Green liquor dregs for the remediation of abandoned mine tailings – opportunities and limitations

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ABSTRACT

The pulp and paper industry in Sweden generates large amounts of waste e.g. *green liquor dregs* (GLD) from sulphate pulping process. GLD is an alkaline residual product with a low hydraulic conductivity. At the same time, residues from former mining activities e.g. tailings and waste rocks may still be found in the surrounding of abandoned mines. GLD's chemical and hydraulic properties make it suitable to cover mining waste deposits to hinder water infiltration and/or to chemically neutralise oxidising tailings aiming at stabilizing the wastes and preventing metal leaching. The aim of the study was to investigate prerequisite of green liquor dregs (GLD) in the treatment of sulphidic copper mining waste.

GLD have a potential to be used to cover tailings deposits since e.g. mixtures of GLD and fly ash reached a hydraulic conductivity of 1-2E-09 m/s. The GLD characterisation enlightened that even though the majority of the falling GLD may fulfil hydraulic conductivity requirements, batches with higher lime content occur and may jeopardize the integrity of the cover. The alkaline capacity of the pulping wastes raised pH in the remediated tailings reducing leaching of e.g. Cu, Co, Cd, and Ni. Addition of 10% pulping waste to tailings on dry weight basis was efficient to reduce copper leaching by a factor 4 to 10. Mixtures including tailings reached hydraulic conductivity between 1 E-8 and 1 E-9 m/s which opens opportunity for tailings stabilisation including both chemical and hydraulic aspects i.e. capping solutions.

INTRODUCTION

The pulp and paper industry in Sweden generates large amounts of waste. While most by-products are internally recycled or used for energy production some of the wastes formed by chemical residues mainly comprising *green liquor dregs* (GLD) from sulphate pulping process are still landfilled. At the same time, residues from former mining activities e.g. tailings and waste rocks may still be found in the surrounding of abandoned mines. Acid mine drainage, i.e. the metal-rich acidic leachate generated when sulphidic mine wastes oxidise, is a serious environmental problem. Former mines are small compared to todays and may be found in remote areas, far from treatment facilities. Therefore, local remediation solutions may be needed to reduce the environmental impact of their remains.

Solidification/stabilisation technique is a method used to chemically and/or physically bind the contaminants in a waste to prevent their leaching into the environment. GLD is an alkaline residual product with a low hydraulic conductivity. GLD's chemical and hydraulic properties make it suitable to cover mining waste deposits to hinder water infiltration and/or to chemically neutralise oxidising tailings aiming at stabilizing the wastes and preventing metal leaching. The aim of the study, performed as a master's thesis, was to investigate prerequisite of green liquor dregs (GLD) in the treatment of sulphidic copper mining waste (Villain 2008).

MATERIAL AND METHODS

Three samples of GLD-(A, B, C) with varying dry content were used (Fig. 1).

Figure 1 Picture of the 3 GLD samples tested

The one presenting the best hydraulic properties was further used for the experiments. Bark sludge (BS) and fly ash (FA1) from wood incineration that are also wastes from the Billerud Karlsborg pulp and paper mill (Northern Sweden), were mixed to GLD to improve its hydraulic properties. Sewage sludge (SS) from Luleå city sewage plant was used as an alternative to BS. GLD-D from Varö Plant was mixed together fly ash (FA2) from Mölndals Energi plant, incinerating mainly peat, and fibre sludge (FS) from Varö Plant. GLD-D used to be separated with a lime filter in the same was as at Billerud plant. In the middle of 2008, the process was modified and polymers were used to flocculate the GLD. The mixtures were made in the field (Hargelius 2008).

Tailings (Tail) were collected at Nautanen former copper mine (region of Gällivare, Northern Sweden) that closed more than a century ago.

a) b)

Figure 2 Experimental set up: a) Constant Head Permeability column tests and b) batch leaching tests.

To evaluate the efficiency of green liquor dregs in stabilising mine wastes, two types of experiments were conducted (Fig. 2):

- Permeability tests: both Constant Rate of Strain and Constant Head Permeability column tests were used to assess the hydraulic conductivity of the GLD and GLD/tailings mixtures.
- Batch leaching tests were used to study the chemical stabilisation i.e. the effect of GLD on the metal leaching of the tailings.

RESULT AND DISCUSSION

GLD characterisation is presented in table 1. GLD are alkaline, with a pH varying between 12 and 13. However its quality varies. The hydraulic conductivity and electric conductivity varied with up to 2 orders of magnitude between the samples. Previous tests performed in 2000 and 2007 by Karlsborg plant indicated hydraulic conductivity between 10^{-8} and 10^{-9} m/s. The wetter samples had a lower hydraulic conductivity compared to the dryer. GLD dry content increases with the presence of calcium oxide residues which are porous. Insuring low calcium oxide concentration during the GLD removal process could be option to improve GLD quality with regard to hydraulic conductivity.

Table 1. GLD characterisation (pH and electric conductivity of leachate from batch tests at L/S 0.2).

Sample	Test type	Dry content (%)	Hydraulic conductivity (m/s)	pH	Electric conductivity (mS/cm)
GLD-A	CHP[a]	55	2.2 E-08	12.1	31.3
GLD-B	CHP	65	2.5 E-07	13.0	177.5
GLD-C	CHP	72	1.2 E-06	12.6	2.3
Karlsborg 2000*	CHP	38	4 E-09		
Karlsborg 2000*	CHP	?	2 E-09		
Karlsborg 2007**	CRS[b]	49	2 E-08		
GLD-A	CRS	58	1-1.5 E-08		
Karlsborg 2007**	CRS	56	4 E-08		
Karlsborg 2007**	CRS	62	4 E-08		

[a]: Constant Head Permeability
[b]: Constant Rate of Strain
*: Pousette et Macsik (2000)
**: Hoffner (2008)

The hydraulic conductivity of GLD may be reduced when amended with FA and organic sludge such as bark and sewage sludge. Table 2 presents the hydraulic conductivity measured in GLD mixtures with different amendments. The hydraulic conductivity was reduced with one order of magnitude when adding FA and BS.

The Constant Rate of Strain test gave lower hydraulic conductivity compared to Constant Head Permeability. The Constant Rate of Strain test is an indirect measurement of hydraulic conductivity when the sample is compressed while the Constant Head Permeability test corresponds better to natural conditions. The compaction achieved during the Constant Rate of Strain test could explain the lower hydraulic conductivity obtained.

Experiments performed with similar materials from a similar pulping plant i.e. Värö plant shown hydraulic conductivity as low as 1-2 E-9 m/s. The GLD-D separated with polymers showed an average lower permeability compared to the one separated with a lime filter. The hydraulic conductivity variability was higher with the GLD separated with a lime filter and several samples showed hydraulic conductivity one order of magnitude higher (10-45 E-9 m/s). Using lime filter leads to lime addition in the GLD which increases its porosity. Therefore, polymer separated GLD is expected to have a lower hydraulic conductivity compared the traditionally lime filtered.

Addition of GLD reduced the hydraulic conductivity of the tailings. Amendment with 30% GLD-A + FA decreased the hydraulic conductivity by one order of magnitude. Mixing BS to the GLD/FA-mixture decreased further the hydraulic conductivity by one order of magnitude. Increasing the amount of additive did not reduce further the hydraulic conductivity. One hypothesis may be that the grain size distribution reaches an optimum at a 70:30 amendment. Furthermore, sample variability may explain part of the variation. GLD-C was the sample showing the highest hydraulic conductivity. The addition of 10% GLD-C to the tailings decreased the permeability by 50%. In pure chemical stabilisation applications, conserving original hydraulic conductivity may be valuable while low hydraulic conductivity is required in capping applications.

Table 2. Hydraulic conductivity in different GLD and GLD-Tailing mixtures.

	Composition				CHP test[a]	CRS test[b]
Sample name	Tail	GLD	FA	BS/SS	Hydraulic Conductivity (m/s)	(m/s)
GLD-A +FA1		70	30		1.6 E-06	4.0 E-08
GLD-A +FA1 +BS		60	30	10		2.0 E-09
GLD-A +FA1 +BS[c]		60	30	10	1.4 E-08	2.5 E-09
GLD-A +FA1 +SS		60	30	10		5.0 E-09
GLD-A +FA2		70	30			2.0 E-09
GLD-A +FA2 +BS		60	30	10		1-2 E-08
GLD-A +FA2 +SS		60	30	10		1-4 E-08
GLD-A +FA2 +SS[c]		60	30	10	1.4 E-07	2.5 E-08
GLD-D + FA2 + FS[d]		60	30	10		9.8 E-9 (±14.6)
GLD-D + FA2 + FS[e]		70	20	10		4.6 E-9 (±4.7)
TAILINGS	100				5.8 E-07	
90 TAIL +10 GLD-C	90	10			2.8 E-07	
70 TAIL + 30(GLD-A+FA1)	70	21	9			2-4 E-08
70 TAIL + 30(GLD-A+FA1)[c]	70	21	9		6.4 E-08	3.5 E-08
70TAIL + 30(GLD-A+FA1+BS)	70	18	9	3	7.7 E-10	
40TAIL + 60(GLD-A+FA1+BS)	40	36	18	6	9.7 E-09	

[a] Constant Head Permeability
[b] Constant Rate of Strain
[c] hydraulic conductivity test performed on the same sample
[d] n=8. Lowest hydraulic conductivity measured 2 E-09 (Hargelius 2008)
[e] n=7. Lowest hydraulic conductivity measured 1.5 E-09 (Hargelius 2008)

The mixture of GLD and FA is hypothesised to cause the flocculation of Ca in the presence of organic matter and increase the porosity in GLD when FA is added to GLD alone. On the other hand, the S-rich tailing addition to GLD+FA leads to the $CaSO_4$ formation hindering the flocculation mentioned above.

The results of the leaching tests showed that GLD amendment was found to be efficient in reducing the release of Cu and Ni (also Co and Cd, results not shown) from the tailings (table 3). On the opposite the concentration of Mo and V (also Cr, results not shown) increased in the leachate after amendment.

Table 3. Metal concentrations after batch leaching test (L/S 10). n=3.

	Tailings		GLD-A		10% GLD-A		10% GLD-C		10%(GLD-A + FA1)		10%(GLD-A + FA1 +BS)	
	mg/kg	Std	mg/kg	Std	mg/kg	Std	mg/kg	Std	mg/kg	Std	mg/kg	Std
Cu	45.6	5.5	<0.01		0.4	0.0	7.0	1.3	5.1	1.1	4.0	1.3
Mo	<0.05		0.1	0.0	0.3	0.0	0.5	0.0	1.4	0.2	1.0	0.0
Ni	0.17	0.06	0.01		<0.005		0.05	0.05	0.01	0.00	0.02	0.01
V	<0.005		0.02	0.01	0.00	0.00	0.02	0.01	0.03	0.01	0.02	0.01
Zn	12.1	1.2	0.1	0.0	1.0	1.5	22.8	35.8	0.9	1.3	1.0	1.2

The concentration of Zn was generally decreased by GLD-A amendment. However, GLD-C amendment leads to increased Zn leaching. The same phenomenon was observed for Pb. No explanation was found to the higher concentration of Zn and Pb in GLD-C.

CONCLUSIONS

GLD have a potential to be used to cover tailings deposits since e.g. mixtures of GLD and fly ash reached a hydraulic conductivity of 1-2E-09 m/s. However, the pulping process is not controlled to ensure even GLD quality. The GLD characterisation enlightened that even though the majority of the falling GLD may fulfil hydraulic conductivity requirements, batches with higher lime content (high dry content) occur and may jeopardize the integrity of the cover and the potential applications of GLD for tailings capping. One outcome of the study was the difference between the results obtained by the Constant Head Permeability and Constant Rate of Strain methods and the difficulty to measure low hydraulic conductivity.

The alkaline capacity of the pulping wastes raised pH in the remediated tailings reducing leaching of e.g. Cu, Co, Cd, and Ni. Addition of 10% pulping waste to tailings on dry weight basis was efficient to reduce copper leaching by a factor 4 to 10. Chemical stabilisation applications may require conserved relatively high hydraulic conductivity compared to the surrounding tailings to avoid water damming. Mixtures including tailings reached hydraulic conductivity between 1 E-8 and 1 E-9 m/s which opens opportunity for tailings stabilisation including both chemical and hydraulic aspects i.e. capping solutions.

Further research should focus on GLD quality assurance. We hypothesise that GLD's dry content could be used as a first quality criterion. The correlation between the Constant Head Permeability and the Constant Rate of Strain methods should also be further investigated.

REFERENCES

Hargelius, K. (2008). *Pilotyta med tätskikt på Ätrans deponi, Fältförsök-Värö-FAVRAB-Hylte*. Ramböll Sverige AB, Region Väst, Gothenburg.

Hoffner, N. (2008). Tests performed by Billerud Karlsborg.

Pousette, K. and Macsik, J. (2000). Kartläggning av restprodukter från Assi-Domän AB. Research report, Luleå University of Technology, Luleå, Sweden.

Villain, L. (2008). *Pulping Wastes and Abandoned Mine Remediation. Application of green liquor dregs and other pulping by products to the solidification/stabilisation of copper mine tailings*. Master's thesis 2008:081, Luleå University of Technology, Luleå, Sweden.