The Importance of Adequate Waste Rock Characterization: A Case Study of Unsuccessful Drainage Quality Prediction

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Abstract

Current Finnish practices in waste rock characterization may result in improper drainage quality prediction. In this paper, we present a case study involving such inadequate predictions. Our results demonstrated that the waste rock materials with relatively low contents of harmful elements and S can still produce poor-quality drainage, and the waste rock characterization approach developed by the government should be re-evaluated. Special attention should be paid to low carbon content, low neutralization potential, and geochemical properties of single rock types rather than average concentrations of the whole rock mass.

Keywords: Aqua Regia Extraction, Geochemical Modelling, AMD-PHREEQC, Acid Mine Drainage, Waste Rock Mineralogy

Introduction

Poor-quality drainage originating from mine waste weathering is a severe environmental issue for mining industry. To design the waste disposal facilities and water management, the waste material should be characterized in an early stage of a mining project. The appropriate characterization methods should be systematically and carefully chosen, as improper characterization of mine waste might result in unexpected costs at later stages.

In Finland, it is a legislative requirement to evaluate if extractive waste is inert or not using aqua regia (AR) leachable element concentrations and S-content of the waste. According to the Finnish Government (2013), mine waste can be classified as inert if, among other criteria, the AR-extractable concentrations of As, Cd, Co, Cr, Cu, Hg, Mo, Ni, Pb, V, and Zn do not exceed the threshold values, i.e. the so-called "PIMA values" defined in the Government Decree on Assessment of Soil Contamination and Remediation Needs (Finnish Government 2007). Furthermore, the sulfidic S concentration should be $\leq 0.1\%$, or the NPR determined by the standard method EN 15875, should be >3 when the sulfidic S concentration is 0.1-1%.

We present a case study, where the waste rock materials of a small gold mine in Finland (Mine A) were inadequately characterized, and the drainage quality prediction was unsuccessful. The objective of this study is to investigate how to avoid similar situations in the future. We evaluated the use of PIMA values for mine waste characterization and demonstrate that relatively low concentrations of harmful elements within waste rock materials can still lead to poor-quality drainage if the mineralogical composition of the waste rock is unfavorable. We revised the original characterization scheme and compared the results with a similar waste rock site in Finland (Mine B). Furthermore,

reactive transport modelling with AMD-PHREEQC was applied to investigate how modelling could be used to support the quantitative prediction of the ultimate drainage quality.

Materials and methods

The Mine site A represents a small-scale open pit gold mine in Finland. It was active in 2013–2016, and during the operation, around 169 000 t of waste rock was excavated and piled to an area of around 6.5 ha at the mine site. The base of the waste rock area is rather impermeable. The quality of the drainage has been monitored, and the drainage waters have been collected for treatment. The waste rock materials were originally characterized in 2012, utilizing composite split drill core samples, and were mainly composed of metagreywacke, feldspar porphyry rock, and vulcanite (ISAVI 2018). The characterization methods included AR extraction (ISO-11466), ABA-test with the determination of the acid production potential (AP) by total S content and the neutralization potential (NP) by the Sobek method (EN-15875), and mineralogical investigation by light microscope. Based on these analyses, the rock materials were not completely inert, but the concentrations of the harmful elements in the rock mass were below the PIMA lower guideline values. Therefore, no major element mobilization as well as generation of poor-quality drainage were expected. To supplement the earlier characterization, further similar geochemical analyses were conducted in 2014 and 2015 for 15-20 kg composite waste rock samples collected from the pile surface.

The Mine A case was compared with that of the Mine B, which is a similar-scale nickelcopper mine in Finland. The latter involves both open pit and underground mine. It was active in 2007–2008, during which around 165 000 t of waste rock was excavated. Some of the waste rock material, which consists mainly of mica gneiss, gabbro, and amphibole rock, has been piled to a waste rock area of around 1.1 ha at the mine site. The Mine B waste rock site has been investigated by Karlsson *et al.* (2018) in 2016. The investigations included a waste rock drainage sample, and three 1520 kg composite waste rock samples collected at the mine site, which were analyzed by AR extraction, ABA-test, and FE-SEM-EDSmethod. Further investigations of the waste rock pile drainage have been conducted by Leskinen (2020).

In addition to the existing published data, more detailed mineralogical investigations by FE-SEM-EDS and XRD methods were conducted at the Research laboratory of the Geological Survey of Finland for the mixed composite samples collected from the Mine A in 2015 and Mine B in 2016. Furthermore, the AMD-PHREEQC code (Muniruzzaman et al., 2020) was applied to the Mine A case to model the evolution of the drainage quality. The simulations involve reactive transport processes by explicitly taking into account the partially saturated water flow, multiphase and multicomponent transport of aqueous and gaseous species, aqueous speciation, and kinetic mineral/dissolution reactions.

Results and discussion

The results show that the drainage concentrations of Al, Co and Ni have been three to tens of times higher at the Mine A compared with the Mine B, even though the drainage of the Mine B waste rock pile has been slightly more acidic (pH 3.3-4.3) than the drainage from the Mine A waste rock pile (3.5-5.0) (Table 1). The drainage of Mine A waste rock pile contained high concentrations of Al (16-215 mg/L), Co (3-9 mg/L), Ni (7-38 mg/L) and SO_4 (1100-4400 mg/L), while the Cu concentrations were low (0.02 mg/L). The drainage of the Mine B waste rock pile contained more Cu (0.1-0.3 mg/L) than the Mine A drainage, but the concentrations of Al (11 mg/L), Co (0.6 mg/L), Ni (7-12 mg/L) and SO₄ (610-990 mg/L) were lower compared with the Mine A drainage.

Based on the geochemical analyses, the environmental management of Mine B waste rock is however expected to be more challenging than that of waste rock from mine A, since the waste rock contains higher contents of harmful elements and acid production potential than the waste rock at the Mine A. The waste rock at the Mine A contained sulfur 0.1-0.7%, carbon <0.05-0.1%, Co 7-37 mg/kg, Cu 57-160 mg/ kg and Ni 19-122 mg/kg, whereas the waste rock at Mine B contained more sulfur (1.7-1.9%) and carbon (0.2-0.3%), and the concentrations of Co (68-80 mg/kg), Cu (198-471 mg/kg) and Ni (648-818 mg/kg) were clearly higher than at Mine A (Table 2). The measured acid production potentials were relatively low (5-21 kg CaCO₃/t) at Mine A, but so were also the neutralization potentials (5-14 kg CaCO₃/t), which resulted in potentially acid producing rock material (NPR 0.5-1.2). At the Mine B, both the AP (53-58 kg $CaCO_3/t$) and NP (13-22 kg $CaCO_3/t$) were higher compared with the Mine A waste rock material and resulted in lower NPR than at Mine A (0.2-0.4).

Mineralogically the Mine A and Mine B waste rock materials were quite similar, the main difference being the presence of carbonates and hornblende and somewhat

Table 1 The waste rock pile drainage qualities at the mines A and B. The pH was measured in the field. The metals as dissolved concentrations, SO_4 as total concentration.

Waste rock pile drainage	рН	AI	Со	Cu	Ni	SO_4
		mg/L	mg/L	mg/L	mg/L	mg/L
Mine A						
October 2014 ¹⁾	4.4	40			14	1200
September 2015 ¹⁾	5.0	16	3	0.02	7	1100
October 2016 ¹⁾	4.1	63			20	1200
August 2017 ¹⁾	3.5	215	9	0.02	38	4400
Mine B						
August 2014 ²⁾	3.4			0.3	12	990
June 2016 ³⁾	3.3	11	0.6	0.2	7	610
August 2017 ²⁾	4.3			0.1	11	830

¹⁾ISAVI (2018), ²⁾Leskinen (2020), ³⁾Karlsson et al. (2021)

Table 2 Waste rock geochemistry of the surface composite samples collected from the mines A and B. AP, NP and NPR determined as instructed in EN-15875.

Waste rock geochemistry	tot S	tot C	Co	Cu	Ni	AP	NP	NPR
	%	%	mg/kg	mg/kg	mg/kg	kg CaCO₃/t	kg CaCO₃/t	
PIMA threshold value			20	100	50			
PIMA lower guideline value			100	150	100			
PIMA upper guideline value			250	200	150			
Mine A								
Meta greywacke ¹⁾	0.2-0.7	<0.05-0.05	16-25	57-102	33-37	6-21	7-14	0.7-1.2
Feldspar porfyr ¹⁾	0.1	0.1	7	160	19	5	5	1.2
Int. Volcanite ¹⁾	0.2-0.3	<0.05	28-37	60-77	105-122	7-10	7-9	0.9-1.0
Mixed surface sample ¹⁾	0.4	<0.05	24	95	88	13	7	0.5
Mine B								
Mixed surface samples ²⁾	1.7-1.9	0.2-0.3	68-80	198-471	648-818	53-58	13-22	0.2-0.4

¹⁾ISAVI (2018) ²⁾Karlsson *et al.* (2018)

higher amount of sulfides in the Mine B samples. The main minerals in the mixed composite sample of the Mine A were quartz (32 wt.%), plagioclase (27 wt.%), biotite (26 wt.%), and chlorite (5 wt.%), whereas the Mine B samples were mainly composed of biotite (26-34 wt.%), plagioclase (17-21 wt.%), quartz (10-19 wt.%), hornblende (3-9 wt.%), and chlorite (1-9 wt.%). The detected sulfides at Mine A rock sample included pyrrhotite (0.5 wt.%), chalcopyrite (0.04 wt.%) and traces of Co-pentlandite, while the Mine B sample included pyrrhotite (1.0-1.5 wt.%), pyrite (0.02-0.7 wt.%), chalcopyrite (0.0-0.03 wt.%) and pentlandite (0.0-0.03 wt.%). In addition, high proportion of unclassified sulfides occurred in Mine B sample as a finegrained mixture with silicates (2.3-3.1 wt.%), with a ratio of around 1:1. Carbonate minerals were not detected in the Mine A sample, whereas the Mine B samples included 0.0-0.05 wt.% dolomite. The SEM images showed that in Mine A waste rock material the Copentlandite existed as small inclusions inside the pyrrhotite grains (Fig. 1). Similar coexistence of pyrrhotite and pentlandite was not detected in the Mine B sample. Inclusions of sulfides inside each other are known to provoke galvanic effects, that enhance the weathering processes (Chopard et al., 2017). In the cases of Mine A and Mine B, the total S

represents the sulfidic S, as besides sulfides no other S-minerals were detected.

AMD-PHREEQC was applied to test the use of modelling in supporting the prediction of drainage quality. Figure 2 shows the simulated drainage quality profiles at the outlet of the Mine A waste rock pile compared to the measured data. The release of acidity, Fe, Ni and Co are due to sulfide mineral oxidation under the presence of atmospheric conditions (a-e). The low pH resulting from the sulfidic reactions leads to the dissolution of aluminosilicates as reflected in the elevated concentrations of Al, Mg and K (f-h). The drainage pH appears to stabilize around 4, which might be a result of gibbsite and/or ferrihydrite buffering. The retention of Ni and Co in the waste rock pile appears to be low, as reflected in their high effluent concentrations. The reactive transport simulation performed with AMD-PHREEQC was able to capture the concentration ranges for different elements relatively well, especially when considering the conceptual simplifications and various assumptions that had to be made about the waste rock pile properties. Nevertheless, this exercise clearly demonstrate that the utilization of a model-based approach, (as used with AMD-PHREEQC in this study) involving even a simple conceptual model, is adequate for more quantitative interpretation

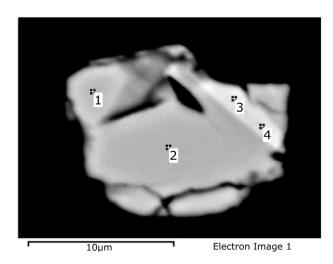


Figure 1 Co-pentlandite inclusion in pyrrhotite in Mine A waste rock. According to the spectrum data; 1: pyrrhotite (S 40.50, Fe 59.50), 2: pyrrhotite (S 40.20, Fe 59.80), 3: Co-pentlandite (S 36.14, Fe 31.86, Co 7.52, Ni 24.48), 3: Co-pentlandite (S 35.93, Fe 34.70, Co 6.37, Ni 23.00). Results in weight%.

of the monitoring data and for the ultimate waste rock management purposes.

High-Ni drainage has also been reported at the Diavik waste rock project by Bailey et al. (2015). At the Diavik type III waste rock test pile, which was constructed in 2006, the rock material was mostly granitic. The average concentration for sulfur was 0.05 wt.%, for carbon 0.03 wt.%, and for Ni 27 mg/kg (measured by the XRF method). The main sulfide mineral was pyrrhotite, which also hosted most of the Ni and Co. Despite the low S, Ni and Co content, basal drainage with pH of <4.5, and high dissolved metal concentrations e.g. for Ni (maximum of 20 mg/L) and Co (maximum of 3.8 mg/L) were measured in 2010, after four years from the construction of the pile.

Based on our results, the main causes for the drainage quality, which is lower than expected at the Mine A site compared with Mine B, were related to low carbon and carbonate content and neutralization potential of the rock material together with the occurrence type of sulfides at waste rock of the Mine A. The main metals detected in the drainage, i.e. Ni and Co, often coprecipitate with and adsorb to secondary minerals in waste piles (e.g. Ribeta *et al.*, 1995), which typically decreases their content in mine site drainage. In addition to affecting the weathering processes of the sulfides and drainage pH, the lower neutralization potential may result in decreased precipitation of secondary minerals, and reduced attenuation of metals in the waste rock pile. Furthermore, the galvanic processes might have enhanced the weathering rates of sulfides in Mine A case, but this should be more thoroughly investigated.

The case study underlines that the Finnish practice, which follows current regulations, to compare waste rock analysis results to the PIMA-threshold values, which are originally meant for soil contaminant assessment, and having a limit value of 0.1 wt.% of sulfidic S for inert waste rock, requires further consideration. For example, according to the Finnish legislation the waste rock from the Diavik test pile would have been classified as inert, which is not a correct classification based on the drainage quality. However, in the case of the Mine A waste rock material, the classification based on the regulations seems to be correct as it was not classified as inert. But as the Ni and Co concentrations of the combined rock mass exceeded only the PIMA threshold values, but not the lower guideline

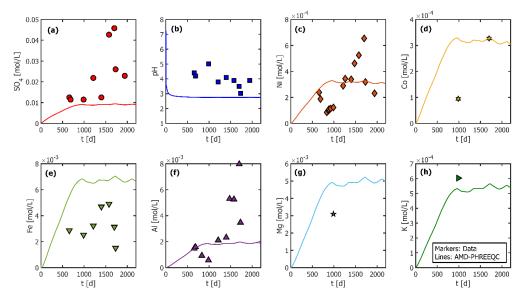


Figure 2 Temporal evolution of the Mine A waste rock pile drainage quality: breakthrough curves of $SO_4(a)$, *pH*(*b*), Ni (*c*), Co (*d*), Fe \in , Al (*f*), Mg (*g*), and K (*h*).

values, only minor amounts of Ni and Co mobilization were expected. It should also be noted, that relying on average concentrations of a waste rock pile material might not result in accurate drainage quality prediction. According to Vriens *et al.* (2019), waste rock cells consisting of 10% of the total waste rock mass may dominate the drainage quality.

To improve the waste rock characterization in the future, and to avoid the underestimation of the harmful element mobilities, special attention should be paid to the neutralization potential and carbon content, and to the single rock types rather than average properties of the rock mass. Our results suggest that rock materials with a low (e.g. <0.1 wt.%) carbon concentration have a high risk to generate poor-quality drainage with high metal concentrations, even though the harmful element concentrations in the rock material are relatively low. However, further investigations are needed to confirm the effect of C content in harmful mobility assessment. Furthermore, detailed investigations including kinetic testing and geochemical modelling are highly recommended to be combined with the basic static tests and geochemical characterization. It should be noted that also several other factors affect the ARD generation, e.g. rock texture, climate, and microbiological activity.

Conclusions

When comparing the geochemistry of the Mine A and Mine B cases, the Mine B waste rock material is expected to have more potential to produce drainage with higher harmful element concentrations. However, the concentrations of Al, Co and Ni were clearly higher in the Mine A drainage. This discrepancy can be explained by the mineralogical differences of the inspected waste rock materials. Especially the lack of carbon and neutralizing minerals in the Mine A rock material may result in reduced attenuation of harmful elements by precipitation and co-precipitation as secondary phases.

This study demonstrates that waste rock material with relative low amounts of harmful elements and S can produce poor-quality drainage. The characterization procedure in the Mine A case should have been more thorough, including detailed mineralogy, kinetic testing, and geochemical modelling, to provide a better prediction of future drainage scenarios. Based on our results, the rock materials with a low (<0.1 wt.%) carbon concentration appear to have a high risk to generate poor-quality drainage with high metal concentrations, which should be taken into account in future waste rock characterization. This indicates that the basis for the Finnish legislative requirements to utilize the PIMA element values and 0.1 wt.% sulfidic S content for inert rock material should be further evaluated. Furthermore, it should be investigated if the C content could have more weight in the evaluation.

References

- Bailey BL, Blowes DW, Smith L, Sego DC (2015) The Diavik Waste Rock Project: Geochemical and microbiological characterization of low sulfide content large-scale waste rock test piles. Applied Geochemistry 65, 54-72, doi:10.1016/j. apgeochem.2015.10.010
- Chopard A, Plante B, Benzaazoua M, Bouzahzah H, Mario P (2017) Geochemical investigation of the galvanic effects during oxidation of pyrite and base-metals sulfides. Chemosphere 166(2), 281-291, doi: 10.1016/j.chemosphere.2016.09.129
- Finnish Government (2013) Government Decree on Mining Wastes 14.3.2013. Finnish Government Decree 190/2013 (in Finnish and Swedish)
- Finnish Government (2007) Government Decree on the Assessment of Soil Contamination and Remediation Needs. Finnish Government Decree 214/2007 (in Finnish and Swedish)
- ISAVI (2018) Documents of the Issue: Rämepuron kaivoksen toiminnan lopettamiseen liittyvien jälkihoitotoimenpiteiden loppuun saattaminen ja ympäristöluvan muuttaminen, Ilomantsi (in Finnish). Regional State Administrative Agency for Eastern Finland, ISAVI/4358/2018. https:// ylupa.avi.fi/fi-FI/asia/1533527, accessed April 12, 2021
- Karlsson T, Alakangas L, Kauppila P, Räisänen ML (2021) A Test of Two Methods for Waste Rock Drainage Quality Prediction: Aqua Regia Extraction and Single-addition Net-acid Generation Test Leachate Analysis. Mine Water and the Environment, published online 21 May 2021, doi: 10.1007/s10230-021-00784-0

- Karlsson T, Kauppila PM, Lehtonen M (2018) Prediction of the long-term behaviour of extractive wastes based on environmental characterization: correspondence of laboratory prediction tests with field data. Bulletin of the Geological Survey of Finland 408, 11-25, doi:10.30440/bt408
- Leskinen J (2020) Water quality of the old Särkiniemi open-pit mine and water treatment testing with industrial by-products (in Finnish). Thesis, Technology, Communication and Transport, Savonia University of Applied Sciences, 64 pp
- Muniruzzaman M, Karlsson T, Ahmadi N, Rolle M (2020) Multiphase and multicomponent simulation of acid mine drainage in

unsaturated mine waste: Modeling approach, benchmarks and application examples. Applied Geochemistry 120 (6):104677, doi:10.1016/j. apgeochem.2020.104677

- Ribeta I, Ptacek CJ, Blowes DW, Jambor JL (1995) The potential for metal release by reductive dissolution of weathered mine tailings. Journal of Contaminant Hydrology 17, 239-273, doi: 10.1016/0169-7722(94)00010-F
- Vriens B, Peterson H, Laurenzi L, Smith L, Aranda C, Mayer KU, Beckie RD (2019) Long-term monitoring of waste-rock weathering at the Antamina mine, Peru. Chemosphere 215, 858-869, doi:10.1016/j.chemosphere.2018.10.105