Remediation of historic waste rock by injection of green liquor dregs – results from a field scale trial, Gladhammar, Southern Sweden

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Abstract

Mining in Gladhammar, southern Sweden started in the 15th century, generating waste rock containing copper, cobalt, and arsenic. During remediation (2011) some waste rock was preserved, due to its geoscientific value, and placed on a geomembrane surface. Eventually, it became apparent that it had a substantial environmental impact (pH 3.8, Cu 96 mg/L, Co 21 mg/L). In 2017, green liquor dregs was injected in order to increase pH and decrease trace element mobility. Ten months after injection pH was 8.3 and concentrations of copper and cobalt 1.3 mg/L and 1.1 mg/L, respectively. Evaluation will continue for at least five years.

Keywords: Mine waste, alkaline, cobalt, copper, arsenic, pH

Introduction

Gladhammar mine in southern Sweden was mined for copper and cobalt already in the 15th century and finished in 1892. Mining resulted in waste rock containing copper, cobalt, lead, and arsenic. Remediation was performed in 2011 and waste rock was mixed with lime and deposited under water in a nearby lake. Gladhammar mining area is type locality for the three minerals Gladite ($PbCuBi_5S_9$), Hammarite ($Pb_2Cu_2Bi_4S_9$) and Lindströmite ($Pb_3Cu_3Bi_7S_{15}$) and hence, authorities decided that some waste rock should be collected and preserved due to its high geoscientific value. Representative waste rock material was collected from eight areas representing the geology at the mine site. The material was then rearranged into eight piles on a geomembrane covered surface (1 000 m^2) with a well collecting all leachates. Eventually, it became apparent that the piles had a large negative impact on the environment, with acidic pH and high concentrations of cationic trace elements like copper, cobalt, and nickel.

A non-invasive remediation of waste rock at Gladhammar was needed. Preferably it should allow for continued geoscientific research and the material being accessible for mineral hunters in the future. Injection of alkaline materials to pre-oxidized waste rock, as a way of increasing pH within acidic waste rock piles and decrease mobility of cationic trace elements, has been developed during more than 10 years (Bäckström et al. 2011). By using alkaline injection, waste rock/acidic leachate is treated and the visual appearance of the area is unchanged. Aim with this project was to verify injection of green liquor dregs, a by-product from the pulp and paper industry, in larger scale.

Methods

Characterisation of waste rock

The waste pile in Gladhammar consists of eight separate piles of varying size (fig. 1). Prior to injection, sampling of waste rock was performed for leaching studies (50 L) and for chemical analysis and mineralogical studies, in order to determine if some of the piles contributed to a significant portion of the load from the remaining waste rock. Leaching studies were performed at liquid to solid ratio (L/S) = 1 in 50 L plastic containers. Waste rock was flooded (barely covered) with deionized water for 3 weeks, where after the overlying water phase was sampled and analyzed for pH, acidity, sulfate and major and trace elements.

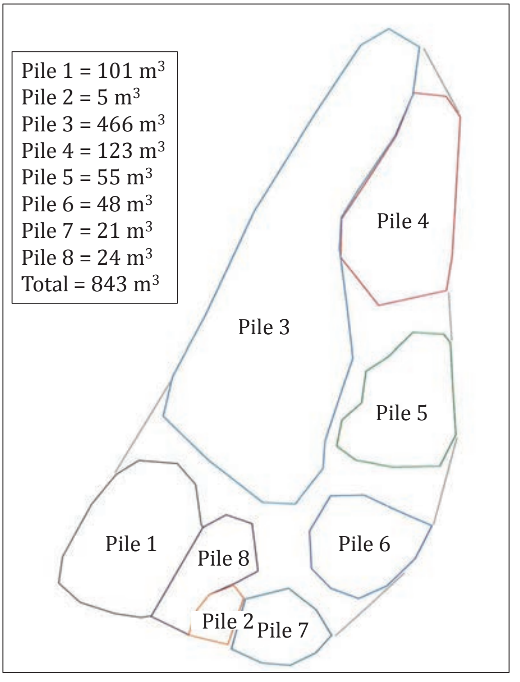

Figure 1 *The waste pile consists of eight separate piles with varying size.*

Analytical results are not available for the waste rock in the waste pile. Instead results from all mining waste prior to the reclamation has been used. Since the waste pile is composed of waste from the entire site this data is thought to be representative for the waste rock.

In table 1 below total concentrations are found for some selected elements in the waste rock. Results also indicate a low content of sulfur and a low buffering capacity (tab. 2).

Performed acid-base accounting indicate that a large portion of the original waste rock is acid generating (tab 2) with an average and median NNP of -24.3 and -17.6 kg $CaCO_3$/tonne, respectively.

Performed sequential extraction (Västervik municipality, 2005) also indicate that arsenic and lead is mainly associated with secondary iron phases within the weathered waste rock.

Injection

Injection was done at 99 points evenly spread over the area (fig. 2). Green liquor dreg was transported from Mönsterås pulp and paper facility and was tipped close to the waste pile. Slurry mixing was done using pan mixer

Table 1 *Selection of problematic elements in waste rock at Gladhammar mining site (Västervik municipality, 2005). Italic indicate half of the used detection limit for the analytical method used (MG-1).*

	CaO (%)	As (mg/kg dw)	Co (mg/kg dw)	Cu (mg/kg dw)	Pb (mg/kg dw)	S (mg/kg dw)
15:1	*0.045*	210	806	3 750	708	5 530
17:1	*0.045*	230	1 820	3 700	821	8 010
29:1	*0.045*	87.7	1 070	4 410	1 050	5 670
15:2	0.129	890	321	1 790	2 380	4 170
27:1	0.213	129	1 450	35 100	1 110	21 500
39:1	2.59	4.18	26.2	4 480	771	7 020

Table 2 *Results from acid-base accounting of waste rock samples from the mining area prior to reclamation (Västervik municipality, 2005). NNP: net neutralising potential.*

	pH	S (%)	NNP (kg CaCO3/ton)
12:1	5.8	0.473	-12.3
15:1	6.1	0.553	-13.2
17:1	5.7	0.801	-24.4
21:1	4.9	0.845	-23.9
24:1	5.3	0.558	-14.9
26:1	5.3	2.15	-65.2
29:1	5.2	0.729	-20.3
36:1	5.4	0.252	-5.4

Figure 2 *Part of the waste pile (parts of piles 3 and 4) and injection points marked.*

and pumping was performed using a slurry pump. A total of 63 tonnes of dry green liquor dreg was injected.

Green liquor dreg

Green liquor dreg (GLD) is a by-product from the pulp and paper industry consisting of $CaCO_3$, 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). Its properties suggest that GLD can be used to construct sealing layers that will prevent oxygen from entering unoxidized mining waste. Due to its alkaline properties GLD is also a promising material to be used as neutralizer for already oxidized mining waste. GLD used in Gladhammar was transported from Södra Cell pulp and paper

Table 3 Total and leachable concentrations (mg/kg dry weight) in green liquor dreg from Södra Cell Mönsterås pulp and paper facility.

	Total	L/S 2	L/S 10
pH	12.7	10.0	10.2
Ca	190 000	NA	NA
As	<2.6	<0.040	<0.050
Co	<2.6	NA	NA
Cu	34	0.37	0.32
Pb	4.0	<0.020	<0.050
S	5 400	1 100	1 130

facility in Mönsterås. Total and leachable concentrations of the GLD are found in table 3.

Results

The piles varied significantly in size of individual pieces, mineralogical grain size, and the proportions between sulfide-, silicate-, carbonate- and secondary- minerals.

Leaching studies (50 L) implicated that one of the piles generated more acid and leached higher concentration of cobalt than the others (Pile 8, fig. 3). Pile 5 generated the highest copper concentrations, but apart from these, pH and leached concentrations of major and trace elements were fairly similar for the different piles.

During injection pH in the well draining the area increased from 3.5 to above 10, due to excess GLD being washed out. One to two months after injection pH was around 7.5 and concentrations of copper and cobalt were 38 mg/L and 4.9 mg/L, respectively.

Discussion

Follow-up measurements of leachates from the waste pile indicate a clear increase in pH (from 3.8 to 8.3), and with markedly decreased levels of cadmium (93 %), cobalt (94 %), copper (98 %), nickel (95 %), lead (99 %), and zinc (97 %). Increased concentrations have been noticed for iron and sulfate in particular, which probably has to do with acidic secondary minerals that were dissolved as pH increased. As iron started to precipitate again as oxidized iron these levels have decreased again. At the second and third sampling after injection there were significantly decreased levels of iron. To summarize, the remediation has worked very well and concentrations of the main problematic elements have decreased considerably.

Conclusions

As a whole the remediation was performed as planned and without any major technical

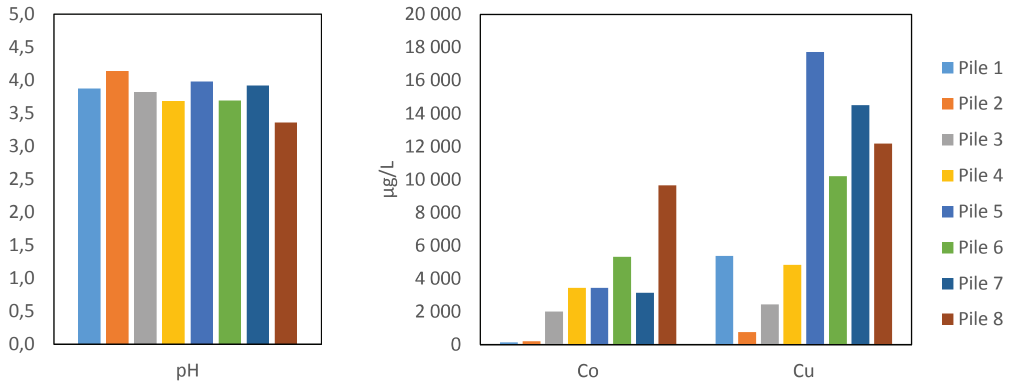

Figure 3 pH, cobalt and copper (µg/L) in leaching studies (L/S = 1) of waste rock from different parts of the waste pile (Piles 1-8).

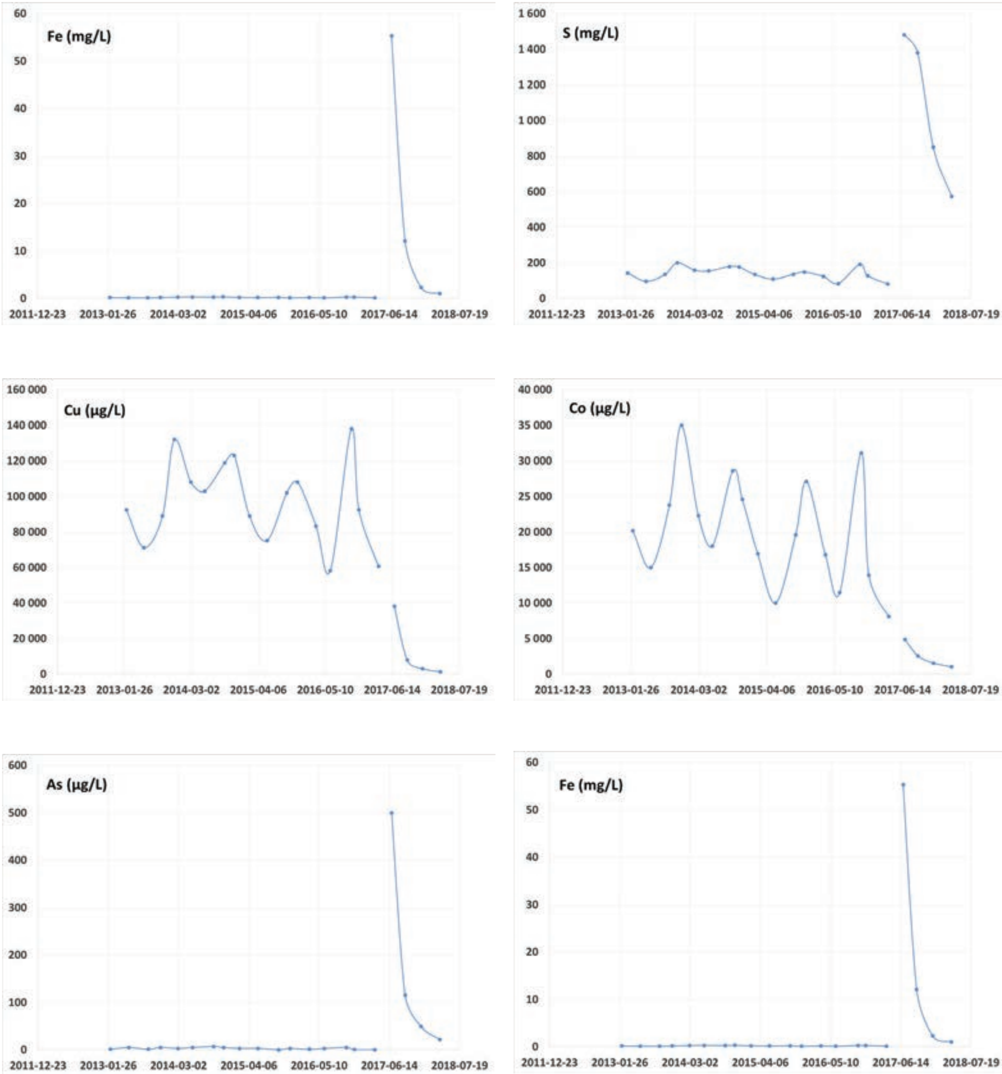

Figure 4 *Selection of data from the monitoring program at the site from February 2013 to March 2018. a) pH, sulfur (mg/L), copper (µg/L), cobalt (µg/L), arsenic (µg/L) and iron (mg/L).*

Table 4 *Reduction or increase (%) in element concentrations for the months September, November and February/March. Comparison made between single measurements after reclamation and average concentrations (n 4 or 5) prior to the reclamation.*

	September	November	February/March
Cu	-93	-97	-98
Co	-90	-94	-94
S	764	421	348
Fe	5 410	930	390
As	3 360	1 350	1 210

problems. Injection of green liquor dreg slurry increased pH in the leachates from around 3.8 to around 8.3. Concentrations of cobalt and copper were reduced with 94 and 98 %, respectively. The appearance of the waste rock did not change, which means that the waste pile is still accessible for mineral hunters and geoscientific research.

With alkaline injection, areas with cultural, historical and geological values can be treated with low visual impact and remnants can be left to all appearances intact. Evaluation of the remediation at Gladhammar will be performed by continuing measurements for at least five years. The pilot study indicates that GLD can be used for full scale applications and that it increases pH and decreases trace element concentrations.

Acknowledgements

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