

Suitability of static tests for acid rock drainage assessment of mine waste rock



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Abstract

In the present study, eight rock samples were analysed with a modified acid-base accounting (ABA) test and the corresponding net acid generation (NAG) test. In addition, the main and trace elements solubilised during the tests were determined with ICP-OES/MS. Both the modified ABA and NAG tests classified the rock samples with a low sulphide-S content (0.1–0.4 %) and low carbonate mineral content (≤ 0.2 %) into the category of ‘potentially acid generating’. The low neutralization potentials of these rocks were partly due to additional acid produced in silicate weathering, upon the hydrolyzation of Fe and Al during the tests. In contrast to the modified ABA, the contribution of slowly reactive carbonate minerals to the neutralisation potential was seen in the NAG test and in the carbonate NP calculation, as they classified the rock samples containing these minerals into the category of ‘non-acid generating’. This supports the use of the carbonate neutralizing potential (NP) and/or the NAG test in mine waste screening. In the NAG test, acid generation and neutralization reactions either raising or decreasing the pH significantly influenced the solubility of trace metals and Al. This suggests that the extract contents could be useful in assessing contaminant mobility during long-term acid generating reactions.

Keywords: Static tests, modified ABA, single NAG test, neutralization potential, acid potential, mine waste, trace element extractability

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1. Introduction

Developers of new mines and operators of existing mines are required to prove that mine waste materials can be stored in a manner that will prevent or

mitigate the generation of acid rock drainage (ARD), both during the operation and long after mine closure (Finnish Mine Waste Decree 717/2009). Acid-

base accounting (ABA) tests, involving the determination of the acid generating potential (AP) and neutralizing potential (NP) of samples, are an essential part of waste characterization for ARD. These tests are designed to measure mining waste's capacity to produce and neutralize acidity, and do not provide information on reaction rates of mineral weathering. The tests are static in nature and allow simple, rapid and low-cost screening of waste samples to characterize whether the waste is either safe for disposal (NP exceeds AP) or potentially acid generating (AP exceeds NP) (Sobek et al., 1978; White et al., 1999; Jambor, 2003).

In the modified ABA test used in the present study (based on the preliminary standard prEN15875), the AP is based on the total sulphur content, assuming that the sulphur is entirely bound by the acid-producing sulphide minerals. The NP is determined by subjecting the sample to acid digestion, and it represents the amount of acid neutralizing carbonate minerals (or a limited range of silicates) in the sample (Kwong & Ferguson, 1997). In this study, the 'modified NP' was determined using hydrochloric acid digestion at ambient temperature in controlled conditions of acidity to provide an end pH in the range of 2.0–2.5, prior to the NaOH titration (Lawrence & Wang, 1997). For comparative purposes, NP was also determined based on the carbonate carbon content. This NP value is referred to as 'carbonate NP'.

The net acid generation (NAG) test is suitable for use both as a stand-alone prediction tool (Miller et al., 1997) and as a supplement to another static tests such as the modified ABA test above (Jambor, 2003). The test involves the reaction of a sample with hydrogen peroxide to rapidly oxidise any sulphide minerals in the sample. During the NAG test, acid generation and acid neutralization reactions can occur simultaneously. Therefore, the end-result represents a direct measurement of the net amount of acid generated by the sample.

The objective of the present study was to evaluate the suitability of a modified ABA test and the corresponding NAG test (AMIRA, 2002) for predicting ARD arising from waste rocks from metal mines and dimension stone quarries as well as crus-

hed aggregate rocks with a low carbonate carbon and sulphide sulphur contents. The largest discrepancies in static tests and their interpretation arise in the assessment of the neutralization potential (Lawrence & Scheske, 1997; Jambor, 2003). Therefore, the present study determined the NP with two methods: by the static NP test prEN15875, submitted for standardization to the European CEN committee, and based on the total carbonate carbon content converted to carbonate NP. Furthermore, the present study examined the metals and metalloids that solubilise during the tests, and evaluated the use of eluate composition in assessing the mobility of contaminants during long-term acid generating reactions. This has received less attention in earlier static test studies.

2. Materials and methods

The study materials consisted of four waste rock samples from metal mines (intermediate and mafic metavolcanic rocks, altered rock), three waste rock samples from dimensional stone quarries (soapstone, diabase, migmatite) and one aggregate rock sample (gneiss, Table 1). The soapstone, diabase, migmatite and mafic volcanic rock samples contained roughly less than 0.5 % sulphide minerals, whereas the intermediate metavolcanic rock (IV) and altered rock samples contained abundant sulphide minerals (≥ 1 %) (Heikkinen et al., 2007; Dagenais & Grondin, 2006; Räsänen, 2005). All the rock samples contained pyrrhotite and/or pyrite, which are obviously initial sources of potential acidity. Compared to the other samples, the mafic volcanic rock II (MVII) contained more chalcopyrite and pentlandite, whereas the intermediate metavolcanic rock sample was rich in arsenopyrite as well as pyrite and pyrrhotite (Dagenais & Grondin, 2006). The diabase, gneiss and mafic volcanic rocks contained only a few carbonate minerals, which were abundant in the soapstone, altered rock and intermediate metavolcanic samples. The migmatite did not contain any carbonates (Table 1).

Prior to analysis, bulk rock samples (rock chips or chunks, and drill cores) were dried at <40 °C and then crushed with a jaw crusher (Mn steel jaws).

Table 1. Mineralogy of the studied rock samples (based on Heikkinen et al. (2007), Dagenais & Grondin (2006) and Räsänen (2005).

Rock name	abbr	Main minerals	Carbonates	Sulphides
Soapstone	SS	tlc, mgt, chl (\pm Fe ox)	mgs	py
Diabase	DB	hbl, pl, am (\pm qtz)		po, py
Mafic metavolcanic rock I	MV I	pl, hbl, qtz, act, chl, bt, ms	cc, ank, Fe-carb, Mn-carb	po, py, gdf
Mafic metavolcanic rock II	MV II	hbl, pl, bt, chl, ep	do \pm cc	po (\pm Ni), cpy, pe, py
Gneiss	GN	pl, qtz, hbl, chl, bt		po (\pm Ni)
Migmatite	MG	crd, qtz, bt, kfs, pl, sill, grt		po
Intermediate metavolcanic rock	IV	qtz, pl, chl, bt, ms (\pm hbl)	cc, ank	apy, py, po, cpy
Altered rock	Alt R	qtz, pl, chl, bt, ms (\pm hbl)	cc, ank (\pm Fe-carb)	py, po, apy

Abbreviations for the minerals: pl = plagioclase, qtz = quartz, am = amphibole, hbl = hornblende, act = actinolite, bt = biotite, ms = muscovite, crd = cordierite, kfs = K feldspar, ep = epidote, sill = sillimanite, grt = garnet, mgt = magnetite, tlc = talc, Fe ox = iron oxide, py = pyrite, po = pyrrhotite, pe = pentlandite, apy = arsenopyrite, gdf = gersdorffite, mgs = magnesite, cc = calcite, do = dolomite, ank = ankerite, Fe-karb = Fe carbonate, Mn-karb = Mn carbonate, chl = chlorite.

After splitting, the crushed subsamples were pulverised in a hardened steel bowl. The grain size of the pulp (>90 %) was <100 μ m. The total element concentrations of the pulverised rock samples were determined with an X-ray fluorescence method (performed on pressed powder pellets). The total sulphur (ISO15178) and carbon (EN13137:2001) contents were determined using a high temperature combustion method. The total inorganic carbon determination included hydrochloric acid pre-treatment. The difference between the total carbon content and the carbon content from the pre-treated samples provided an estimate of the carbonate carbon content. In addition to the totals, main and trace element concentrations in the pulverised rock samples were determined with the hot *aqua regia* extraction method and ICP-OES (Niskavaara, 1995).

The static test for the modified NP determination followed the instructions of the preliminary standard prEN15875. Originally, it was a modification of the method by Lawrence and Wang (1997). The standard prEN15875 method does not include the Fizz test to determine the amount of acid needed, as in the modified ABA test by Lawrence & Wang (1997). In contrast, the addition of the acid is based on the determination of total carbon content (EN13137:2001). Hydrochloric acid (1.0 mol/l) was added to 2 g of

pulverized subsample mixed with demineralised water until pH 2.0–2.5 was reached at 24 hours. After the pH stabilization, sodium hydroxide solution (0.1 mol/l) was used to titrate the solution to an end-point of 8.3. The volume of NaOH required is a measure of how much of the input HCl the sample has consumed and therefore reflects the neutralization potential. The NP value from the back-titration was calculated as CaCO₃ equivalents in kg/t. In comparison, carbonate NP was calculated by multiplying the carbonate carbon concentration by 83.34 to yield the NP in units of kg CaCO₃/t. The AP was calculated from the total S content of a sample, based on the assumption that each mole of sulphur present produces two moles of acid (Jambor, 2003). Because one mole of Ca carbonate (i.e. calcite [CaCO₃]) will neutralize the two moles of acid, the sulphur content (%) was multiplied by 31.25 to yield the AP in units of kg CaCO₃ equivalent per one ton of mine waste.

The procedure for the NAG test followed the instructions of the AMIRA handbook (2002). A mixture of a 250 ml of 15 % (m/V) H₂O₂ and 2.5 g of pulverised sample was allowed to react for about 12 hours and was then boiled until the visible reaction ceased. After cooling, pH and electric conductivity (EC) were measured from the NAG solution. The suspension was then titrated with NaOH (0.1 mol/L) to pH 4.5 and 7.0 (AMIRA,

2002). The NAG values were calculated from the consumption of NaOH in the titration, and expressed as kg H₂SO₄/t.

The AMIRA guidebook (2002) recommends using the net acid producing potential (NAPP) together with the NAG test for the classification of acid generation. The NAPP is calculated as the difference (subtraction) between the maximum potential acidity (MPA) and the acid neutralizing capacity (ANC), and it represents the balance between the capacity of a sample to generate acid (MPA) and its capacity to neutralise acid (ANC). In the present study, the ANC was converted from the NP value of the modified NP test (NP/50*49) and the MPA from the total S content in units of kg H₂SO₄/t (S % * 30.6) (AMIRA, 2002).

In addition, portions of NP and NAG extracts were separated before titrations by pipette to analyse elements solubilised during the addition of acid in the modified NP test and during the sulphide oxidation with H₂O₂ in the NAG test. Element concentrations were determined from the extracts by ICP-OES/MS.

3. Results and discussion

The majority of the rock samples analysed with the modified NP and NAG tests had a low total S concentration (<0.4 %), while two samples contained

more than 1 % S (Table 2). The soapstone (SS) and diabase (DB) samples fulfilled the inert waste criterion of 0.1% for the maximum total sulphide S content set by the Finnish Mine Waste Decree 717/2009. The samples of mafic metavolcanic rocks (MVI and MVII), gneiss (GN) and migmatite (MG) exceeded the S limit of inert waste, having a S content between 0.2 % and 0.4 % (Table 2). Carbonate C concentration of these rocks was low or below the detection limit (diabase, migmatite). The intermediate metavolcanic rock (IV) and altered rock (Alt R) had high sulphide S and carbonate C concentrations (>2 %).

High total concentrations of MgO and CaO in samples of diabase, mafic (MVII) and intermediate (IV) metavolcanic rocks indicated not only the presence of carbonate minerals (see *aqua regia* extractable Mg and Ca in Table 4) but also the presence of Mg- and Ca-bearing silicates that may provide some neutralisation capacity (Table 2). These samples contained moderately reactive silicates such as hornblende, actinolite and anorthite (Ca-plagioclase) to attenuate acid production (Table 1; cf. Jambor et al., 2002). According to Jambor et al. (2002), highly calcic members of the plagioclase feldspars yield a greater neutralizing potential than the sodic members do. Gneiss and migmatite, with a lower total content of Mg and Ca, mainly consist of Na-bearing plagioclase and/or K feldspar (Table 1),

Table 2. Total S, C, non-carbonate C and carbonate C concentrations, and total main element oxide concentrations of the studied rock samples. See keys for abbreviations of the rock samples in Table 1; n.d. = no data.

Totals		SS	DB	MVI	MVII	GN	MG	IV	Alt R
S	%	0.07	0.12	0.19	0.31	0.33	0.35	2.50	8.92
C	%	4.48	0.08	0.91	0.07	0.22	0.15	2.54	7.08
C, non carbonate	%	0.08	0.07	0.74	<0.05	0.15	0.15	0.31	3.11
C, carbonate	%	4.40	<0.05	0.18	0.05	0.06	<0.05	2.23	3.97
SiO ₂	%	36.1	50.4	68.7	45.2	65.3	66.3	43.1	45.5
Fe ₂ O ₃	%	17.6	14.6	9.01	10.7	5.98	6.33	11.0	20.6
Al ₂ O ₃	%	1.98	13.8	10.7	9.36	15.9	17.6	13.2	6.31
MgO	%	34.3	6.69	4.56	20.0	2.49	2.02	5.73	1.69
CaO	%	0.75	10	0.23	8.00	1.49	1.26	10.3	3.82
Na ₂ O	%	<0.07	2.31	1.72	0.21	2.46	1.98	2.29	2.11
K ₂ O	%	n.d.	0.37	0.19	0.13	3.67	3.18	1.19	0.98

which weather very slowly and have hardly any input into acid neutralisation (Kwong & Ferguson, 1997; Lawrence & Wang, 1997). In comparison, the altered rock, which consisted of reworked metasedimentary and metavolcanic materials, had a somewhat greater CaO content than gneiss and migmatite due to the presence of Ca-bearing carbonate minerals.

The modified NP/AP ratios (NPR) of all the other rocks, except for soapstone, varied in the range of <1 to 2, which classified them as 'possibly' or 'likely acid generating' materials (Table 3; ST/EIP-PCB/MTWR_BREF_FINAL July 2004). Based on the Finnish Mine Waste Decree 717/2009, this type

of waste is not inert. A waste with S content < 1 % and NPR < 3 is classified as inert. Only the soapstone sample fulfilled this criterion.

Contrary to the modified NP value, the neutralization capacity based on carbonate NP was considerably higher for the soapstone (SS), and somewhat higher for the mafic metavolcanic rock I (MVI) and altered rock (Alt R) samples, and classified them as 'non-acid generating', 'not potentially acid generating' and 'possibly acid generating' materials, respectively (Table 3). These rocks contain slowly weatherable carbonates such as magnesite and ankerite, which potentially increase the long-term neutralization capacity (Table 1). In contrast, the NP/AP

Table 3. Results of the modified ABA and single NAG tests and carbonate NP determinations of the studied rock samples.

		SS	DB	MV I	MV II	GN	MG	IV	Alt R
AP ¹⁾	kgCaCO ₃ /t	2.2	3.8	5.59	9.6	10.2	10.9	85.0	289
NP (prEN15875)	kgCaCO ₃ /t	53.6	6.65	9.34	6.07	6.82	4.38	182	89.5
Carbonate NP ²⁾	kgCaCO ₃ /t	367	0.83	14.6	4.18	5.26	n.d.	186	331
Acid-base account (equivalent NPR ratios of CaCO₃)									
NP(prEN15875)/AP		25	1.8	1.7	0.6	0.7	0.4	2.1	0.3
Carbonate NP/AP		168	0.2	2.6	0.4	0.5	n.d.	2.2	1.1
Classification,		>4	1-2	1-2	<1	<1	<1	2-4	<1
NP(prEN15875)/AP ³⁾		none	possibly	possibly	likely	likely	likely	low	likely
Single NAG test									
EC	mS/m 25°C	16.6	10.5	14.0	17.9	23.5	36.4	54.1	252
NAG-pH		9.0	4.1	7.0	4.9	3.5	3.2	8.7	2.8
NAG pH 4.5	kg H ₂ SO ₄ /t	0.0	0.2	0.0	0.0	1.6	3.8	0.0	13.5
NAG pH 7.0	kg H ₂ SO ₄ /t	0.0	1.0	0.0	1.3	3.8	6.6	0.0	44.1
Acid-base account (equivalent ratios of H₂SO₄)									
ANC ⁴⁾	kg H ₂ SO ₄ /t	52.5	6.5	9.2	5.9	6.7	4.3	178	87.7
MPA ⁵⁾	kg H ₂ SO ₄ /t	2.1	3.7	5.5	9.4	10.0	10.7	83.2	283
NAPP ⁶⁾	kg H ₂ SO ₄ /t	-50.4	-2.8	-3.68	3.4	3.3	6.4	-95.1	195
ANC/MPA		24.5	1.8	1.7	0.6	0.7	0.4	2.1	0.3
NAG _{pH4.5} /NAPP		0.0	-0.1	0.0	0.0	0.5	0.6	0.0	0.1
Classification ⁷⁾		NAF	PAF-LC	NAF	UC	PAF-LC	PAF	NAF	PAF

¹⁾ Acid potential = 31,25*S %

²⁾ Neutralization potential = 83,34*C_{carb} %

³⁾ ST/EIPPCB/MTWR_BREF_FINAL July 2004, Price et al. 1997

⁴⁾ Acid neutralization capacity = NP/50*49 kg H₂SO₄/t

⁵⁾ Maximum potential acidify = 30,6* S%

⁶⁾ Net acid producing potential = MPA-ANC

⁷⁾ NAF = non acid forming (negative NAPP and NAG_{pH3.5}, NAG = 0), PAF = potentially acid forming (positive NAPP, NAG_{pH<4.5}, and NAG>5), PAF-LC = potential acid forming, low capacity (NAG £5), UC = Uncertain, if positive NAPP and NAG_{pH>4.5}

ratio based on the carbonate NP was smaller for the rock samples with a low carbonate content or without carbonates than the modified NP/AP ratio (Table 2 and 3). This suggests that the dissolution of silicates was responsible for neutralization during the modified NP test (Kwong & Ferguson, 1997). Therefore, the neutralization capacity of diabase, mafic metavolcanic rock II (MVII), gneiss and migmatite mainly seems to have resulted from silicate weathering and hardly at all from carbonate minerals.

Instructions for the NAG procedure determine four categories for waste classification: 'non-acid forming' (NAF), 'potentially acid forming with lower capacity' (PAF-LC), 'potentially acid forming with a high capacity' (PAF or PAF-HC) and 'uncertain' (UC; AMIRA, 2002). Based on the NAG pH and NAPP values, the soapstone, MVI and intermediate metavolcanic (IV) rock samples were 'non-acid forming' materials (Table 3 and Fig. 1). Diabase and gneiss had a low capacity for potential acid generation, whereas migmatite and the altered rock were unambiguously acid-forming materials. In contrast to the diabase, gneiss and migmatite, the NAG (pH 4.5) value for MVII was zero, cor-

responding to the category 'non-acid generating', but the NAG (pH 7.0) value was >0 and classified it as 'potentially acid generating' (Table 3). Consequently, MVII is placed in the 'uncertain' category in Figure 1.

In the NAG test, the titration at pH 4.5 includes acidity due to free acid (i.e. H_2SO_4 from sulphide oxidation) as well as from the hydrolysis of soluble Al and Fe (Miller et al., 1997; AMIRA, 2002). The NAG pH 7.0 titration value includes additional acidity due to other metals that precipitate as hydroxides between pH 4.5 and 7.0 (AMIRA, 2002). As seen in Table 4, a considerable part of the Cu and Ni was soluble in the NAG extract of MVII. Copper and Ni obviously precipitate during the back-titration to pH 7, which causes the increase in the NAG pH 7 value (Jennings et al., 2000). In contrast, both NAG pH 4.5 and 7 values indicated that the diabase, gneiss, migmatite and altered rock samples were potentially acid generating (Table 3).

The results of the modified NP and NAG tests and carbonate NP revealed differences in classifying the acid-generating character of the rock samples. The hydrochloric acid treatment in the modified NP test mainly solubilised reactive carbonate

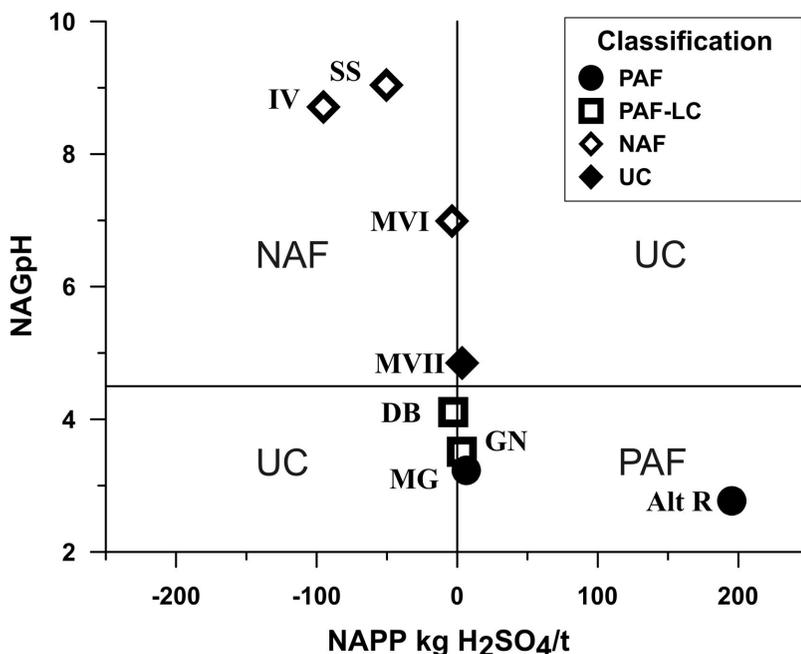


Fig. 1. Distributions of the studied rock samples in the NAG pH/NAPP diagrams.

minerals (e.g. calcite) (see Ca extractability in Fig. 2a). However, the acid added during the test did not solubilise all the carbonates that may have neutralization potential in the long term (Table 3). Based on this, carbonate NP determination should be included in mine waste screening. The results showed that the dissolution of silicates in the samples with a low carbonate content or without carbonates yielded a minor neutralizing potential (Table 3). According to Kwong & Ferguson (1997) and Jambor et al. (2002), silicates rarely contribute sufficient NP to surpass the threshold value (e.g. 20 kg CaCO₃/t) needed to neutralize potential acidity produced by the sulphide oxidation during the test. This is despite silicate alteration (e.g. clay mineral transformation) may contribute to ARD neutralization and metal attenuation under field conditions (Alpers & Nordstrom, 1990; Blowes et al., 1992).

Hydrogen peroxide is an aggressive reagent for oxidizing sulphides, while it less strongly attacks carbonates and silicates (AMIRA, 2002). The extractability of S during the NAG test varied from 30 % to 95 % of the S totals, while it was expectedly much lower (<10 %) during the modified NP test (Fig. 2b). According to the experiments by Jennings et al. (2000), H₂O₂ oxidation liberates acidity from Fe sulphides (pyrite, marcasite, pyrrhotite), but also from arsenopyrite, chalcopyrite and sphalerite, similarly to the sulphide oxidation caused by oxygen. However, the extractability of As was low during the NAG test, especially from the intermediate

metavolcanic rock that contained abundant arsenopyrite. This indicates that a single addition of the H₂O₂ solution, as used in the present study, may not be sufficient to oxidize all the slowly reactive arsenopyrite (AMIRA, 2002). Furthermore, the coprecipitation of As with Fe during the test can also reduce the As content in the NAG extracts (Jennings et al., 2000).

Table 4 presents the concentrations of some of the main and trace elements in extracts produced by the modified NP test and NAG test in comparison to their *aqua regia* extractable concentrations. As can be seen, the concentrations of extractable Fe and Al were much higher in the NP than the NAG extracts. This suggests that hydrochloric acid of the NP test markedly dissolved silicates, resulting in slightly increased NP values for the low carbonate and non-carbonate rock samples. However, the increase in the neutralization capacity via silicate dissolution did not raise the NP values over the AP values in MVII, gneiss or migmatite, as was the case for diabase (Table 3). Hydrolyzation of Fe and Al generates some additional acidity in these rocks (Kwong & Ferguson, 1997), further contributing to their classification as 'likely acid generating materials'. In contrast, the low concentrations of Fe in NAG extracts and the reddish brown colouring of the residues suggest the precipitation of Fe during the test, which obviously leads to acid release and therefore influences the NAG pH, in addition to the release of sulphuric acid from sulphide oxidation

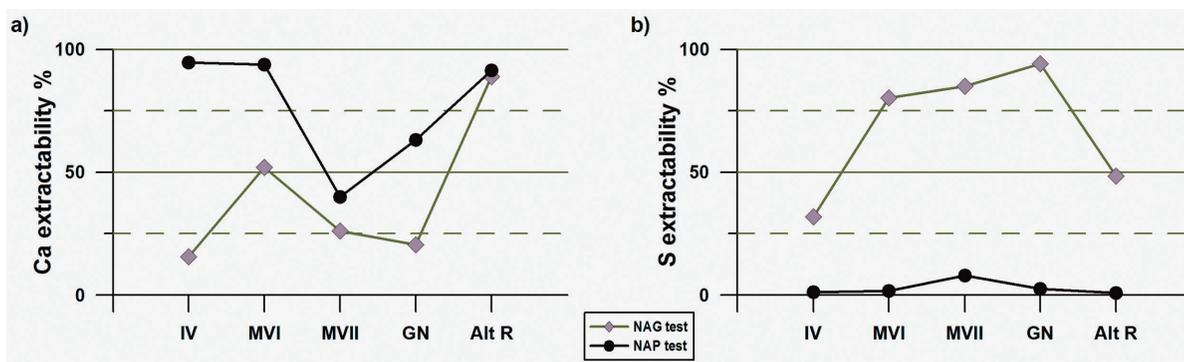


Fig. 2. (a) Ca and (b) S extractability (%) in the NP and NAG extracts of the studied rock samples. See keys for abbreviations in Table 1.

(Miller et al., 1997; Jennings et al., 2000). The exception to the behaviour of Fe was the sample of altered rock, which showed high extractability of Fe at a very low NAG pH (<pH 3) that maintains the solubility of Fe³⁺ instead of re-precipitation (Table 3). Furthermore, a decrease in the NAG pH below 5 is followed by an increase in Al extractability, which upon hydrolysis generates some acid.

Furthermore, the release of trace metals unambiguously depends on the NAG pH (Table 4, Fig. 3). As seen for samples of MVII, diabase, gneiss,

migmatite and altered rock in Figure 3, the relative extractability of Cu and Ni was markedly elevated when the NAG pH dropped below 5.0, regardless of their *aqua regia* extractable concentrations or the total sulphide S content. Furthermore, the concentrations in the NAG extracts were greater than in the NP extracts (except in MVI and IV), which had a lower solubility of sulphur indicating minor decomposition of metal sulphides in the NP test. The pH dependence of trace solubility in the NAG extract (before the titration) is analogous to the see-

Table 4. Main and trace element concentrations in the hot aqua regia (AR), NP and NAG extracts of the studied rock samples. No NP extract data from the SS, DB and MG rock samples, keys for rock sample abbreviations in Table 1.

	Ca mg/kg	Mg mg/kg	K mg/kg	Al mg/kg	Fe mg/kg	S mg/kg	As mg/kg	Co mg/kg	Cr mg/kg	Cu mg/kg	Mn mg/kg	Ni mg/kg	Zn mg/kg
Soapstone (SS)													
AR	4890	89600	<50	4100	93400	802	226	104	858	38	1530	814	25
NAG	1330	1520	<20	34	<20	473	6	0	2	0	<1	1	<1
Diabase (DB)													
AR	11100	3140	1020	13300	25900	1200	1	16	35	138	190	31	37
NAG	606	150	199	96	<20	1070	0	7	0	89	15	17	16
Mafic metavolcanic rock I (MVI)													
AR	1290	26300	321	37900	61700	1980	19	32	240	84	390	208	158
NP	1210	2390	98	4550	5450	35	1	10	19	22	75	39	34
NAG	666	1080	21	55	61	1590	<0.07	0	11	0	3	0	2
Mafic metavolcanic rock II (MVII)													
AR	2720	40000	374	28200	32000	2790	1	54	326	1650	409	778	99
NP	1090	1400	213	952	1200	223	0	4	8	115	31	49	13
NAG	710	883	313	41	<20	2370	1	10	2	781	22	127	50
Gneiss (GN)													
AR	1510	13800	18400	28900	38100	2060	3	17	65	87	353	62	93
NP	954	528	833	1290	2180	51	1	3	4	2	41	10	6
NAG	309	316	875	254	<20	1940	0	6	0	39	18	26	20
Migmatite (MG)													
AR	632	6280	4270	16900	20300	3140	1	14	92	113	53	66	41
NAG	360	254	297	455	95	2720	0	9	2	90	8	45	11
Intermediate metavolcanic rock (IV)													
AR	69000	32700	2180	29700	69900	25200	15120	39	45	100	1270	51	76
NP	65300	1820	675	1800	3330	282	103	3	4	11	783	5	6
NAG	10800	14	591	74	10	8030	60	0	0	1	1	<0.1	2
Altered rock (Alt R)													
AR	27000	9190	2600	7220	143000	88600	142	42	141	379	2530	187	624
NP	24700	5560	566	1440	23200	762	2	4	44	29	1120	21	217
NAG	24000	7030	733	479	14600	43000	2	20	5	189	2110	94	425

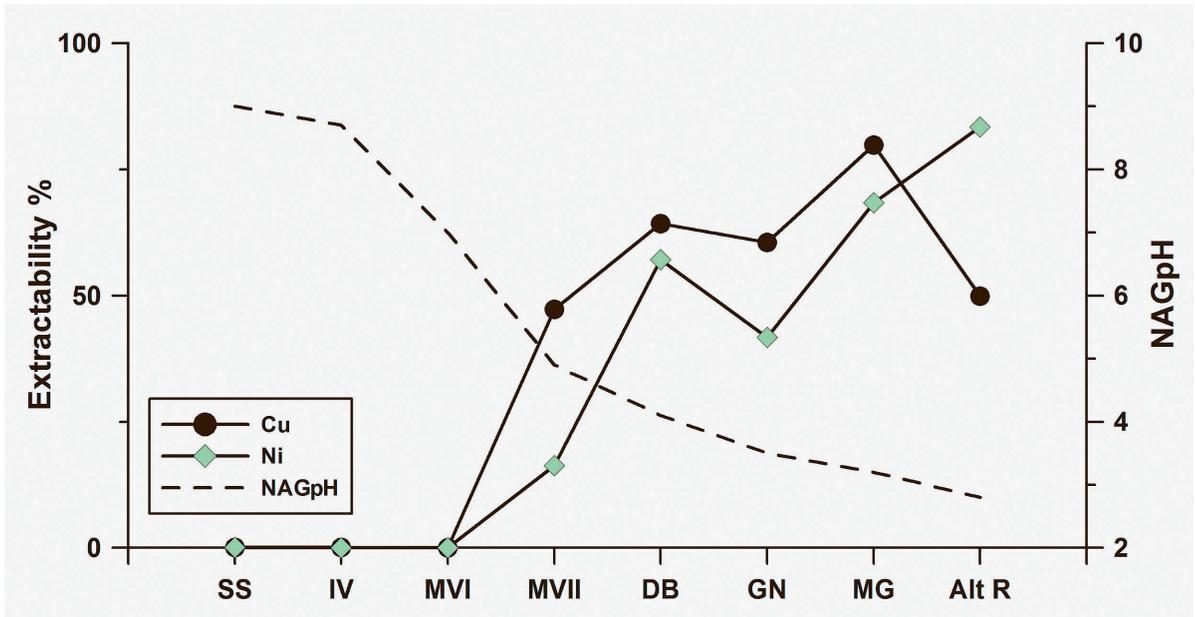


Fig. 3. NAG pH and extractability (%) of Cu and Ni in the NAG extracts of the studied rock samples. See keys for abbreviations in Table 1.

page chemistry in the surroundings of actual waste deposits (Heikkinen et al., 2009). The solubilisation of traces during the NAG test can be interpreted to represent their maximum potential release via sulphide oxidation in the long term (Jennings et al., 2000; Weber et al., 2004; Lei & Watkins, 2005). The acidic and Ni-rich seepage from crushed gneiss aggregates in the basal structure of a municipal waste disposal facility is also consistent with this interpretation (Table 4, Räisänen, 2005). Hydrolyzation of Al released in silicate weathering (obviously chlorite), following pyrrhotite oxidation, was the main source of acidity in this seepage (Räisänen, 2005; cf. Kwong & Ferguson, 1997).

Several studies have reported the discrepancy in ARD classification between the NAG tests and the ABA tests that rely on hydrochloric or sulphuric acid treatment (O'Shay et al., 1990; Lapakko & Lawrence, 1993; Jennings et al., 2000). This was partly also seen in this study. Both the NP and NAG tests classified diabase, gneiss, migmate and MVII into the category of 'potentially acid generating'. However, the acid production of the diabase sample, with an S content below the limit (<0.1 %) for inert waste, may have been overestimated due to

the additional acid released via hydrolysis of Fe and Al during the tests (Kwong & Ferguson, 1997). Further research is needed to assess whether this reaction is valid in the actual environment, as it was in the case of gneiss aggregates. The rock sample (MVI) with slowly reactive carbonate minerals proved to be 'not potentially acid generating'/'non acid forming' according to the NAG test and the carbonate NP/AP ratio, but 'possibly acid generating' according to the NP(prEN15875)/AP ratio (ST/EIPPCP/MTWR_BREF_FINAL July 2004). However, the slow dissolution rate of these carbonates (i.e. ankerite) may promote ARD in the short term, and the prediction based on the NAG test or carbonate NP may therefore overestimate their actual neutralization capacity in the short term (Lei & Watkins, 2005).

Several studies have reported the importance of mineralogical investigations together with the static test (Lawrence & Scheske, 1997; White et al., 1999; Jambor, 2003; Weber et al., 2004; Lei & Watkins, 2005; Heikkinen, 2009). It is also our aim in the future to examine the behaviour of different minerals during the NP and NAG tests, and to identify secondary precipitates that form.

4. Conclusions

The majority of the rock samples (diabase, gneiss, migmatite, mafic metavolcanic rocks MVI and MVII) analysed with the modified NP and NAG tests had low total S and carbonate C concentrations (<0.5 %). The intermediate metavolcanic rock, altered rock and soapstone samples contained more than 2 % carbonate C. The first two mentioned rocks had high S contents (>2 %), whereas the soapstone had a low S concentration (<0.1 %). Both the modified ABA and the NAG test classified diabase, gneiss, migmatite and MVII into the category of 'potentially acid generating'. However, in case of the diabase, classified as inert waste based on the low S content (<0.1 %), the tests may overestimate the acid generation potential. Nevertheless, hydrolyzation of Fe and Al released in silicate weathering, following Fe sulphide oxidation, can be one additional source of acidity attenuating the neutralization potential in low sulphide bearing wastes, as it proved to be in the case of gneiss. Furthermore, the tests unambiguously classified soapstone as 'non acid generating' and the altered rock as 'potentially acid generating'. The intermediate metavolcanic rock and MVI with slowly reactive carbonate minerals proved to be 'low and possible acid generating', respectively, according to the carbonate NP/AP ratio and the modified ABA, but 'non acid generating' (NAF) according to the NAG test. This supports the use of the NAG test comparatively to the modified NP in mine waste screening. In the NAG test, acid generation and neutralization reactions either raising or decreasing the pH significantly influenced the solubility of trace metals and Al. Since H₂O₂ oxidation liberates acidity from Fe sulphides similarly to the sulphide oxidation caused by oxygen, we suggest that the NAG extract contents could be useful in assessing contaminant mobility during long-term acid generating reactions.

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