Green liquor dregs from pulp and paper industry used in mining waste management: a symbiosis project (GLAD) between two Swedish base industries

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Abstract Mining has been and still is an important industry in Sweden. Leaching from sulfidic mining waste is however a serious environmental issue that can bring acidity and metals in solution. Simultaneously, green liquor dreg (GLD) with potential to decrease oxygen transport to the waste and neutralize acid leachate, is generated by the pulp and paper industry and deposited in landfills. The aim of the project is to promote valorisation of GLD, identify hinders and create a database providing information about the material and its variability to enhance establishment of circular economy for the pulp and paper mill waste.

Key words Waste rock, alkaline by-product, sealing layer, injection

Introduction

Sweden is EU´s principal Fe producer and one of the main producers of Au, Pb, Ag, Zn and Cu. Thereby the Swedish mining industry is of utmost importance from a European perspective. Mining operations may however have detrimental effects on soil, water and biota. Major long-term environmental effect is formation of acid mine drainage in sulfide-bearing mining waste. Simultaneously, Swedish paper and pulp industry – another important base industry, produces large amounts of alkaline residuals. Green liquor dreg (GLD) is the largest residual fraction, approximately 300 000 tonnes/yr is retrieved in the chemical recovery cycle at Swedish sulfate pulp mills. Today, GLD is exempted from taxes for disposal and there is no sustainable alternative for reutilization of GLD; the material is deposited or used to cap the mills´ own or municipal waste landfills.

Reclamation of mine waste

Today the most common method to prevent oxidization of sulfidic mining waste is to cover the waste material to prevent oxygen/water ingress. Today there are two main strategies used to prevent oxygen reaching the waste; 1) installing dry covers with a low permeability sealing layer or 2) disposing the waste under water. Both methods are based on the fact that oxygen diffusion is four orders of magnitude slower through water than through air. In Northern Europe climate conditions, the sealing layer method delay infiltration of oxygen through the cover by creating saturated condition (comparable to a suspended groundwater surface) in the sealing layer acting as an oxygen barrier. The second most common method is to dispose the mining waste below the water surface in a flooded open pit or in the tailings pond. Other approaches, which still are at the development level, aim at inhibiting the sulfide mineral to prevent the oxidation.

Sealing layer methods have limitations when the mining waste already has oxidized and when high concentrations of ferric iron is present. In such cases, the oxidation of the mining waste will continue, using ferric iron instead of oxygen and alkaline amendment is often used in order to increase pH and reduce trace element mobilization.

The 4-year GLAD project (2016-2020) (GLD vs ARD) was created around the hypothesis that GLD can be used as an effective agent in the remediation of acid generating mining waste. GLD consist of calcium carbonate, Na_2CO_3, Na_2S and insoluble solids (Pöykiö et al. 2006; Martins et al. 2007; Nurmesniemi et al. 2005). Studies have shown that GLD typically has low hydraulic conductivity (10^{-7}-10^{-9} m/s) and is strongly alkaline (pH 11-13) (Nurmesniemi et al. 2005). We agree with previous authors, that the properties suggest that GLD can be mixed together with natural materials, such as till, to construct sealing layers that will prevent oxygen from entering unoxidized mining waste. We also see a potential that GLD is a promising material to be used as neutralizer for already oxidized mining waste.

At the moment there are at least two new GLD-based methods that take advantage of different properties of the GLD and are getting closer to commercial use. Mäkitalo (2015) describes laboratory characterization and firmly established pilot experiments where GLD is mixed with coarse till. The GLD/till mixture fulfills the requirements for construction of sealing layers. In the application, the physical qualities (water retention capacity and low hydraulic conductivity) of the GLD is used and the buffering potential is merely a bonus that may affect the underlying waste. In another new application (Bäckström et al. 2011), GLD is injected into oxidized mining waste. Adhesive properties of the GLD decreases infiltration of water and the pH is increased which in turn reduces trace element mobility.

For acceptance of GLD, mining companies and authorities require production and quality control of critical factors over time. GLD is a residual material with generally negative monetary value for the producers and consequently, limited efforts have been made to monitor and control their quality. One key point in the GLAD project is to establish a GLD-property database with information about critical parameters for different types of applications. The database will make it easier for mining companies and “middle hands” (consultants and entrepreneurs) to compare and select materials for remediation. The database will also be a useful tool to guide the paper/pulp industry to target appropriate applications for the material and provide better knowledge of the quality criteria´s to be adhered to.

Methods

The GLAD Project

Project GLAD aims to fill the knowledge gap on production and quality requirements that currently is hindering the use of GLD for remediation of mine tailings and waste rock, and will help to valorize GLD through two work packages; WPA: *The right GLD for the right application* and WPB: *Economical, environmental and legal requirements*. A short summary of project activities is shown in tab. 1.

Table 1 *Work packages and major activities in GLAD Project (2016-2020).*

Description of activity	Outcome
WPA: The right GLD for the right application	
Visits and interviews at mills	Processes and parameters affecting GLD quality
Sampling/analyses	Variation of GLD quality over time (short and long term)
GLD Database	Matching, select materials for the right application
WPB: Economical, environmental and legal requirements	
Logistics, transport	Type of transport (road, rail, water), distances, CO_2-tax
Storing, quality	Interim storage, middleman, quality control
Policy	Environmental authorities, permits, long-term effect

Project approach

Academia initiated the GLAD project with the ambition to fill knowledge gaps regarding the use of GLD in mining waste mitigation, asking; what is left to study and what kind of further information is needed in order to "close the loop"? – Or in other words: What is needed before a complete value chain for GLD can be established?

In the project, the pulp and paper industries are motivated to take part in the discussions on how we can turn a costly waste stream into a valorized material. Another, just as important, reason for the mills to participate in the project is to be an active part in solving environmental problem by returning waste into the value chain according to the principles of sustainability.

Key drivers for the mines to participate in the GLAD project is the foreseen technical and financial potential in the usage of GLD in remediation projects. The reason is partly economical as the use of a by-product instead of a commercial product generally is associated with lower costs. There is also another important benefit in that natural resources can be saved if by-products are used for remediation instead of natural resources. Also the mining industry welcomes all research and development projects on new technologies for more efficient treatment of mining waste.

Another important group of participants in the project are representatives for the "middleman-companies/actors". They play an important role as they seek to add value by utilizing residual materials from one industry as a resource for another. For instance, practical obstacles such as storage and logistic that turn up along the way from the mill to the mine and they are able to identify and present suggestions for their solution. Eventually, over time all three actors need to determine how the final business model will look like.

A conceptual outline of GLAD project is shown in fig. 1. In order to establish a successful business model for the “flow” of GLD from left to right (from mill to mine) questions have to be answered regarding:

• GLD characteristics from different producers
• Which GLD to use for a certain location and application
• GLD-logistics, -storage, and responsibility for GLD storage

No matter how good the laboratory or field test-results are, – no real business will appear unless all/ or most, technical, economical and practical issues have been resolved.

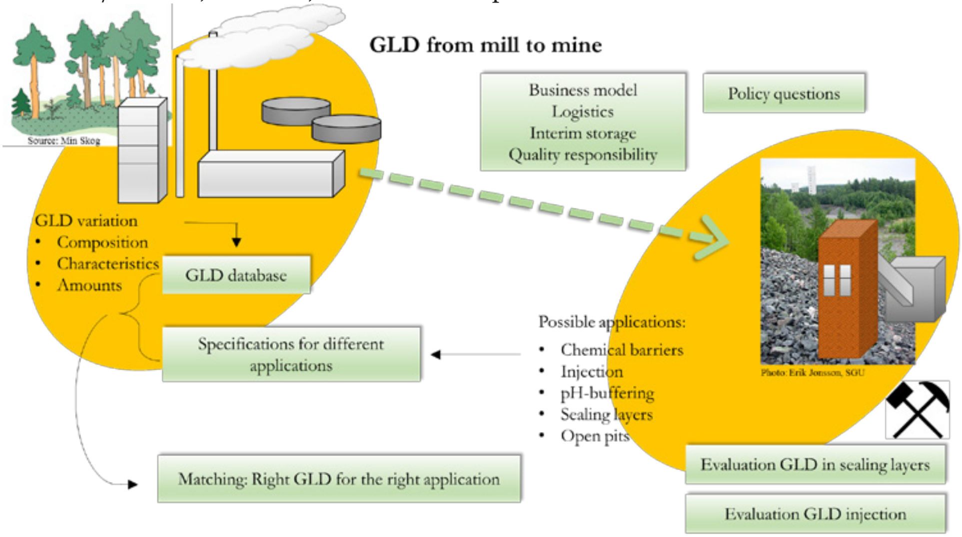

Figure 1 *Conceptual outline of the GLAD project. Work packages/major activities are described in green boxes.*

Results and Discussion

Visits at mills

The 18 paper/pulp-mills in the project were visited during fall 2016 in order to discuss the different processes and parameters that are affecting the GLD properties. One purpose with the action is discuss with staff and operators at the mills what changes in process or procedure have a potential to easily and positively change the GLD for a new intended purpose. Historically, GLD has not been in focus at the mills, *i.e.* the processes and handling at the mills have not been optimized to achieve or maintain a specific GLD quality.

Analyses of GLD

In order to determine the degree and character of variations in quality of GLD between different mills and different batches, GLD will be sampled at several mills at four occasions 2017 and 2018.

The investigated properties will be: Total element concentrations (by alkaline fusion and acid digestion followed by ICP-MS analysis), organic contaminants, cellulose derivates, mineralogy (XRD and SEM), water retention capacity (WR), hydraulic conductivity (HC), porosity, and organic content (determined as total organic content).

Leaching properties will be determined by standardized leaching tests (L/S 2, L/S 10) and sequential leaching test and leaching solutions will be analyzed for pH, redox potential, electrical conductivity, alkalinity, total organic content, sulfate, chloride, fluoride, nitrate, phosphate and element concentrations. Anions will be determined by capillary zone electrophoresis or ion chromatography.

ATR-FTIR analysis: By analyzing all GLD samples with ATR-FTIR and relate the obtained spectra's to the measured quality parameters (both chemical and physical) a multivariate model can be created using PCA and PLS. This model will be able to quickly determine both quality and changes with time for the same mill. The method and model can also be applied in a field situation to quickly determine the quality in different batches.

There are no records of eco toxic decomposition products of cellulose to GLD, but there is a potential risk which must be addressed. Samples of GLD from several different mills will be characterized with respect to human toxicity and eco toxicity: 1) simulated gastro intestine system leaching in order to determine toxicity when ingested, 2) skin exposure, inhalation etc., and 3) eco toxicity tests (fish and aquatic organisms).

Evaluation of the test results will show the industry and the environmental authorities that there are low risks in the handling, use and environmental application of GLD and that the application has no adverse effects on neither human health nor the environment (primarily the aquatic environment).

GLD Database

Characterization of the GLD as well as the relevant information about the process generating the GLD will be compiled in an open database, where it is possible to compare different GLDs between different facilities, but also to compare with the requirements demanded by different reclamation methods. The database will be used to shift the view of GLD as "only a by-product" to a potential product and provide an incentive to slightly change the production in order to achieve a better GLD product. Reclamation projects will also have a new source of information that enables logistical planning and the selection of the "right" GLD material for their chosen method and remediation project.

GLD quality varies depending on the production parameters and *e.g.* production incidents may lead to a batch with exceptional properties that should be separated for special purposes from the standard quality. There is also a need to develop a procedure for the operator at the mills to be aware of the quality of GLD, control it and ensure that different quality material do not impair the standard quality.

Criteria for quality control will be defined based on the use *i.e.* sealing layer, injection, etc. The aim is to identify key parameters that could be controlled by technicians at the paper mill and ensure that "different" material is not mixed with "standard" quality material.

GLD is expected to gain a higher degree of acceptance from authorities by becoming more transparent regarding what the benefits are using GLD, its content, properties and environmental impact.

Logistics and transport

The project will also study the logistical aspects connected to the application of GLD: volumes, transports, and interim/on-site storage.

Transportation costs may be a financial hurdle in many projects and therefore different solutions for transportation will be investigated including the possibility to use returning empty transports.

Storing and quality responsibility

Handling of GLD on the mining site and alternatives for temporary storing needs to be investigated. Possible GLD quality changes during aging also have an impact on the possibility to store GLD either at a mining site prior to reclamation or at a mill site prior to transportation.

Arrangements where a "middleman"-company (consultant or entrepreneur) assigned for the project guarantees delivery of a certain volume with a certain quality (*e.g.* d.w.) are expected to be developed.

Policy questions

Market based instruments, *e.g.* deposit tax for GLD, affects how GLD will be seen in the future – as a cost-efficient, sustainable amendment for mine waste remediation, or as a by-product with limited, or no, area of application For the moment GLD is exempt from waste taxation (500 SEK/ton) but what will happen if the tax for depositing of waste also would include GLD?

In the GLAD project, two new approaches of using GLD for mine waste mitigation are evaluated (GLD/till mixing and injection). Both trials have a background in experiences from trials that have been running for several years which gives a good starting point. The long-term based pilot scale tests are fundamental in the project. Results from "real world trials" are critical in proving to the authorities that our suggested use of GLD is a suitable, long-term treatment method of acid generating mining waste.

Conclusions

Two major work packages have been identified in order to develop a successful, market-based business model for using GLD in mine waste applications. These are: 1) Establishment of a robust database with information on volumes and quality of GLD at different mills and 2) Economical, environmental and legal requirements; all crucial parameters that more or less determine how the proposed new methods for GLD utilization will be accepted in practice.

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