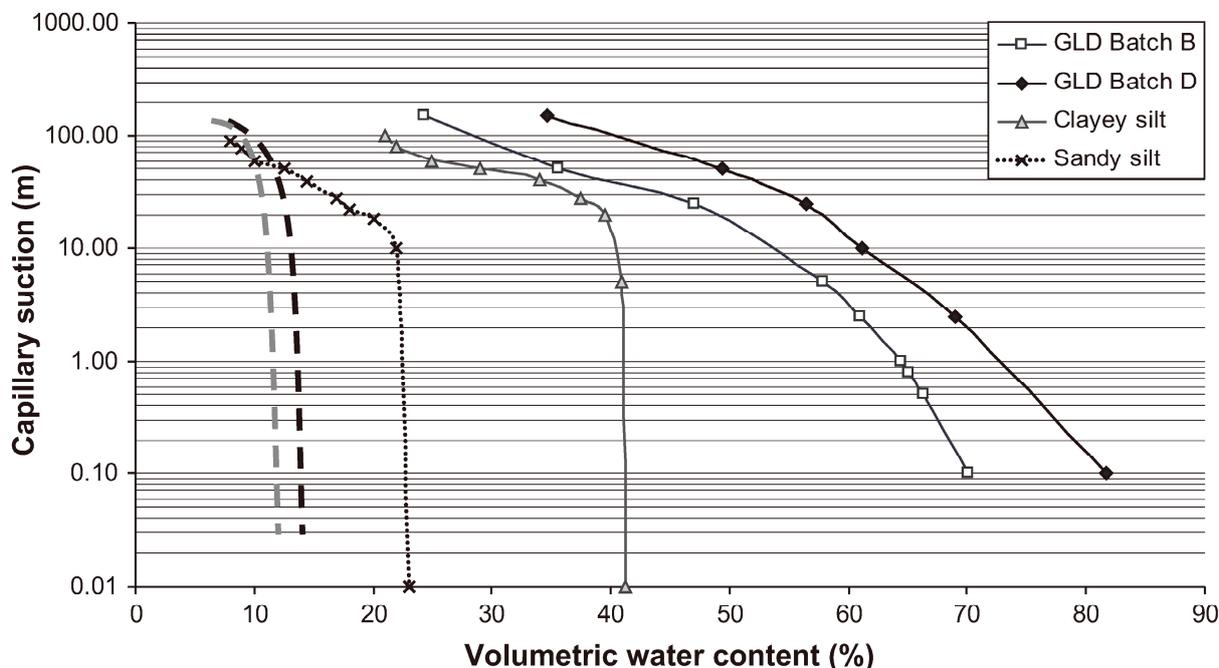
**Table 3.** Surface area, pH, hydraulic conductivity, bulk density, compact density and porosity of GLD batches A, B, C and D. The analyses were performed on duplicate samples, except for hydraulic conductivity and pH which were measured in triplicate.

GLD batch	Surface area (m <sup>2</sup> /g)	pH	Hydraulic conductivity (m/s)	Bulk density (g/cm <sup>3</sup> )	Compact density (calculated) (g/cm <sup>3</sup> )	Compact density (by pycnometer) (g/cm <sup>3</sup> )	Porosity (%)
A	12.1 ± 0.1	11.0 ± 0.1	N/A	N/A	N/A	N/A	N/A
B	16.8 ± 0.1	10.0 ± 0.0	1 × 10 <sup>-8</sup> ± 7 × 10 <sup>-9</sup>	0.67 ± 0.00	2.60 ± 0.00	2.57 ± 0.00	73.2 ± 0.4
C	21.4 ± 0.0	10.6 ± 0.1	N/A	N/A	N/A	N/A	N/A
D	20.4 ± 0.2	10.1 ± 0.0	1 × 10 <sup>-8</sup> ± 7 × 10 <sup>-9</sup>	0.44 ± 0.00	2.47 ± 0.00	N/A	82.2 ± 0.1

The WRC curves for batches B and D are presented in Figure 2. Compared with five sealing layers made of clayey till, commonly used in glaciated terrains [1], the WRC is significantly higher for GLD. The acid neutralizing capacity pattern was similar between pH 7.8 and 11, for the four batches of GLD with a large buffering at pH 8. Small differences were found between pH 2 and 7.8. To maintain pH > 6, the average neutralization capacity was high with the average value 18.5 mmol H<sup>+</sup>/g dry weight for the four batches of GLD.

The shear strength of GLD was assessed at 11.8 ± 1.6 kPa after one month curing time. This is a low value compared with other materials used for construction of sealing layers. Clayey till and Ca-bentonite have 4 times higher values and Na-bentonite 6 times higher values [26].

**Figure 2.** Water retention characteristics of GLD batches B and D. The results for two types of silt are also included for comparison [27]. The area between the dashed lines indicates the water retention capacity (WRC) of five sealing layers made of clayey till reported by Höglund *et al.* [1].



## 4. Discussion

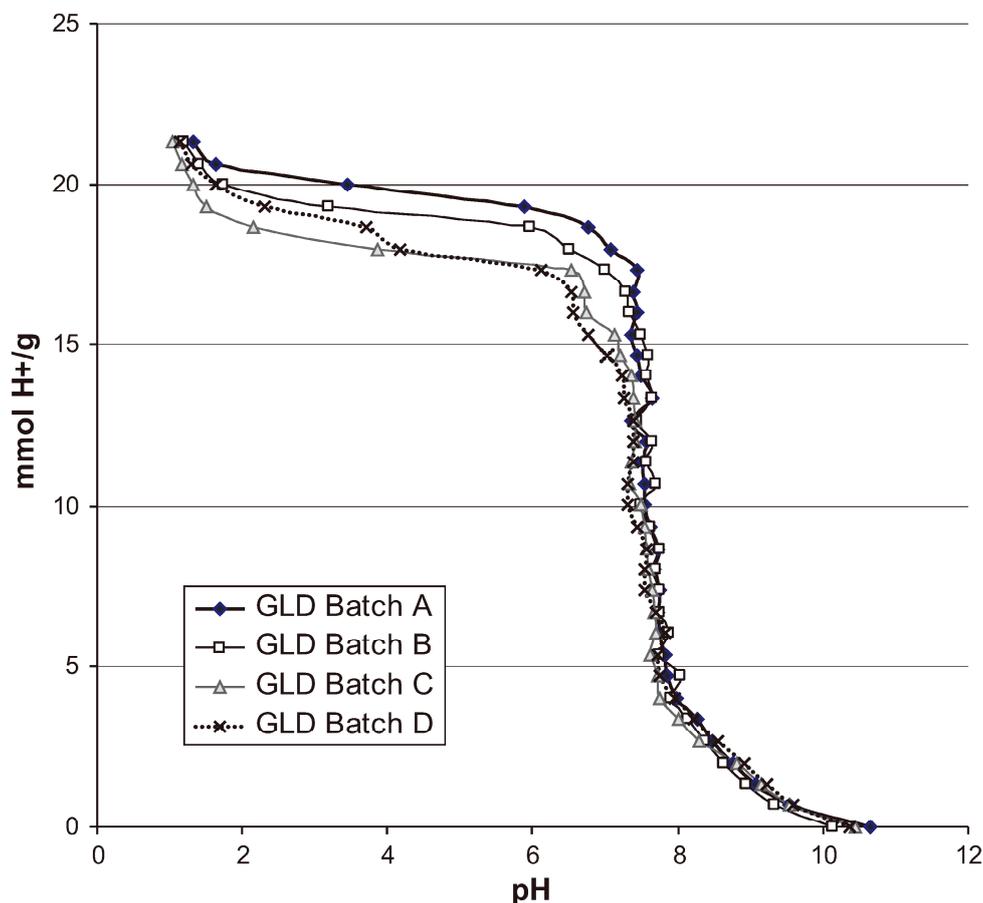
### 4.1. Material Variation

To enable the reuse of GLD, the effect of varying material compositions on the desired function should be understood to identify possible limitations. The dry content of GLD monitored at the Billerud mill ranges between 29% and 72%, commonly within the range 36% and 54%. Increasing dry content is a consequence of larger amounts of lime mud scraped off from the filter coating. This decreases the relative concentration of non-process elements.

The XRD analysis indicated the presence of calcite and small amounts of brucite, which is in agreement with Martins *et al.* [28], while no other buffering minerals were detected. Calcite crystals were detected by SEM analysis. The chemical analysis showed large amounts of sulphur but no crystalline forms of this element was detected. However, Martins *et al.* [28] found gipsite in GLD, not detectible by XRD. Ettringite and gypsum are other solid forms of sulphate that may be present in small amounts and therefore not picked up by XRD due to the instruments detection limit. It is likely that mainly amorphous and liquid forms of sulphate are present in GLD and can therefore not be detected with XRD. Based on the ANC, up to 75% of the GLD content is  $\text{CaCO}_3$ , assuming that the source of alkalinity that is buffering around pH 8.3 is only  $\text{CaCO}_3$ . 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 (Figure 3). The observed variation in the chemical and mineralogical composition of the GLD can be caused both by the origin of the wood and the efficiency of the GLD retrieval. The variation between batches had no strong effect regarding the hydraulic conductivity, buffering capacity, 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 residual product on a large scale. Therefore potential negative effects of the quality variation on the intended application of the material should be addressed.

**Figure 3.** Acid neutralization capacity for GLD batch A, B, C and D.



#### 4.2. Use of GLD in Sealing Layers

A sealing layer applied on reactive mine waste should function as a barrier for oxygen transport. Pore size and degree of saturation affect the effective diffusion coefficient,  $D_e$ , which in turn affects the oxygen flux through the material. The porosity forms channels for oxygen diffusion if the pores are not saturated.  $D_e$  increases with increasing pore size and quantity [29] and the oxygen penetration decreases when the particles are irregularly shaped compared to a more regular structure [30]. Decreasing particle size is correlated to increasing total porosity [29]. GLD is a fine-grained material. Comparing the particle size distribution of GLD with sealing layers made of clayey till [1] shows that GLD particles are significantly smaller with a  $d_{50}$  of 12  $\mu\text{m}$  compared to 60  $\mu\text{m}$  for the till. A sealing layer should be homogeneous to achieve uniform water saturation and GLD has a small particle size throughout the material. As the porosity of GLD is high, >70%, oxygen diffusion may occur if it dries. Oxygen diffusion decreases sharply as the degree of saturation increases above 85% [1]. WRC is a hydraulic property affecting the transport of fluids in the material. GLD has very high water retention potential, much higher compared to other cover materials (Figure 2) such as clayey till. The high WRC

is assumed to be due to the grain structure together with the ionic charge of the particles. Although the particle size falls into the range of silt, the WRC is more comparable to clayey materials than silty materials, especially at high under-pressures. Due to the high WRC, GLD has good potential to reduce the oxygen flux through a sealing layer by 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.

A sealing layer should consist of a material that decreases water infiltration. Decreasing the particle size of a material is usually correlated to decreasing its hydraulic conductivity [31,32]. Hydraulic conductivity is negatively correlated to porosity in the case of fine-grained material [33,34] and the specific surface area [32]. 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, resulting in high grade of saturation. Our results showed that GLD has adequate characteristics, such as a small particle size, high porosity and average surface area of 18 m<sup>2</sup>/g, to limit the water flow through the material. The tests confirmed a relatively low hydraulic conductivity, between  $1 \times 10^{-8}$  and  $7 \times 10^{-9}$  m/s. However, it did not reach the recommended minimum hydraulic conductivity [1] of  $1 \times 10^{-9}$  m/s.

There are several advantages of using GLD over virgin material such as till and other natural soils for construction of sealing layers. Opening quarries is not only costly but also has a significant environmental impact. A shortage of fine-grained cover material close to the mines is often an issue [2]. 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. Based on the results, GLD with low hydraulic conductivity would be most suitable to use for construction of sealing layers. However, the small variations observed between the batches of GLD from Billerud are not expected to lead to complications if used for barrier applications. GLD has previously been used in applications such as a stabilization agent for road construction [15].

Ideally, the material used as a sealing layer should both decrease oxygen penetration, water infiltration and simultaneously function as a chemically reactive barrier retaining heavy metal ions originating from the mine waste. A major concern when using residual products is assessing their potentially negative impact on the environment. Both undesired alteration of the material, which may alter its sealing function, and side effects on underlying mine waste caused by GLD leachates are potential issues to be addressed. The GLD from Billerud, however, has low content of most potentially harmful metals. The leaching data indicated that a large amount of the K and S content was leached. It is possible that the sulphate leached from the GLD may increase the chance of gypsum precipitation and could decrease the chance of jarosite formation in the underlying sulphidic waste [35]. It can be concluded that calcite was not dissolved despite of the repeated leaching test. The pH remained at a high level (pH 11.6). The leaching behavior is likely to change if the material is acidified resulting in a lower pH. Due to the production process of GLD (burned at high temperatures) it does not contain organic matter meaning that GLD is not susceptible to organic matter degradation that may harm the integrity of the sealing layer [28]. The material also lacks elements that are likely to interact and transform into harmful substances or oxidize easily, thereby changing its initial structure and properties. The  $\zeta$ -potential is similar to those of kaolinite and montmorillonite at lower pH, but the clay minerals show a larger negative charge at high pH [36]. The  $\zeta$ -potential had a negative correlation with

pH which can be related to its high content of  $\text{CaCO}_3$  and is consistent with other electrokinetic studies on calcite summarized by Guichet *et al.* [37]. For pH below 8, the presence of  $\text{CaCO}_3$  decreases leading to more free  $\text{Ca}^{2+}$  in solution [37]. The measured  $\zeta$ -potential should therefore be less negative for pH below 8, which is consistent with the result. The electrical properties of calcite are a controversial topic. Electrokinetic measurements have shown to be dependent on  $\text{CO}_2$  partial pressure and have yielded different results on calcites of various origins [37]. The calcite in the GLD has a negative  $\zeta$ -potential at all pH levels, which is not the case with kaolinite. This indicates that the GLD particles are relatively stable and resist the formation of aggregates [38]. This, together with the high WRC, suggests 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 buffering capacity of GLD is high, which is consistent with its high carbonate content. To maintain  $\text{pH} > 6$ , the average neutralization capacity was 18.5 mmol  $\text{H}^+$ /g dry weight for the four batches of GLD. The high buffering capacity indicates that GLD could act as an alkaline barrier. The high grade of saturation will minimize oxygen intrusion into the underlying sulphidic waste, slowing down oxidation. Only small amounts of alkalinity would therefore be consumed by the mine waste, resulting in a long lasting sealing layer. This is in agreement with Jia *et al.* [22] who showed that it is feasible to use GLD as a cover material to immobilize trace metals in tailings. Leaching experiments have shown that the amount of elements released was below the leaching limits for non-hazardous waste regulated by the European Union [25], making it a good candidate for sealing layer applications. In addition, it has been shown that addition of 10% green liquor dregs to reactive, sulphide-rich tailings reduced leaching of metals such as Cu, Co, Cd and Ni [39]. A probable explanation is that GLD increases pH, thereby immobilizing metal ions by precipitation of secondary minerals and absorption to mineral surfaces [1].

#### 4.3. Limitations

The results indicate that the application of GLD may be effective in the Swedish subarctic climate since the neutralization capacity is expected to last for a long time because the dissolution of buffering compounds such as  $\text{CaO}$ ,  $\text{Ca}(\text{OH})_2$  and  $\text{CaCO}_3$  will be slow due to the low hydraulic conductivity of the material and low precipitation. However, the applicability of a GLD sealing layer may not be suitable in all environments. Waste rock piles have to be carefully engineered diverting the water away from the pyritic waste. In climate zones with very high annual precipitation, there is a risk of water flow on top of the sealing layer. This may harm the integrity of the sealing layer or slowly dissolve the chemical compounds compromising its long-term function. The function may also be compromised if the material dries, which is a risk in arid regions.

Although GLD has shown desirable properties to function as a sealing layer, some practical issues have to be addressed beforehand. The material is very sticky, making it difficult to handle on a large scale. In addition, the total amount of GLD annually produced is small in comparison with the amount of mine waste. In Sweden, as an example, the annual production of GLD is *ca.* 240,000 t produced in many mills spread over the country, many situated far away from the mining areas. Logistics and transport economics must be considered. During 2010, 89 million tons of mine waste was produced, most of it from mines where sulphide-bearing ores were mined [40].

The shear strength of GLD was assessed at  $11.8 \pm 1.6$  kPa after one month curing time, which is low compared to the shear strength of bentonite and clayey till. Such low shear strength is insufficient for engineering applications [26]. It is important that the material exhibit sufficient compressive strength to 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 is 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. A mixture with the proportions 7:2:1 of tailings: GLD: fly ash was found to be geotechnically satisfactory but its function as oxygen barrier remains to be proven [41]. GLD may also be frost sensitive, which is a common problem with silty soils, causing damage to the cover (*i.e.*, frost heave) when used at shallow depths in cold regions.

## 5. Conclusions

GLD has the potential to be used as sealing layer in dry covers on mine waste since it has relatively low hydraulic conductivity, a high WRC and small particle size. Although the chemical and mineralogical composition varied between the different batches, these variations were not reflected in properties such as hydraulic conductivity and WRC. Leaching of contaminants from the GLD is not a concern for the environment. However, GLD is a sticky material, difficult to apply on mine waste deposits and the shear strength is insufficient for engineering applications. Improving the mechanical properties is therefore necessary. Mixing the GLD with tailings and additives such as fly ash is a promising methodology to increase the shear strength and even lower the hydraulic conductivity, but further research is necessary before using such mixtures for construction of sealing layers on an industrial scale.

GLD shows a high buffering capacity indicating that it could act as an alkaline barrier. Due to the low hydraulic conductivity, the buffering capacity will not be consumed in a very long time in subarctic regions. A practical evaluation of the use of GLD taking the climate/geographical region into consideration needs to be pursued. Covers on mine waste should be efficient in a very long-term perspective. Therefore, the effects of aging on GLD properties should be studied.

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## Authors Contributions

Experimental design was conducted by Maria Mäkitalo. Leaching experiments were conducted by Yu Jia. Maria Mäkitalo, Christian Maurice and Björn Öhlander contributed to the preparation and writing of the manuscript.

## Conflicts of Interest

The authors declare no conflict of interests.

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