



A Test of Two Methods for Waste Rock Drainage Quality Prediction: Aqua Regia Extraction and Single-addition Net-acid Generation Test Leachate Analysis

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Abstract

The mobility of contaminants from mine waste can be assessed using different extraction methods. Aqua regia (AR) extraction is the most commonly used method in Finland. Another method is the analysis of leachate from net acid generation (NAG) tests, which is primarily designed for acid production potential assessment. We investigated the performance of single-addition NAG test leachate analysis and AR extraction in drainage quality prediction, using waste rock and drainage water samples from several Finnish waste rock sites. Our objective was to improve interpretation of the AR and single-addition NAG test leachate analysis results in drainage quality prediction. The AR extraction effectively reflected elements that occurred in elevated concentrations in drainage water, though it over-predicted Al, As, Cd, Co, Cu, and Ni in some circumneutral drainages, and Cr in general. The single-addition NAG test leachate analysis also performed well in assessing the mobility of contaminants including Al and Cr at acid mine drainage sites. As the contaminants tend to precipitate in neutral NAG test solution, the usability of the method in neutral mine drainage cases should be further investigated. Furthermore, the conclusions presented in this study are limited to waste rock samples collected from the surface of piles; future work will examine waste rock history, dump cores, drainage quality changes, etc. in more detail.

Keywords Mine waste characterisation · Drainage water · NAG test · ARD · NRD

Introduction

One of the main environmental issues associated with metal sulfide mining is generation of contaminated acid rock drainage (ARD) or neutral rock drainage (NRD) (e.g. Dold 2014; Heikkinen and Räisänen 2009; MEND 1991; Nieva et al. 2018; Price 2003; Singer and Stumm 1970). Mine waste facilities such as waste rock piles and tailings impoundments are the main sources of ARD and NRD (MEND 1991; Price 2003). Designing appropriate waste facilities and drainage

water management systems is important for mitigating the potential consequences of ARD or NRD but requires sufficient data about the long-term behaviour of the wastes. Thus, it is important to characterise mine wastes and assess their behaviour before actual mining activities begin.

The short- and long-term behaviour of mine wastes can be predicted by geochemical laboratory tests including static tests and longer-term kinetic tests, geochemical modelling, and using analogues from similar, older, mine waste sites (Kauppila and Räisänen 2015; Lapakko 2002; Muniruzzaman et al. 2018; Nordstrom and Nicholson 2017; Price et al. 1997; White III et al. 1999). The acid production potential of mine waste is usually determined based on different acid–base accounting (ABA) tests (Price 2009; Sobek et al. 1978), with the standardised method SFS-EN 15875 (SFS-EN 2012) being widely used in Europe. Another commonly used method is the single-addition net acid generation (NAG) test (AMIRA 2002; Miller et al. 1997), which involves the reaction of a sample with hydrogen peroxide (H₂O₂) to rapidly oxidise any sulfide minerals present. The ARD potential can also be calculated based on

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the mineralogy of the sample (Dold 2017; Karlsson et al. 2018b).

The mobility of contaminants from mine waste can be assessed using different extraction and selective leaching methods. Extraction with aqua regia (AR), a 3:1 mixture of hydrochloric acid and nitric acid (Doležal et al. 1968; Niskavaara 1995), is the most commonly used extraction method in mining environmental and mineral exploration studies in Finland. AR is intended to dissolve elements bound especially to sulfide phases, but in addition to sulfides, it also partly dissolves some silicates, and all carbonates and secondary precipitate minerals. As sulfides are the main primary sources of contaminants in mine wastes (e.g. Lapakko 2002), a sulfide-specific leaching method is useful in environmental studies to assess the potential mobility of elements (Niskavaara 1995). Based on previous studies, the AR-extractable concentrations of waste rocks indicate these contaminants are most likely to be of concern in mine waste drainage (Fosso-Kankeu et al. 2015; Karlsson and Kauppila 2016; Karlsson et al. 2018a; Price et al. 1997). In Finland, AR extraction is also the preferred method for evaluating whether mine waste is inert (Finnish Government 2013) and for assessing soil contamination (Finnish Government 2007; Reinikainen 2007). According to 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 or the background values (if the latter are naturally higher than the former), i.e. the so-called “PIMA values” defined in the Government Decree on Assessment of Soil Contamination and Remediation Needs (Finnish Government 2007).

Another method for contaminant mobility prediction is the analysis of leachate from the single-addition NAG test, which is primarily designed to determine the potential generation of acid in mine wastes (Barnes et al. 2015; Charles et al. 2015; Karlsson and Kauppila 2016; Karlsson et al. 2018a; Räisänen et al. 2010). The NAG test uses H_2O_2 to liberate acidity from Fe-sulfides. Räisänen et al. (2010) suggested that NAG leachate element concentrations could be useful for assessing contaminant mobility in long-term acid-generating reactions. Unlike AR, which cannot be used for drainage pH prediction, the NAG test combines the ‘acid generating’ and the ‘fast reacting’ acid neutralisation components and can predict the likely final pH of leachate from sulfidic mine waste. The extractability of trace elements during the NAG test can be considered representative of their potential mobilization in the long-term (Jennings et al. 2000; Lei and Watkins 2005; Weber et al. 2004). Analysis of NAG test leachate could also potentially be scaled to field conditions and used for preliminary prediction of mine waste seepage water quality (Barnes et al. 2015).

The objectives of the study were to: (1) improve the interpretation of AR extraction and single-addition NAG test leachate analysis results, (2) evaluate the functionality of NAG test leachate analysis as a proxy for natural sulfide oxidation, and (3) evaluate acid AR extraction for the preliminary assessment of mobility of contaminants. To achieve these objectives, we inspected the results of single-addition NAG test leachate analysis and AR extraction for waste rock samples collected from the surface of piles from various Finnish mine waste sites. We compared the AR and single-addition NAG test leachate results to actual measured drainage water compositions for selected surface composite samples. We also investigated and described waste rock characteristics and drainage water quality at several selected Finnish waste rock sites.

Materials and Methods

The rock materials analysed consisted of 49 waste rock samples (denoted 1–38, 101–111) collected from a total of 17 different locations: 14 active and closed metal mines, two industrial mineral mines and one dimension stone quarry in Finland (Table 1). Sampling was conducted during multiple field campaigns from 2013–2016.

Waste rock samples 1–38 consisted of a single rock type or mixed composite waste rock samples without corresponding drainage water data. Samples 101–111 were those used in Karlsson et al. (2018b) and consisted of ≈ 15 –20 kg of heterogeneous rock material of particle size of ≈ 5 –10 cm randomly collected from the surface of waste rock piles above drainage points, where water samples were collected for comparison. At Mine B, two sets of waste rock and water samples were taken from the same spot, the first in 2014 and the second in 2016. Mine C and Mine G have two different waste rock piles, an inactive older one and a new active one, which were sampled separately.

Waste rock drainage water samples were collected from small seepage streams flowing from the base of the waste rock piles at waste rock sampling sites 101–111. In two cases (Mine C new and Mine A), there was no visible flow, and thus samples were taken from a pond at the base of the waste rock pile. The quality analysis of waste rock drainage water included field analysis of pH and electrical conductivity (EC) and laboratory analysis of dissolved elements. The field measurements were conducted using a portable multi-parameter YSI probe, which was calibrated to pH 4 and 7 before every field trip. For dissolved element analysis, the drainage water samples were filtered in the field through 0.45 μm filters into polyethylene bottles that had been rinsed twice with sample water and acidified with concentrated HNO_3 .

Table 1 Sources of samples analysed and details of mine sites, including the major minerals, carbonates, sulphides and secondary minerals

| No | Mine site | Mine type | Waste facility active | Rock/sample type | Main minerals (> 5%) | Carbonates | Sulfides | Secondary minerals |
|-----|------------|-----------|-----------------------|--------------------------------|---------------------------|------------|---------------------|--------------------|
| 1 | Mine A | Cu–Zn | 1973–1986 | Chlorite biotite schist | qtz, bt, chl | | po | |
| 2 | Mine B | Ni | 1970–1993 | Serpentinite | srp, crs, ol | | | |
| 3* | Mine B | Ni | 1970–1993 | Composite serpentinite | ol/srp, tlc | cc | | gö/li |
| 4* | Mine B | Ni | 1970–1993 | Composite mica schist | qtz, pl, bt, ms | | po, py, pe, ch | gö/li, ja |
| 5* | Mine B | Ni | 1970–1993 | Composite mica schist | qtz, ms, bt, pl | | po, pe, ch, py, sph | gö/li |
| 6* | Mine B | Ni | 1970–1993 | Composite serpentinite | srp, ol | cc, sid | po, pe, ch | |
| 7 | Mine C old | Talc–Ni | 1982–2004 | Graphite schist | gr, po, qtz, bt, pl | | po, py | |
| 8 | Mine C old | Talc–Ni | 1982–2004 | Soapstone | carb, tlc | carb | po, py | |
| 9 | Mine D | Cu | 1966–1984 | Skarn rock | grt, ch, cpx | | ch, po | |
| 10 | Mine D | Cu | 1966–1984 | Amphibolite | hbl, pl, ep, cpx, zs | | py, ch, po | |
| 11 | Mine D | Cu | 1966–1984 | Skarn rock | grt, cpx, pl | | | |
| 12 | Mine J | Ni–Cu | 1988–1992 | Graphite biotite schist | qrt, pl, bt, gr, kfs, po | | po | |
| 13 | Mine J | Ni–Cu | 1988–1992 | Tonalite | pl, bt, qtz | carb | po, ch | |
| 14 | Mine J | Ni–Cu | 1988–1992 | Amphibole tonalite | pl, am, qtz, bt | | po, ch, py | |
| 15 | Mine K | Zn–Cu | 1984–1985 | Garnet biotite schist | qtz, pl, bt, grt | | py, po, ch | |
| 16 | Mine L | Cr | 1968–2003 | Soapstone | tlc, carb, crm | carb | | |
| 17 | Mine L | Cr | 1968–2003 | Soapstone | tlc, carb, crm | carb | | |
| 18* | Mine R | Ni–Cu–PGE | 2012– | Composite mixed waste rock | di/am, srp | dol | | gö/li, gy |
| 19* | Mine R | Ni–Cu–PGE | 2012– | Composite mixed waste rock | di/am, srp, hbl | dol | | gö/li, gy |
| 20* | Mine R | Ni–Cu–PGE | 2012– | Composite mixed waste rock | di/am, srp, pl | cc | po, pe, ch | gö/li |
| 21 | Mine M | Zn–Cu–Pb | 1758–1958 | Cordierite kyanite rock | ky, qtz, crd, po, ch | | po, ch, py | |
| 22 | Mine M | Zn–Cu–Pb | 1758–1958 | Chlorite muscovite talc schist | tlc, ms | | py, ch | |
| 23* | Mine N | Cu–Ni–Zn | 2011– | Composite mixed waste rock | pl, qtz, bt, phl, py | cc, dol | py, po, sph, pe | gy |
| 24 | Mine G | Au | 2011– | Biotite schist | qtz, bt, pl, mgt | | py | |
| 25 | Mine G | Au | 2011– | Soapstone | tlc, carb | | py | |
| 26 | Mine O | Au | 2014–2016 | Vulcanite | qtz, pl, bt, chl | | po | |
| 27 | Mine O | Au | 2014–2016 | Greywacke | qtz, pl, bt, ms | | po | |
| 28* | Mine O | Au | 2014–2016 | Composite mixed waste rock | qtz, bt, pl, chl | | po, ch | |
| 29* | Mine I | Ni | 2007–2008 | Composite mica schist | bt, pl, qtz, chl | | po, py, pe, ch | gö/li |
| 30* | Mine I | Ni | 2007–2008 | Composite mica schist | bt, pl, qtz, chl, hbl, am | | po, py, ch | gö/li |

Table 1 (continued)

| No | Mine site | Mine type | Waste facility active | Rock/sample type | Main minerals (> 5%) | Carbonates | Sulfides | Secondary minerals |
|------|-------------|-----------|-----------------------|---------------------------------------|---------------------------|--------------|-----------------|--------------------|
| 31 | Mine P | Diabase | 1994– | Metadiabase | am, pl | | py, po | |
| 32 | Mine P | Diabase | 1994– | Metadiabase | am, pl | | py, po | |
| 33 | Mine Q | Cu–Zn–Ni | 1972–1985 | Biotite schist | qtz, bt, po, py | | po, py, ch | |
| 34 | Mine Q | Cu–Zn–Ni | 1972–1985 | Metapyroxenite | cpx, po | carb | po | |
| 35 | Mine Q | Cu–Zn–Ni | 1972–1985 | Amphibole chlorite biotite schist | bt, am, chl, po | | po | |
| 36 | Mine Q | Cu–Zn–Ni | 1972–1985 | Kyanite quartzite | qtz, ky | | py, po | |
| 37 | Mine Q | Cu–Zn–Ni | 1972–1985 | Serpentinite | srp, ol | carb | po | |
| 38* | Mine Q | Cu–Zn–Ni | 1972–1985 | Composite mixed waste rock | qtz, pl, bt | cc | po, sph, py | gö/li, gy |
| 101* | Mine A | Cu–Zn | 1973–1986 | Composite waste rock, drainage sample | qtz, chl, pl, bt | cc | po, ch, py | gö/li, gy |
| 102* | Mine B 2014 | Ni | 1970–1993 | Composite waste rock, drainage sample | qtz, bt, pl, srp, po, ms | dol | po, py, ch, sph | gö/li |
| 103* | Mine B 2016 | Ni | 1970–1993 | Composite waste rock, drainage sample | pl, bt, qtz, ms | | po, py, ch, sph | gö/li |
| 104* | Mine C old | Talc–Ni | 1982–2004 | Composite waste rock, drainage sample | qtz, chl, pl, mgs, tlc | mgs, dol, cc | po, py, pe | gö/li, gy |
| 105* | Mine C new | Talc–Ni | 2004– | Composite waste rock, drainage sample | qtz, bt, mgs, pl, am, tlc | mgs, dol, cc | po, py, pe | |
| 106* | Mine D | Cu | 1966–1984 | Composite waste rock, drainage sample | pl, hbl, aug, qtz | cc | ch, po, py | |
| 107* | Mine E | Au | 2011–2013 | Composite waste rock, drainage sample | pl, qtz, kfs, bt, am, hbl | | po | |
| 108* | Mine F | Au | 2011– | Composite waste rock, drainage sample | pl, kfs, bt, qtz | dol, sid, cc | ch, po | gö/li |
| 109* | Mine G old | Apatite | 1975–2000? | Composite waste rock, drainage sample | bt, cc, hbl, phl, dol | cc, dol | po | |
| 110* | Mine G new | Apatite | 2000?– | Composite waste rock, drainage sample | pl, kfs, bt, aug | cc | py, po | |
| 111* | Mine H | Ni | 2007–2008 | Composite waste rock, drainage sample | bt, pl, qtz, hbl | | po, pe, py | gö/li |

Minerals are presented in descending order of concentration. The amounts of detected secondary minerals were low (0.1–0.01%). Samples marked with an asterisk were analysed by FE-SEM on milled samples and other samples by light microscopy on thin sections of whole rock alb, albite; am, amphibole; ap, apatite; aug, augite; bt, biotite; carb, undefined carbonate; cc, calcite; ch, chalcopyrite; chl, chlorite; cpx, clinopyroxene; crd, cordierite; crm, chromite; crs, chrysotile; di, diopside; dol, dolomite; ep, epidote; gö, göthite; gr, graphite; grt, garnet; gy, gypsum; hbl, hornblende; ilm, ilmenite; ja, jarosite; kfs, k-feldspar; ky, kyanite; li, limonite; mgs, magnesite; mgt, magnetite; ms, muscovite; ol, olivine; opx, orthopyroxene; pe, pentlandite; phl, phlogobite; pl, plagioclase; po, pyrrhotite; py, pyrite; qtz, quartz; rt, rutile; sid, siderite; sph, sphalerite; srp, serpentine; tlc, talc; tt, titanite; zr, zircon; zs, zoisite

The drainage water and surface waste rock samples were analysed in laboratory of Labtium Oy Eurofins Labtium Oy, which has been accredited by FINAS (Finnish Accreditation Service) using the ISO/IEC 17025 standard (ISO/IEC 2005). Drainage water dissolved element concentrations were analysed by ICP-OES and ICP-MS. The rock samples were first dried at $40\text{ }^\circ\text{C}$ and then crushed (> 70% 2 mm). For the different laboratory analyses, the crushed samples were split using a riffle splitter and/or the cone and quartering method and milled in a steel container. The XRF method (Criss and Birks 1968) was used to obtain the total elemental concentrations. The XRF method is not suitable for some elements, e.g. Cd and Co. The total concentrations of C and S were determined using the ISO 10694 (ISO 1995a) and ISO 15178 (ISO 2000) standards respectively, using a pyrolytic method (Leco) and infrared (IR) detection. Non-carbonate C was determined after hydrochloric acid treatment by pyrolysis and IR detection. The amount of carbonate C was calculated based on the difference between total C and non-carbonate C (ISO 1995a). Main and trace element concentrations were determined with a hot AR extraction method and ICP-OES/MS techniques (Niskavaara 1995), using a modified version of the ISO-11466 standard (ISO 1995b) to dissolve the samples.

The single-addition NAG test was performed following instructions in the AMIRA handbook (AMIRA 2002). The test involves mixing 250 mL of 15% (m/V) H_2O_2 with 2.5 g of pulverised sample. The laboratory uses ultra-pure H_2O_2 when analysing NAG test leachate for trace element concentrations, as recommended by Ross and Verburg (2015). The mixture reacted for 12 h, after which it was boiled until the visible reaction ceased. After cooling, EC, pH and concentrations of dissolved main and trace elements in the NAG leachate were determined by ICP-OES/MS, and the suspension was titrated with NaOH (0.1 mol/L) to pH 4.5 and 7.0 (AMIRA 2002).

The quality of drainage water and waste rock analysis was assured by the accredited laboratory by analysing control samples and providing the quality control analysis results along with the sample results. In addition, laboratory duplicates for 10 waste rock and three drainage water samples were analysed. The quality of the drainage water samples was further checked by taking double and blank (laboratory distilled water) samples during the field campaigns after approximately every 10 samples.

Results

Geochemistry of the Surface Waste Rock Samples

Geochemical analysis results, including total S, total C, carbonate C, total elements, NAG test leachate pH, and element

concentrations in AR and NAG test leachates, are presented in supplemental Table S-1. AR-extractable concentrations are also compared with the reference values defined by Finnish Government (2007) in Table S-1. For samples 101–111, the above-mentioned parameters are also presented in Table 2.

Total S concentration in the samples varied from 0.05% in several samples to 10.4% of the skarn rock sample no. 9 from Mine D. The median of all samples was 0.6%. Of 49 samples, 11 had a very low S concentration of 0.1% or less. Total C concentration in the samples varied from 0.05% in several samples to 9.5% for the graphite schist sample no. 7 from Mine C old site (median 0.3%). Carbonate C concentration in the samples varied from 0.05% to 6.5% (median 0.1%). The pH of NAG test leachate varied from 2.4 to 10.8 (median 4.1). Based on NAG pH 4.5, 26 of the 49 samples were classified as potentially acid forming (AMIRA 2002).

Based on the AR-extractable element concentrations, only the garnet biotite schist sample from Mine K (sample no. 16) was classified as inert (Table S-1). All the other samples contained contaminant concentrations exceeding the PIMA threshold values for harmful elements set by Finnish Government (2007). In particular, the Ni, Cu, and Cr concentrations exceeded the upper guideline values for 31 out of 49, 27 out of 49, and 11 out of 49 samples, respectively. Zn concentrations exceeded the upper PIMA guideline value for six samples, As concentrations for five samples, and Co concentrations for one sample.

On average, AR extracted $\approx 40\%$ of the total (XRF detectable) Al and Cr. For Fe, Mn, and Zn, the average AR extractable amount was $\approx 60\text{--}70\%$, for As and Ni $\approx 80\%$, and for Cu and S > 90%. For Cd and Co, the AR results could not be compared with the total element concentrations, as no XRF results were available for Cd and Co. In general, the element concentrations in NAG test leachate were substantially less than the AR-extractable concentrations. The only exception was Cd, for which the NAG test leachable concentration was higher than the AR-extractable concentration in nine of the 49 samples (Table S-1). This might be due to the relatively low Cd concentrations, which were approaching the limit of quantification.

Ratios of element concentrations in single-addition NAG test leachate to AR-extractable concentrations (NAG/AR ratios) are presented in Fig. 1. Data points were removed if the extractable concentrations were below the detection limit (e.g. Zn for samples no. 16 and 17), or if the detection limit for NAG analysis exceeded the AR-extractable concentration (e.g. Fe for sample no. 8).

In general, for most of the elements analysed the NAG/AR ratio was markedly lower than 1.0, indicating that the concentrations in NAG leachate were lower than those in AR solution. In addition, the NAG/AR ratio was higher when the NAG test leachate pH was low, and vice versa (Fig. 1).

Table 2 Total elemental (XRF), tot-S, tot-C, carb-C, NAG test pH, element concentrations in AR and NAG test leachate and ratio of NAG test and AR-extractable concentrations (NAG/AR) of the samples 101–111

| | tot-S (%) | tot-C (%) | C carb (%) | NAG pH | Al (mg/kg) | As (mg/kg) | Cd (mg/kg) | Co (mg/kg) | Cr (mg/kg) | Cu (mg/kg) | Fe (mg/kg) | Mn (mg/kg) | Ni (mg/kg) | S (mg/kg) | Zn (mg/kg) | |
|----------------------------|-----------|-----------|------------|--------|------------|------------|------------|------------|------------|------------|------------|------------|------------|-----------|------------|------|
| PIMA threshold value | – | – | – | – | AR | 5 | 1 | 20 | 100 | 100 | – | – | 50 | – | 200 | |
| PIMA lower guideline value | – | – | – | – | AR | 50 | 10 | 100 | 200 | 150 | – | – | 100 | – | 250 | |
| PIMA upper guideline value | – | – | – | – | AR | 100 | 20 | 250 | 300 | 200 | – | – | 150 | – | 400 | |
| 101 | Mine A | 1.6 | 0.5 | <0.05 | 3 | XRF | 68,241 | 55 | – | 85 | 2035 | 65,254 | 558 | 60 | 14,030 | 569 |
| | | | | | | AR | 30,300 | 44.8 | 1.8 | 21.7 | 1925 | 59,800 | 481 | 55 | 14,600 | 542 |
| | | | | | | NAG | 1090 | 0.3 | 2.1 | 13.3 | <0.5 | 1285 | 93 | 40 | 10,850 | 459 |
| | | | | | | NAG/AR | 0.04 | 0.01 | 1.17 | 0.61 | – | 0.02 | 0.19 | 0.73 | 0.74 | 0.85 |
| 102 | Mine B | 3.4 | 0.9 | 0.1 | 2.6 | XRF | 80,937 | <20 | – | 503 | 347 | 88,824 | 511 | 1023 | 27,110 | 257 |
| | | | | | | AR | 21,200 | 6.6 | 2.4 | 49.8 | 133 | 80,100 | 482 | 963 | 30,800 | 246 |
| | | | | | | NAG | 1010 | <0.05 | 0.9 | 46.4 | 2.5 | 2450 | 145 | 964 | 19,200 | 196 |
| | | | | | | NAG/AR | 0.05 | – | 0.38 | 0.93 | 0.02 | 0.03 | 0.3 | 1 | 0.62 | 0.8 |
| 103 | Mine B | 2.5 | 1 | <0.05 | 2.6 | XRF | 86,756 | <30 | – | 104 | 423 | 65,604 | 333 | 335 | 23,730 | 229 |
| | | | | | | AR | 23,900 | 1 | 0.8 | 20.2 | 83.6 | 63,900 | 392 | 332 | 22,200 | 231 |
| | | | | | | NAG | 1270 | <0.1 | 0.9 | 16.5 | <1 | 2230 | 95 | 322 | 14,700 | 158 |
| | | | | | | NAG/AR | 0.05 | – | 1.13 | 0.82 | – | 0.03 | 0.24 | 0.97 | 0.66 | 0.68 |
| 104 | Mine C | 1.4 | 2.1 | 1.3 | 7.5 | XRF | 26,291 | 30 | – | 1420 | 60 | 51,476 | 503 | 1040 | 11,190 | 170 |
| | | | | | | AR | 13,500 | 28 | 1.4 | 55.3 | 374 | 39,500 | 418 | 944 | 13,200 | 94 |
| | | | | | | NAG | 8 | <0.05 | 0.02 | 1.3 | 2 | <20 | 4 | 8 | 12,300 | 4 |
| | | | | | | NAG/AR | 0 | – | 0.01 | <0.01 | 0.04 | – | 0.01 | 0.01 | 0.93 | 0.04 |
| 105 | Mine C | 2.3 | 3.2 | 1.4 | 3.8 | XRF | 43,219 | 90 | – | 920 | 90 | 60,358 | 542 | 730 | 18,370 | 180 |
| | | | | | | AR | 20,400 | 103 | 1.8 | 38.5 | 258 | 59,200 | 485 | 694 | 22,700 | 148 |
| | | | | | | NAG | 55 | <0.05 | 0.9 | 25.9 | 1.1 | 28 | 156 | 413 | 19,900 | 89 |
| | | | | | | NAG/AR | <0.01 | – | 0.5 | 0.67 | <0.01 | <0.01 | 0.32 | 0.6 | 0.88 | 0.6 |
| 106 | Mine D | 0.4 | <0.05 | <0.05 | 4.1 | XRF | 87,285 | <30 | – | 197 | 1956 | 60,988 | 1015 | 107 | 3419 | 90 |
| | | | | | | AR | 12,900 | 0.7 | 0.2 | 12.5 | 21 | 16,000 | 235 | 32 | 3280 | 26 |
| | | | | | | NAG | 47 | <0.1 | 0.2 | 6.9 | <1 | <50 | 39 | 16 | 2540 | 15 |
| | | | | | | NAG/AR | <0.01 | – | 1 | 0.59 | – | 0.17 | 0.5 | 0.77 | 0.58 | |
| 107 | Mine E | 0.1 | <0.05 | <0.05 | 7.5 | XRF | 76,176 | 206 | – | 121 | 273 | 42,733 | 759 | <20 | 1215 | 56 |
| | | | | | | AR | 12,800 | 220 | 0.2 | 14.5 | 69.6 | 22,600 | 456 | 17 | 1010 | 32 |
| | | | | | | NAG | 28,500 | 25.3 | <0.02 | 15.2 | 3 | 63 | 12 | <2 | 1000 | 7 |

Table 2 (continued)

| | tot-S (%) | tot-C (%) | C carb (%) | NAG pH | Al (mg/kg) | As (mg/kg) | Cd (mg/kg) | Co (mg/kg) | Cr (mg/kg) | Cu (mg/kg) | Fe (mg/kg) | Mn (mg/kg) | Ni (mg/kg) | S (mg/kg) | Zn (mg/kg) | | |
|-----|---------------|-----------|------------|--------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|--------|------|
| 108 | Mine F | 0.1 | 0.9 | 0.8 | 9.2 | NAG/AR | 2.23 | 0.12 | – | 0.22 | 0.01 | <0.01 | 0.03 | – | 0.99 | 0.22 | |
| | | | | | | XRF | 67,448 | 20 | – | 820 | 100 | 53,049 | 833 | 395 | 815 | 75 | |
| | | | | | | AR | 17,600 | 19.5 | 0.9 | 25.7 | 631 | 87 | 35,950 | 577 | 177 | 985 | 45 |
| 109 | Mine G old | 0.1 | 2.8 | 2.8 | 10.8 | NAG | 10 | 1.2 | <0.01 | 7.6 | 1 | <20 | <1 | 4 | 535 | <1 | |
| | | | | | | NAG/AR | <0.01 | 0.06 | – | 0.01 | 0.01 | – | – | 0.02 | 0.54 | – | |
| | | | | | | XRF | 48,139 | <20 | – | 40 | 40 | 67,982 | 1015 | 30 | 740 | 80 | |
| 110 | Mine G new | 0.2 | 0.8 | 0.8 | 10.5 | AR | 27,800 | <5 | 1 | 20.6 | 23 | 47,700 | 725 | 19 | 951 | 47 | |
| | | | | | | NAG | 85 | <0.05 | <0.01 | <0.5 | <1 | 2 | <20 | <1 | 402 | 1 | |
| | | | | | | NAG/AR | <0.01 | – | – | – | 0.06 | – | – | – | 0.42 | 0.02 | |
| | | | | | | XRF | 74,589 | <20 | – | 90 | 60 | 60,708 | 720 | 60 | 1720 | 60 | |
| 111 | Mine H | 1.7 | 0.3 | 0.2 | 2.7 | AR | 15,700 | <5 | 0.7 | 20.9 | 65 | 46,300 | 598 | 42 | 1990 | 50 | |
| | | | | | | NAG | 317 | <0.05 | <0.01 | <0.5 | 1.6 | 2 | <20 | <1 | 1150 | 6 | |
| | | | | | | NAG/AR | 0.02 | – | – | – | 0.02 | 0.04 | – | – | 0.58 | 0.12 | |
| | | | | | | XRF | 78,292 | <30 | – | – | 186 | 187 | 83,229 | 720 | 763 | 15,720 | 134 |
| | | | | | | AR | 34,000 | 6.6 | 0.1 | 75.3 | 166 | 72,100 | 496 | 818 | 15,700 | 108 | |
| | | | | | | NAG | 1320 | <0.1 | 0.1 | 60.4 | <1 | 131 | 869 | 122 | 758 | 13,900 | 28 |
| | | | | | | NAG/AR | 0.04 | – | 1 | 0.8 | – | 0.66 | 0.01 | 0.25 | 0.93 | 0.89 | 0.26 |

Tot-S, tot-C, carbonate-C and NAG test pH data for samples 101–111 are taken from Karlsson et al. (2018b). The AR-extractable concentrations of potentially harmful elements defined in Government Decree (Finnish Government 2007) were compared to the PIMA reference values. Those exceeding the PIMA threshold value are marked with italics, those exceeding the lower guideline value with bold and those exceeding the upper guideline value with bolditalics. The NAG test leachate Al concentration in the Mine F sample was erratically high (28,500 mg/kg) and consequently not taken into account

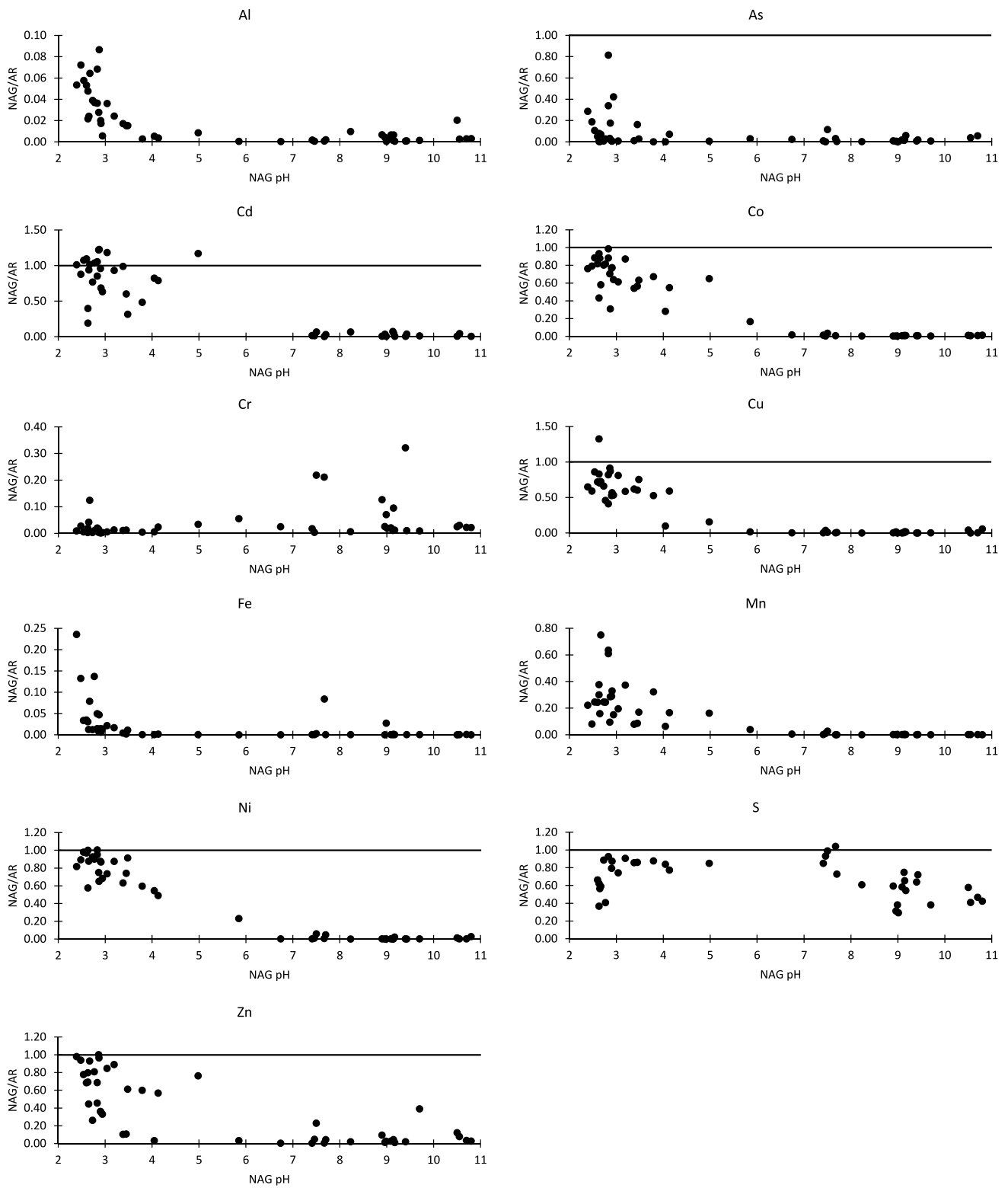


Fig. 1 Ratio of NAG test leachate concentration to AR-extractable concentration of Al, As, Cd, Co, Cr, Cu, Fe, Mn, Ni, S and Zn (Y-axis) as a function of NAG test leachate pH (X-axis). The NAG/AR ratio 1.0 is marked with a horizontal line

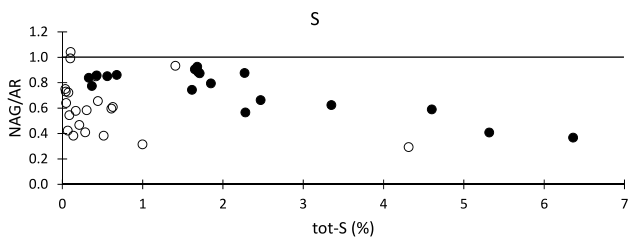


Fig. 2 Ratio of NAG test leachate concentration to AR-extractable concentration for sulphur (S) as a function of total S concentration. Samples with NAG pH > 7 presented as white dots. The NAG/AR ratio 1.0 is marked with a horizontal line

This was particularly true for Al, As, Cd, Cu, Co, Ni, Zn, Fe, and Mn. The NAG/AR ratios of Cd, Co, Cu, Mn, Ni and Zn were clearly lower at pH 5–6 than in more acidic conditions, but were still above or ≈ 0.2. However, when the NAG pH > 6, the ratios dropped close to 0.01, except for Zn, which showed some sporadic higher ratios at higher NAG pH. In contrast to these metals, Cr showed higher NAG/AR ratios at pH > 7 than at low pH. In general, the leachability of Cr was lower in the NAG test than in AR extraction (ratio < 0.3). Leachability of Al and Fe in the NAG test was generally low in comparison with their extractability in AR, with NAG/AR ratios below 0.1 and 0.25, respectively (Fig. 1). For Al, As, and Fe, the NAG/AR ratio was mainly below 0.01 when the NAG pH was > 4. For S, NAG/AR ratios above 0.8 were abundant when the NAG pH was < 8, but not when NAG pH > 8. In general, the NAG test leachate pH did not clearly affect the NAG/AR ratios of S. Samples with < 0.2 wt.% of total S had NAG/AR ratios ranging from ≈ 0.4 to 1 and a NAG pH > 7 (Fig. 2). For samples with a lower NAG pH and a total S ≈ 2 wt.%, the NAG/AR ratio for S was above 0.7 and decreased below 0.4 when the total S was ≈ 6 wt.% (Fig. 2).

Drainage Water Quality

The pH of the drainage samples ranged from 3.3 (Mine H) to 7.7 (Mine C new) with a median value of 6.7 (Karlsson et al. 2018b). EC ranged from 597 μS/cm (Mine D) to 4577 μS/cm (Mine C old) with a median value of 1731 μS/cm (Table 3). The drainage water concentrations were compared with the Finnish stream water medians presented by Lahermo et al. (1996). The concentrations were > 100×Finnish stream water medians for SO₄ at eight of the 10 target waste rock sites (seven of eight mines), for Ni and Co at six waste rock sites (five mines), for Cu at four waste rock sites (four mines), for Al, Mn, and Zn at two waste rock sites (two mines), and for Pb at one waste rock site (one mine). The Cd concentrations were relatively high at five waste rock sites (five mines): Mines A, B, C old, D, and H, where the concentrations in drainage water exceeded

Table 3 Drainage water quality at seepage points below the areas where the composite waste rock samples 101–111 were collected

| Mine waste site | Rock sample | Al (μg/l) | As (μg/l) | Cd (μg/l) | Co (μg/l) | Cr (μg/l) | Cu (μg/l) | Fe (mg/l) | Mn (mg/l) | Ni (μg/l) | Pb (μg/l) | S (mg/l) | Zn (mg/l) | SO ₄ (μg/l) | EC (μS/cm) | pH |
|-----------------|-------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|----------|-----------|------------------------|------------|------|
| Mine A | 101 | 8700 | 2.9 | 12 | 171 | <0.2 | 246 | 1.2 | 1.5 | 590 | 87 | 192 | 3.3 | 439 | 3.9 | 1270 |
| Mine B 2014 | 102 | 10,100 | 1.3 | 1.7 | 116 | 0.9 | 245 | 0.2 | 5 | 4520 | 0.2 | 673 | 829 | 2000 | 4.0 | 3013 |
| Mine B 2016 | 103 | 18,500 | 1.2 | 1.9 | 127 | 1.6 | 367 | 0.2 | 7.3 | 5940 | 0.4 | 666 | 901 | 2090 | 3.5 | 2993 |
| Mine C old | 104 | 23 | 14 | 0.8 | 65 | 0.4 | 6.9 | <0.05 | 0.5 | 4123 | <0.05 | 1298 | 114 | 3195 | 7.3 | 4577 |
| Mine C new | 105 | 13 | 12 | 0.6 | 29 | <0.2 | 0.2 | <0.05 | 0.6 | 724 | <0.05 | 372 | 72 | 917 | 7.7 | 1998 |
| Mine D | 106 | 12 | <0.05 | 1.5 | 138 | <0.2 | 2199 | <0.03 | 0.4 | 436 | 0.1 | 88 | 195 | 281 | 6.7 | 597 |
| Mine E | 107 | 9.6 | 5.7 | 0.4 | 2.4 | 0.2 | 3.8 | 0.03 | 0.03 | 11 | <0.05 | 475 | 11 | 1400 | 7.0 | 2182 |
| Mine F | 108 | 133 | 22 | 0.03 | 12 | 6.9 | 1.8 | 3.2 | 1.9 | 17 | 0.8 | 29 | 4.0 | 812 | 6.7 | 818 |
| Mine G old | 109 | 56 | 0.9 | <0.02 | 4.4 | 1.1 | 0.3 | 57 | 9.1 | 0.7 | <0.05 | 20 | 6.6 | 61 | 6.5 | 1137 |
| Mine G new | 110 | 21 | 0.1 | 0.04 | 1.7 | 0.3 | 1.7 | <0.05 | 0.8 | 2.7 | <0.05 | 118 | 66 | 350 | 7.0 | 1731 |
| Mine H | 111 | 10,600 | 1.6 | 1.2 | 576 | 0.9 | 231 | 6.3 | 2.9 | 6830 | 0.5 | 219 | 410 | 610 | 3.3 | 1232 |
| Stream waters | | 95 | 0.4 | <0.02 | 0.2 | 0.5 | 0.6 | 0.7 | 0.03 | 0.5 | 0.2 | – | 3.6 | 3.5 | 5.9 | 44 |

The median concentrations in Finnish stream waters are presented for comparison (Lahermo et al. 1996). pH values are from Karlsson et al. (2018b). The concentrations > 100×Finnish stream water medians and Cd concentrations exceeding the maximum permissible concentrations for inland surface waters (European Commission 2008) are marked with italics

the maximum permissible concentrations for inland surface waters ($\leq 0.45\text{--}1.5\ \mu\text{g/L}$, depending on classification based on water hardness) as defined in the European Commission Directive on environmental quality standards applicable to surface water (European Commission 2008). In addition, the Cd concentrations in Mine C new and Mine E drainage water exceeded the permissible mean annual concentrations ($\leq 0.08\text{--}0.25\ \mu\text{g/L}$) stipulated in the Directive (European Commission 2008). It should be noted, that As, Co, and Ni were abundant also in some circumneutral drainage waters (Table 3).

Based on acidity and contaminant concentrations, drainage water from Mines A, B, and H waste rock sites can be classified as ‘high-acid’ and ‘high-metal,’ whereas drainage water from the Mines C old and D waste rock sites can be classified as ‘near-neutral’ and ‘high-metal.’ In contrast, drainage water from the Mines C new, E, F, G (old and new) waste rock sites was ‘near-neutral’ and ‘low-metal’ (Plumlee et al. 1999) (Fig. 3).

Discussion

Comparison of NAG test leachate analysis and AR extraction

As expected, AR dissolution appeared to be more efficient in dissolving various minerals than the single-addition NAG test. The presumption was that the NAG test would leach elements bound to sulfide minerals and other more readily leachable mineral phases (Räisänen et al. 2010), and that AR would also partly leach some silicate mineral phases (Doležal et al. 1968; Niskavaara 1995). When comparing the single-addition NAG test and AR leachate results, the NAG test leachate concentrations were generally much less than the corresponding AR-extractable concentrations. This was particularly true for the elements originating from silicates and oxides, e.g. Al, Cr, and Fe.

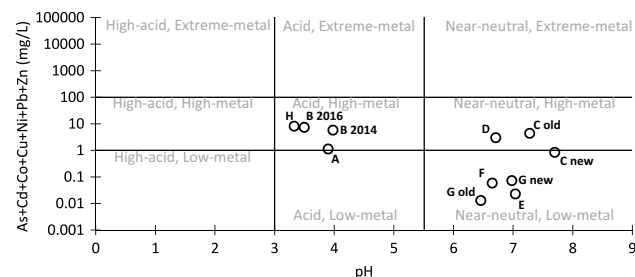


Fig. 3 A modified (the metalloid As added to the metal sum) Ficklin diagram (Plumlee et al. 1999) showing the quality of drainage water at the target waste rock facilities where water sampling was conducted

The greater leaching of Cd, Co, Cu, Ni, Zn, and S compared with the other elements in the single-addition NAG test can be mainly explained by the oxidation of sulfide species, since they are chalcophile elements which occur typically in sulfides. In addition, the leaching of existing secondary minerals related to sulfide oxidation can increase the concentrations of chalcophile elements in the NAG test leachate. For example, Cu occurs mainly in sulfides and rarely in silicates (Koljonen 1992). Cobalt and Ni occur commonly together, mainly in sulfides, but also in mafic silicates, e.g. olivine, pyroxene and amphibole (Heikkinen and Räisänen 2009; Koljonen 1992). Zinc occurs both in sulfides and silicates. Silicates such as olivine, pyroxenes, amphiboles and biotite usually contain some Zn (Koljonen 1992). Cadmium usually occurs with Zn, replacing it in the crystal structure of minerals (Koljonen 1992). Lower NAG/AR ratios can also be related to the ability of AR to partly leach and etch silicates potentially bearing harmful elements (Chao and Sanzalone 1977; Doležal et al. 1968; Räisänen et al. 1992), which might not be as soluble in the single-addition NAG test or in natural environments.

Incomplete sulfide oxidation in the single-addition NAG test has been previously documented (Stewart 2005; Parbhakar-Fox et al. 2018). According to AMIRA (2002), the single-addition NAG test is not suitable for samples containing $> 1\%$ sulfide S and high contents of readily available neutralising minerals (carbonates). This is because sulfides of high-S samples oxidise incompletely due, for example, to the catalytic decomposition of peroxide by metal ions released during sulfide oxidation. In the single-addition NAG test sulfide oxidation can already be incomplete in samples containing $> 0.7\ \text{wt}\%$ of pyritic sulphide (Stewart 2005). Parbhakar-Fox et al. (2018) recommend multi-addition NAG test for low sulfide-S (i.e. $< 0.3\ \text{wt}\%$) carbonate-bearing samples, and the use of $30\% \text{H}_2\text{O}_2$ for high sulfide-S materials (i.e. $> 0.3\ \text{wt}\%$). It is also recommended that the multi-addition NAG test should supersede the single-addition NAG test entirely (Parbhakar-Fox et al. 2018).

According to our results, low S content in a sample does not guarantee a high NAG/AR ratio for S. Samples with low ($< 0.2\ \text{wt}\%$) total S can have NAG/AR ratios of wide range ($\approx 0.4\text{--}1$). In general, samples with a lower NAG pH (≤ 7) appear to be more dependent on the S content; the NAG/AR ratios for S decrease when the total S increases. As also stated by Parbhakar-Fox et al. (2018), the use of multi-addition NAG tests would enhance sulfide oxidation, which might lead to lower NAG test pHs and more realistic predictions of contaminant mobilization.

In addition to peroxide decomposition, the available sulfide surface area could also be related to NAG/AR S variation. The kinetics of sulfide oxidation is controlled by (for example) micro-textures (Parbhakar-Fox et al. 2013), mineral associations (Kwong 1993), and the precipitation

of secondary minerals on sulfide surfaces (Al et al. 1997). If these factors affect the NAG test results, the NAG test results could also better reflect the sulfide oxidation process and effect of secondary mineral formation in the natural environment. The impact of these factors could not be verified in this study, as more detailed mineralogical investigation of the NAG test residues would be needed.

Results of the single-addition NAG test were dependent on the final pH of the test. In particular, the concentrations of Cd, Co, Cu, Ni, and Zn showed clear pH dependence. Their NAG/AR ratio was relatively high, (up to 0.5–1) when the NAG pH was acidic (<4.50), but dropped mainly to ≈ 0.1 or less when the NAG test leachate pH was between 5 and 6. A decrease in element concentrations with higher pH in NAG test leachate has also been noted in previous studies (Barnes et al. 2015; Charles et al. 2015; Karlsson and Kauppila 2016; Karlsson et al. 2018a; Räisänen et al. 2010) and can be explained by the formation of secondary precipitates during the test at higher pH (Charles et al. 2015), coinciding with decreasing Al and Fe concentrations and retention of elements by adsorption at elevated pH (Barnes et al. 2015).

Interpretation of Single-addition NAG test leachate Analysis and AR Extraction Results in Drainage Quality Prediction

The performance of AR and single-addition NAG test methods in drainage quality prediction varied for different elements. Overall, the elevated AR-extractable As, Cd, Co, Cu, Ni, and Zn concentrations reflected elevated concentrations in the drainage, especially in acidic water systems. For Al, As, Cd, Co, Cu and Ni, elevated AR-extractable concentrations did not correspond to elevated drainage concentrations in some circumneutral water systems. The NAG test method predicted elevated drainage concentrations for Al, Cd, Co, Cu, Ni, and Zn, but only when the NAG test leachate pH was low. The abundance of As and Ni in some circumneutral drainage waters suggests that the single-addition NAG test leachate concentrations were not useful drainage quality indicators in these cases. The AR-extractable Cr concentrations were high in many cases and did not correlate with the low drainage concentrations. In contrast, the acidic NAG test leachate concentrations of Cr were low, reflecting low drainage concentrations. Cr is bound mainly to silicates and oxides (e.g. Salminen et al. 2005), and therefore has poor mobilisation in rock weathering processes (e.g. Koljonen 1992; Räisänen et al. 2010). Similarly, a high AR-extractable Al concentration did not correspond to a high drainage concentration, especially in circumneutral drainage systems, likely because AR extraction partly leaches some silicates that are not significantly weathered in circumneutral natural environments (e.g. biotite; Doležal et al. (1968)). In this study, the abundance of biotite, an Al-bearing silicate,

corresponded with high AR extractable Al concentrations (e.g. see samples 1, 25, 26, 28, 29, 34, 101, and 112). It should be noted that the leachable concentrations in AR extraction and in acidic, single-addition NAG tests are not intended to provide a direct measure of the concentrations of contaminants in drainage water, but only to indicate where elevated concentrations are likely (Fig. 4).

In general, elevated concentrations of contaminants in the AR-extractable fraction of surface waste rock samples were reflected in elevated concentrations in drainage water (Fig. 5). Similar results have been reported in previous studies (Price et al. 1997; Fosso-Kankeu et al. 2015; Karlsson and Kauppila 2016; Karlsson et al. 2018a). It can be generalised that if the AR-extractable sum of As, Cd, Co, Cu, Ni and Zn is > 1 000 mg/kg, there is a high risk for a high-metal drainage (the sum of harmful metals and metalloids > 1 000 $\mu\text{g/L}$, as in Plumlee et al. 1999). In the cases of Mine A and Mine C new, the water samples were collected from a pond, which may have been diluted by other water sources and therefore had lower overall drainage concentrations. Thus, and when considering the higher drainage concentrations in the case of Mine C old with similar rock material, it can also be assumed that the Mine C new drainage could be classified as ‘high-metal’ water.

Overall, the analysis of single-addition NAG test leachate is also a suitable method for predicting contaminants in waste rock and its drainage water. However, as the leachable concentrations of contaminants in the single-addition NAG test decrease when the NAG test pH increases, high concentrations in NAG test leachate can only indicate elevated concentrations in drainage water under acidic NAG test conditions, as also stated by Barnes et al. (2015). Nonetheless, as can be noted in the case of Mine D site, the NAG test can predict contaminant mobilization in neutral drainage if the test pH is sufficiently low for the contaminants not to precipitate, but in then the test pH does not reflect the drainage pH. In general, if the sum of As, Cd, Co, Cu, Ni, and Zn in NAG test leachate is > 500 mg/kg, there is an elevated risk for high-metal drainage. As discussed above, < 500 mg/kg in NAG test leachate does not exclude the risk for high-metal drainage in circumneutral drainage systems. The usability of the method in neutral mine drainage cases should be further investigated.

According to the results of this study, the presence of Ca- and Mg-bearing minerals resulted in unrealistically high NAG test pH values. The NAG test pH of several samples was abnormally high, up to 10.8 (sample 109 from Mine G old), although the related drainage pH was circumneutral. In general, high (> 8) NAG pH values seem to be related to the presence of Ca and Mg bearing minerals, e.g. carbonates, diopside/tremolite, serpentine, olivine, and talc (for example, see samples 2, 3, 6, 8, 16, 17, 18, 19, 20, 25, 37, 109, and 110). Parbhakar-Fox et al. (2018)

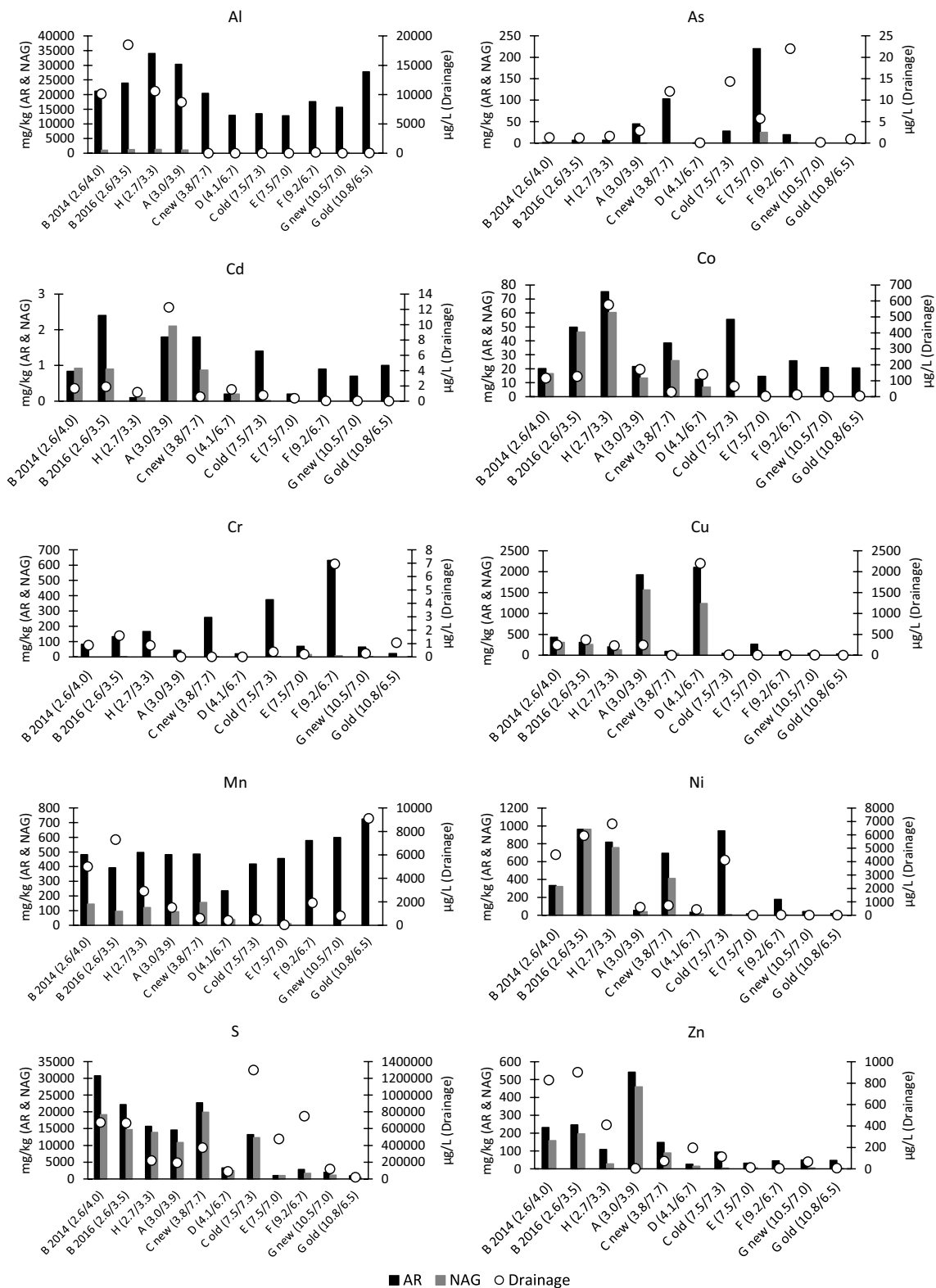


Fig. 4 NAG test leachate concentrations and AR-extractable concentrations of Al, As, Cd, Co, Cr, Cu, Mn, Ni, S and Zn in composite waste rock samples and in the corresponding drainage water. The

NAG test and drainage pH values are shown in brackets after the sample name (NAG test/drainage)

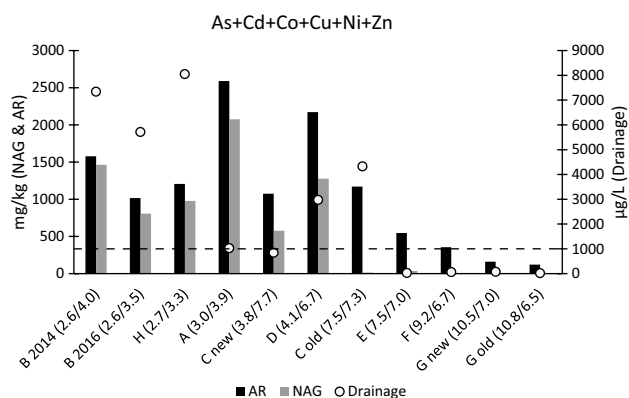


Fig. 5 The sums of NAG test leachate As, Cd, Co, Cu, Ni and Zn concentrations and AR-extractable concentrations in composite waste rock samples and in the corresponding drainage water of the mine sites. The NAG test and drainage pH values are shown in brackets after the sample name (NAG test/drainage). The mine sites are presented in the order of increasing NAG pH. The dashed black line presents 1000 µg/L in drainage

recommended multi-addition NAG test for low sulfide-S (< 0.3 wt%) carbonate-bearing samples, but according to this study, the commonly used single-addition NAG test was not representative for samples containing Ca and Mg silicate. It can be assumed that samples with high contents of Ca and Mg bearing carbonates and silicates will result in abnormally high, single-addition NAG pH, and NAG test leachate analysis gives a poor prediction of contaminant mobilization due to enhanced precipitation processes.

Waste rock characterisation and drainage quality predictions made using data from small-scale laboratory tests have limitations. For example, mineral assemblage and surface area, rock texture, and mineral impurities may affect the weathering rate, as would a small sample size and crushing of the samples (Dold 2017; Jambor 2003; Paktunc 1999; Parbhakar-Fox and Lottermoser 2015; White III et al. 1999). Representative sampling is key to successful waste rock characterisation (Price 2009). To assess drainage water quality based on AR and single-addition NAG test leachate analysis of waste rock samples, only composite surface samples were collected for this study, which should be considered when interpreting the results. More comprehensive waste rock sampling techniques were presented by McLemore et al. (2014). In addition, drainage water samples represented only one sampling campaign. For drainage water quality measurements, a more long-lasting monitoring campaign is recommended, as the contaminant concentrations in mine waste drainage water may display wide annual and seasonal fluctuations (Alakangas et al. 2010; González et al. 2020; Heikkinen et al. 2009; Søndergaard et al. 2007). Future work will examine waste rock history, dump cores,

drainage quality changes etc. in more detail. It should also be noted that the concentrations measured in this study do not necessarily represent any official mine waste or drainage concentrations monitored at the mine sites.

Small-scale laboratory tests such as AR extraction and NAG test leachate analysis are useful for preliminary screening in the drainage water quality assessment of waste rocks, but more thorough and site-specific investigations such as kinetic testing and geochemical modelling should still be conducted. Although the single-addition NAG test and AR prediction results have known limitations (e.g. Parbhakar-Fox and Lottermoser 2015; Parbhakar-Fox et al. 2018), the test is still widely used. The results of this study indicated that the analysis of single-addition NAG test leachate can be used in site-specific drainage water quality assessment at potentially acid forming (PAF) waste rock sites, both in assessing the acid production potential and in predicting which contaminants might occur in elevated concentrations in the drainage water. For non-acid forming (NAF) rock types containing high amounts of Ca- and Mg-bearing carbonates and silicates, the AR extraction better predicts which elements will be potentially mobilized. In these cases, the multi-step NAG test might also produce more realistic predictions, but this needs further verification. Although many elements tend to precipitate in higher pH single-addition NAG test leachates, H₂O₂ seems to leach most potential contaminants efficiently. Our results indicate that a H₂O₂-based leach might be more selective for contaminant mobility assessment than the more aggressive AR extraction, which also partially leaches many silicates.

Conclusions

The most widely-abundant contaminants at Finnish waste rock drainage sites investigated in this study were Co, Ni, Cu, and Cr. Cd, Co and Ni had high concentrations at five of the eight investigated mine sites, and Cu was abundant at four mine sites. These elements also appeared in some circumneutral water systems. In waste rocks, AR-extractable Co, Ni, Cu, and Cr often exceeded the PIMA guideline values.

Elevated concentrations of contaminants in the AR-extractable fraction of surface waste rock samples seemed to reflect elevated concentrations in the drainage water. If the AR-extractable sum of As, Cd, Co, Cu, Ni, and Zn was > 1000 mg/kg, there was an elevated risk for high-metal (> 1000 µg/L) drainage. Elevated AR-extractable Al, As, Cd, Co, Cu, and Ni concentrations reflected elevated concentrations in acidic drainage water, but overestimated contaminant mobility in some circumneutral drainage cases, and Cr in general. For example, the abundance of biotite, an Al-bearing silicate, correlated with high AR extractable Al

concentrations, although Al is not mobile in circumneutral drainage systems.

Analysis of single-addition NAG test leachate was also useful for assessing the mobility of Al, Cd, Co, Cr, Cu, Ni, and Zn in acid drainage cases. In some high-metal NMD cases, the predicted mobilities were too low. The usability of single-addition NAG test leachate analysis in neutral mine drainage cases should be further investigated. Most of the contaminants precipitated when the leachate pH was above 3–6. If the sum of As, Cd, Co, Cu, Ni, and Zn in NAG test leachate was > 500 mg/kg, there seemed to be high risk for a high-metal drainage. On the other hand, < 500 mg/kg in NAG test leachate did not exclude the risk for high-metal drainage in circumneutral systems. The presence of Ca- and Mg-bearing minerals such as carbonates, diopside/tremolite, serpentine, olivine, and talc can result in unrealistically high NAG test pH values. Use of multi-addition NAG tests for low sulfide, carbonate, and Ca- and Mg-silicate bearing samples is recommended.

Sulfides appeared to be incompletely leached in the single-addition NAG test, even when their concentrations were low (tot-S < 0.2 wt%). Using the multi-addition NAG test would enhance sulfide oxidation, which might lead to lower NAG test pHs and provide more realistic predictions of contaminant mobilization. The multi-addition NAG test or another H₂O₂-based leach might be more selective for element mobility assessment in the circumneutral cases than the more aggressive AR extraction. Further investigations and verification are needed.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s10230-021-00784-0>.

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