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TECHNICAL ARTICLE

Evaluation of pH Testing Methods for Sulfidic Mine Waste

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Abstract Environmental assessment of solid mine waste is required throughout the life of a mine. This has driven the need for tools and practices to understand the current state of net acidity in mine wastes. Rinse and paste pH tests are commonly used in the initial screening of waste to provide a preliminary evaluation of its current net acidity. Such pH tests are particularly useful for assessing the chemistry of first flush waters draining sulfidic rocks and wastes. In this study, we compared nine different pH tests (rinse and paste pH tests as well as soil tests of the International Organization for Standardization ISO 10390:2005; American Society for Testing and Materials ASTM D4972-01 2007; Standards Australia AS4969.2-2008), using three different sulfidic rock samples and the acid–base accounting standard KZK-1. We observed significant variability in measured pH for the same samples using the different test methods. We show that different rinse and paste pH methods using different grain sizes and extraction solutions can result in different risk classification for ARD assessments. We recommend carrying out pH measurements using 0.01 M $CaCl_2$ solution, which results in more rapid, reproducible, and precise analyses than using deionised water.

Keywords Acidity · Testing · Rinse pH · Paste pH · Risk classification

Introduction

Anthropogenic activities contribute to acidification of the Earth's air, water, and soils (Rice and Herman 2012). At mine sites, the weathering of sulfidic rocks and wastes often cause acid rock drainage (ARD), which in turn may acidify and contaminate ground and surface waters (cf. Lottermoser 2010). A thorough understanding of acidification and metal contamination processes is required due to detrimental and long term effects of ARD on the environment, and because of the colossal liability costs associated with current and future ARD remediation (approximately US $100 billion; Tremblay and Hogan 2001).

Geochemical tools including rinse and paste pH tests are routinely used in ARD risk assessments of mine wastes and mine workings. However, rinse and paste pH tests are not predictive tests. Materials disturbed by mining processes can have neutral to alkaline rinse and paste pH values, but a high acid generating potential due to unoxidised sulphides.

Regardless, in acid base accounting, rinse and paste pH tests are often used in conjunction with the net acid generation (NAG) pH test. The NAG pH oxidizes the sulphides using hydrogen peroxide, and methods using the total sulfur and carbonate content are used to assess the net acid producing potential (NAPP) (e.g. Smart et al. 2002) or net neutralizing potential (NNP) of sulfidic rocks and wastes (e.g. Price 2009).

Rinse and paste pH tests involve the measurement of pH in slurries comprising crushed or pulverised rock and water. These tests indicate the presence of readily soluble

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acidity or alkalinity, and are generally thought to provide a preliminary indication of the chemical response of a sample with respect to water quality (e.g. Sobek et al. 1978). A number of different pH testing methodologies have been established that assess the current state of acidity of sulfidic rocks in the laboratory (e.g. Morin and Hutt 1997; Smart et al. 2002; Sobek et al. 1978), with the tests varying in their experimental designs and sample requirements. For example, the sample grain size for testing purposes has been recommended as <0.075 mm (Smart et al. 2002), <0.25 mm (Sobek et al. 1978), and <2 mm (Morin and Hutt 1997; Price 2009). Furthermore, the analytical protocols used to prepare the supernatant or paste rely on different solid:solution ratios, ranging from 1:1 (Morin and Hutt 1997; Price 2009), to 1:2 (Smart et al. 2002), and 2:1 (Sobek et al. 1978). Moreover, the equilibration time between the sample and extracting solution also varies, from instant pH measurement (Sobek et al. 1978) to a period of equilibration ranging from 10 min (Price 2009) to 12–16 h (Smart et al. 2002). While rinse and paste pH tests differ in sample grain size, solid:solution ratios, and equilibration time, they all recommend the use of distilled or deionised (DI) water to produce a solution or paste that resembles the leaching of rocks in nature (Smart et al. 2002; Sobek et al. 1978). Until now, there has been no attempt to compare rinse and paste pH tests and to validate their application, despite the diversity of such tests and their established use in ARD risk assessment.

There has been extensive research within the soil science community on the most appropriate method to measure soil pH, particularly soils with low ionic conductivity. In this context, the use of 0.01 M $CaCl_2$ relative to distilled water has been shown to: (1) reduce the junction potentials through coagulation of soil particles in suspension; (2) stabilise the ionic conductivity, which can vary due to seasonal fluxes in soluble salts; (3) eliminate variability observed in pH measurements of moist and dry soils; and (4) reduce fluctuations in pH observed with different shaking times (Conyers and Davey 1988; Davey and Conyers 1988; Sumner 1994). Furthermore, there are numerous standard methods from national (e.g. Australian Standard) and international (e.g. International Organisation for Standardisation (ISO)) bodies for soil pH testing. By contrast, no standard pH methods exist for sulfidic rock testing.

In this paper, we compare commonly used pH tests that form the first step in assessing the potential of sulfidic rocks and mine wastes to produce ARD. We investigated the use of 0.01 M $CaCl_2$ for pH testing of unweathered sulfidic rocks, particularly waste rocks containing fresh sulphides brought to the surface during underground mining operations, and which suffer from low ionic conductivity due to the lack of exposure to weathering. We also review which variable of the analytical protocols (i.e. extraction solution, solid:solution ratio, or grain size) leads to the most pronounced variation in measured pH. Furthermore, new data on the abrasion pH of selected minerals measured using 0.01 M $CaCl_2$ are presented to assist in the interpretation of rinse and paste pH results. Consequently, this contribution adds to our existing knowledge of testing methods for sulfidic rocks and wastes, and makes recommendations on the use of pH tests in ARD risk assessments.

Methods

Sample Selection

Two bulk sulfidic rock samples were collected from the Mount Lyell Cu mine (41°04′S, 145°34′E), from the run-of-mine ore stockpile (CMT-ROM1) and waste rock dump (CMT-WRD1). Mt Lyell ore and waste rocks consist of chalcopyrite and pyrite within a quartz–sericite–chlorite gangue (cf. Hills 1990; Raymond 1996). The Mt Lyell ore sample (CMT-ROM1) derived from underground workings represents a freshly extracted, unweathered sulfidic ore. By contrast, the Mt Lyell waste rock sample (CMT-WRD1) has been subjected to limited weathering (possibly months) since the waste was extracted from underground workings and placed into the above-ground waste repository.

A third bulk sulfidic rock sample was obtained from an abandoned waste rock dump at the historic Royal George Sn mine (41°49′S, 147°53′E). Royal George ore and waste rocks contain cassiterite, pyrite, and chalcopyrite, and the gangue minerals feldspar, quartz, biotite, and tourmaline (cf. Green 1990; McIntosh Reid and Henderson 1929). The Royal George sample (RG-WRD1) represents oxidised material that has been exposed to atmospheric conditions since abandonment of the site in the 1920s (Hills 1990).

A suite of sulfidic waste rock samples (n = 35) was collected from waste rock piles at the historic Croydon Au mine (18°12′S, 142°14′E). The waste rocks contain major quartz, potassium feldspar, muscovite, plagioclase, minor illite, kaolinite, pyrite, arsenopyrite, sphalerite, and galena, and traces of pyrrhotite and chalcopyrite (Parbhakar-Fox et al. 2014; Van Eck and Child 1990).

Several mineral specimens (n = 22) were obtained from commercial suppliers for abrasion pH test work. Materials included carbonates (calcite, dolomite, malachite, azurite, siderite, magnesite), silicates (plagioclase, K-feldspar, olivine), sulphides (pyrite, pyrrhotite, chalcopyrite, sphalerite, arsenopyrite, galena), sulfates (celestine, gypsum, jarosite), and native sulfur.

Accuracy of the various pH testing methods was evaluated using the acid–base accounting reference material KZK-1, which is a sericite schist made from a mixture of drill cores from the Kudz Ze Kayah copper–lead–zinc project, Canada (CANMET Certificate of Analysis KZK-1, 2007). The tested material was received already processed to −74 µm and contains quartz, albite, muscovite, biotite, rutile, ilmenite, ankerite, calcite, monazite, zircon, pyrite, and pyrrhotite. Trace amounts of clinochlore, kaolinite, and sphalerite are also present.

Sample Processing

Sulfidic rock samples from Mt Lyell and Royal George (CMT-WRD1, CMT-ROM1, RG-WRD1) were processed into three different grain size fractions (<0.075, <0.25, and <2 mm) to evaluate the different pH test methods. Bulk samples were homogenised, passed through a steel jaw crusher, and dry sieved to yield different size fractions. In addition, bulk samples were crushed using a chrome steel ring mill to produce sufficient sample masses of the <0.075 mm fraction. Similarly, waste rock samples from the Croydon Au mine were processed to different grain size fractions (<0.075 and <2 mm). Mineral specimens were crushed and then dry sieved to the <0.075 mm fraction.

pH Tests

The three sulfidic waste rock samples (CMT-ROM1, CMT-WRD1, RG-WRD1) were subjected to nine different pH tests [i.e. the rinse and paste pH tests of Sobek et al. (1978) and Smart et al. (2002), and soil tests of the International Organization for Standardization ISO 10390:2005, American Society for Testing and Materials ASTM D4972-01 (2007), and Standards Australia AS4969.2-2008]. The samples were further tested at the commercial laboratory, Intertek (Perth) using the 1:5 soil pH test of Rayment and Lyons (2010), which is similar in experimental design to ISO 10390:2005. Each test required particular solid:solution ratios (1:1, 2:1, 1:2, 1:5, 1:40), extracting solutions (DI water, $CaCl_2$, KCl), sample masses (5–25 g), solution volumes (5–50 mL), grain size fractions (<0.075, <0.25, <2 mm), equilibration times (0, 1, <3, <16 h), and procedural steps (Table 1).

Sieved size fractions (<0.075 and <2 mm) of the Croydon waste rock samples were used to understand the control of grain size on the resulting rinse and paste pH. Measurements using both the ISO 10390:2005(E) and ASTM D4972-01(2007)(E) pH methods (Table 1) were carried out on both size fractions, using 0.01 M $CaCl_2$ as the extracting solution.

The pH of mineral samples was measured by adapting the abrasion pH method of Stevens and Carro (1948). Their method relied on measuring the pH of mineral–water suspensions using pH indicator paper to establish the current acidity release of individual minerals. Our modified abrasion pH method included the use of 0.01 M $CaCl_2$ and an operationally defined grain size (<0.075 mm). The pH and electrical conductivity (EC) of each mineral was measured by mixing 10 g of <0.075 mm fraction with 10 mL of the 0.01 M $CaCl_2$ solution. The paste was stirred for 10 s and the pH and electrical conductivity (EC) recorded after 10 min.

A Mettler Toledo S47 SevenMulti™ dual pH/conductivity meter was used to measure the pH and EC of the samples' supernatant or paste. The pH of all samples was measured by an InLab®Expert Pro electrode and the EC by an InLab®731 probe. The pH electrode was calibrated using a four-point calibration with buffer solutions (pH 2, 4, 7.0, 9.21) at 25 °C. The InLab®Expert Pro pH electrode is especially designed to measure slurries and suspensions because the reference electrode is in the form of a gel and in direct contact with the sample solution through two open junctions. Such a configuration reduces the likelihood of blockage and contamination associated with fine-pored ceramic junctions used in conventional electrodes. The EC probe was calibrated using three conductivity solutions (500, 1413 and 12.88 $\mu S\ cm^{-1}$) at 25 °C.

The Mettler Toledo SevenMulti™ dual pH/conductivity meter was calibrated at the start of each analysis period and after a break in analysis. During long analysis runs, the pH meter was checked using the pH 4 buffer solution and recalibrated if necessary. Measurements of pH were carried out by working with one sample type at a time to prevent offsets due to sudden shifts in sample pH. When switching from neutral pH to acidic pH samples or vice versa, it is important to allow the pH probe to adequately equilibrate before recording the pH by discarding the first three measurements. For CMT-WRD1 and RG-WRD1, the pH value was recorded using the automatic end-point criterion, which determines the end of an individual reading once the measurement signal changes less than 0.03 mV in 8 s and by no more than 0.1 mV in 30 s. The low EC of CMT-ROM1 meant that pH measurements were significantly delayed using this endpoint stability criterion, so the pH measurement was manually recorded after 1 min for this sample.

Distilled water was prepared in a conventional glass distillery. Throughout pH testing, the EC and pH of DI water were monitored, yielding an average EC value of 7 $\mu S\ cm^{-1} \pm 40$ ($n = 26$) and a pH value of 5.44 ± 0.25 ($n = 26$). Deviations from the theoretical pH value of 5.65 (Langmuir 1997) likely reflect the fact that precise pH measurements in low-ionic strength waters are very difficult to achieve (Covington et al. 1985). The EC of electrolyte solutions 0.01 M $CaCl_2$ and 1 M KCl yielded values of 1594 ± 16 ($n = 10$) and $114{,}000 \pm 769$ ($n = 10$) $\mu S\ cm^{-1}$, respectively. The pH of electrolyte solutions 0.01 M $CaCl_2$ and 1 M KCl, prepared for the pH tests were 6.40 ± 0.04 ($n = 10$) and 6.56 ± 0.04 ($n = 10$), respectively.

Table 1 Details summarising the protocols of the pH methods evaluated

Test	Solid: solution ratio	Extracting solution	Mass	Grain size (mm)	Equilibration time (h)	Procedure	Stirred or not during measurement
Rinse pH (Sobek et al. 1978)	1:1	DI water	10 g:10 mL	<2	0	Wet sample by capillary action to saturate, then stir to form a thin paste	Stir
Paste pH (Sobek et al. 1978)	2:1	DI water	10 g:5 mL	<0.25	0	Allow water to wet sample by capillary action to saturate the soil, then stir to form a thin paste	Stir
Paste pH (Smart et al. 2002)	1:2	DI water	25 g:50 mL	<0.075	12–16	Stir continuously while adding DI water	Not specified
ASTM D4972-01(2007)	1:1	DI water	10 g:10 mL	<2	>1	Mix the suspension thoroughly and let stand for 1 h	Do not stir
ASTM D4972-01(2007) (E)	1:1	0.01 M $CaCl_2$	10 g:10 mL	<2	>1	Same as just above	Do not stir
ISO 10390:2005	1:5	DI water	5 mL:25 mL	<2	>2	Shake or mix suspension for 1 h and allow it to stand for between 1 and 3 h	Stir
ISO 10390:2005 (E)	1:5	0.01 M $CaCl_2$	5 mL:25 mL	<2	>2	Same as just above	Stir
ISO 10390:2005 (E)	1:5	1 M KCl	5 mL:25 mL	<2	>2	Same as just above	Stir
AS4969.2-2008	1:40	1 M KCl	2 g:80 mL	<0.075	>12	Machine-shaken for 4 h; let stand between 12 and 16 h	Stir

ASTM American Society for Testing and Materials, *ISO* International Organization for Standardization, *AS* Australian Standard, *E* electrolyte

Five replicates of each sulfidic rock sample (CMT-ROM1, CMT-WRD1, RG-WRD1) were analysed for each of the nine pH tests. One pH test was performed for each rock type by Intertek (Perth), as part of the acid–base accounting (ABA) analyses. Three replicates of each Croydon waste rock sample were analysed using the ISO 10390:2005(E) and ASTM D4972-01(2007)(E) pH methods. Each mineral sample was also analysed in triplicate. Moreover, each replicate was measured for both pH and EC three times, resulting in multiple measurements per sample and allowing the calculation of median values and percentiles. The differences between the median and the first and third quartiles are reported as the lower and upper limits, which were generally equal to or larger than the internal precision of the pH measurements. The accuracy of pH measurements for rinse and paste pH tests has been questioned by Price (2009), who stated that pH cannot be detected to an accuracy of more than 0.2–0.5 pH units. However, the accuracy of laboratory measurements is usually better than about 0.02 pH units because buffer solutions have an absolute accuracy in the 0.01–0.02 pH unit range (Langmuir 1997). In this study, we report a mean standard deviation for the total number of measurements ($n = 685$), arising from the different pH tests and four different samples, as 0.04 pH units.

Sample Characterisation

Particle surface area analyses were carried out on each grain size fraction of the three bulk samples (CMT-ROM1, CMT-WRD1, RG-WRD1), following the single point BET method (Brunauer et al. 1938) and using a Micrometrics Flowsorb II 2300 at Intertek, Melbourne. This method determines the surface area by measuring the amount of nitrogen gas adsorbed to the solid surface as the sample is cooled to the temperature of liquid nitrogen. Approximately 1 g of each sample was used, which was outgassed at 200 °C for 1 h prior to analysis. In an effort to assess the precision of the surface area analysis, sample RG-WRD1 <2 mm was repeatedly analysed ($n = 4$), resulting in a standard deviation of 0.11 $m^2\ g^{-1}$.

Total concentrations of selected elements (Ag, As, Bi, Cd, Co, Cu, Mo, Ni, Pb, S, Sb, Se, Tl, Zn) were determined for each size fraction, using a four acid digestion procedure (HF, HNO_3, $HClO_4$, HCl) and inductively coupled plasma mass spectrometry (ICP-MS) at Intertek (Perth). Quality control/assurance of the data was applied by in-house standards, submission of sample replicates, and the repetitive processing of several aliquots of the standard reference material NIST-2780. The difference between the measured and certified concentrations of elements in NIST-2780 was less than 12 % from the reference values. Replicate elemental analyses of CMT-ROM1 <0.075 mm deviated by <6 % on average.

Powdered samples of each grain size fraction were assessed for their ability to generate acid. These tests included the 1:5 soil pH test (cf. Rayment and Lyons 2010; 1:5 solid/water ratio, shaken for 1 h and measured after 4 h) and NAG pH measurements (cf. Smart et al. 2002) of samples to provide a preliminary evaluation of the material's net acidity. The total sulfur (S_{total}) content of samples was assumed to represent the maximum potential acidity (MPA) calculated in kg H_2SO_4/t. The acid neutralising capacity (ANC) of rocks was determined by standard acid reaction and titration. The difference between MPA and ANC yielded the NAPP.

The mineralogy of samples was determined at Federation University (Australia). X-ray diffraction (XRD) traces were obtained from portions of the powdered samples after micronising with Siemens D500 and D501 diffractometers using Fe-filtered CoK_α radiation. The operating conditions were 40 kV/30 mA, step scan 0.02θ/2θ at 1°/2θ/min, fixed 1° divergence and receiving slits, and a 0.15° scatter slit. Mineral phases were identified using computer-aided search/match of the 2010 ICDD PDF4/minerals subfile. SiroQuant^{TM} (version 3.0) was applied to obtain semi-quantitative mineral abundances (wt%).

Results

Sample Characteristics

Geochemical analyses demonstrate that sulfidic rock samples from Mt Lyell (CMT-ROM1, CMT-WRD1) have distinctly elevated Cu values, whereas the Royal George sample (RG-WRD1) is characterised by significant As contents (Table 2). Such element distributions are consistent with the known mineralogy of the Mt Lyell (cf. Hills 1990; Raymond 1996) and Royal George deposits (Green 1990; McIntosh Reid and Henderson 1929) and the XRD analyses completed by this study (Supplemental Table 1).

The highest S_{total} contents were observed in sample CMT-WRD1 (11.0–14.5 wt%), followed by CMT-ROM1 (5–7.5 wt%) and RG-WRD1 (1.6–3.0 wt%). Consequently, all bulk samples had elevated MPA values (49–445 kg H_2SO_4/t), with the highest values present in CMT-WRD1 (337–445 H_2SO_4/t) and the lowest in RG-WRD1 (49–91 kg H_2SO_4/t; Table 2). The highest ANC value was observed in calcite- and dolomite/ankerite-bearing CMT-ROM1 (average of 46 kg H_2SO_4/t), while the lowest ANC value was measured in RG-WRD1 (<3 kg H_2SO_4/t; Table 2). Therefore, all tested samples had positive NAPP values (+52 to +440 kg H_2SO_4/t). In addition, all tested grain size fractions of each rock type reported low NAG pH values (2.2–2.9). Median NAG pH values were 2.9 for CMT-ROM1 and 2.2 for CMT-WRD1 and RG-WRD1, demonstrating their likelihood to produce acid in the long term. Also, plotting

Table 2 Geochemical composition (mg/kg), particle surface area (m^2/g), and static test data of sieved sulfidic rock samples (grain size fractions <0.075, <0.25, and <2 mm for CMT-ROM1, CMT-WRD1, and RG-WRD1) that were used in the pH tests

	CMT-ROM1 < 0.075	CMT-ROM1 < 0.25	CMT-ROM1 < 2	CMT-WRD1 < 0.075	CMT-WRD1 < 0.25	CMT-WRD1 < 2	RG-WRD1 < 0.075	RG-WRD1 < 0.25	RG-WRD1 < 2
Geochemistry									
Ag	2.3	3.1	2.6	0.9	0.8	0.6	32.9	48.1	22.6
As	27	38	35	99	109	93	4268	6136	2980
Bi	1.9	3.0	2.7	5.1	6.4	4.8	40.1	59.5	38.0
Cd	0.15	0.18	0.18	BDL	BDL	0.05	13.43	21.02	3.46
Co	157	187	184	92	78	61	107	51	28
Cu	9662	11,228	9737	689	757	362	379	447	359
Mo	61.9	90.8	83.1	4.9	5.2	4.3	1.3	2.1	1.1
Ni	26.5	28.5	27.9	9.7	9.8	6.4	3.5	3.7	BDL
Pb	17.9	25.6	25.4	20.9	30.2	29.9	164.9	226.8	78.0
S (wt%)	5.0	7.5	7.5	11.0	14.5	11.9	1.6	3.0	1.7
Sb	1.2	1.35	1.09	1.05	1.52	1.68	8.93	12	6.05
Se	6.9	10.4	8.5	9.7	11.6	7.4	8.2	13.4	6.2
Tl	0.37	0.43	0.41	0.65	0.56	0.39	2.72	2.92	1.95
Zn	246	257	260	26	21	16	818	1123	174
Particle surface area	2.06	1.04	0.32	2.61	1.68	1.13	2.05	1.61	0.57
Static test data									
1:5 pH (Rayment and Lyons 2010)	7.8	7.8	7.6	4.8	4.1	4.4	5.2	4.5	4.3
NAG pH	2.9	2.8	2.9	2.2	2.2	2.1	2.3	2.2	2.2
ANC (kg H_2SO_4/t)	53	44	42	8	5	4	-3	-4	-2
MPA (kg H_2SO_4/t)	154	228	228	337	445	363	49	91	52
NAPP (kg H_2SO_4/t)	101	184	186	329	440	359	52	95	54

BDL below detection limit

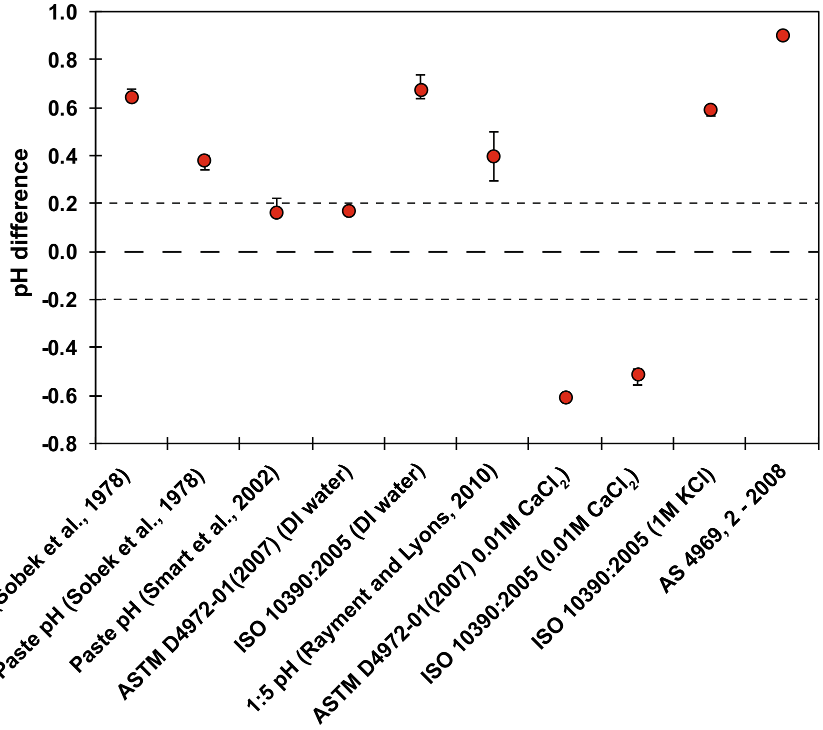

Fig. 1 The difference between the certified pH value and the median pH value (n = 3) for nine different pH methods for the acid–base accounting standard KZK-1. The *dashed lines* show the accepted inter-laboratory range. The 1:5 pH test (Rayment and Lyons 2010) was measured by Intertek, Perth

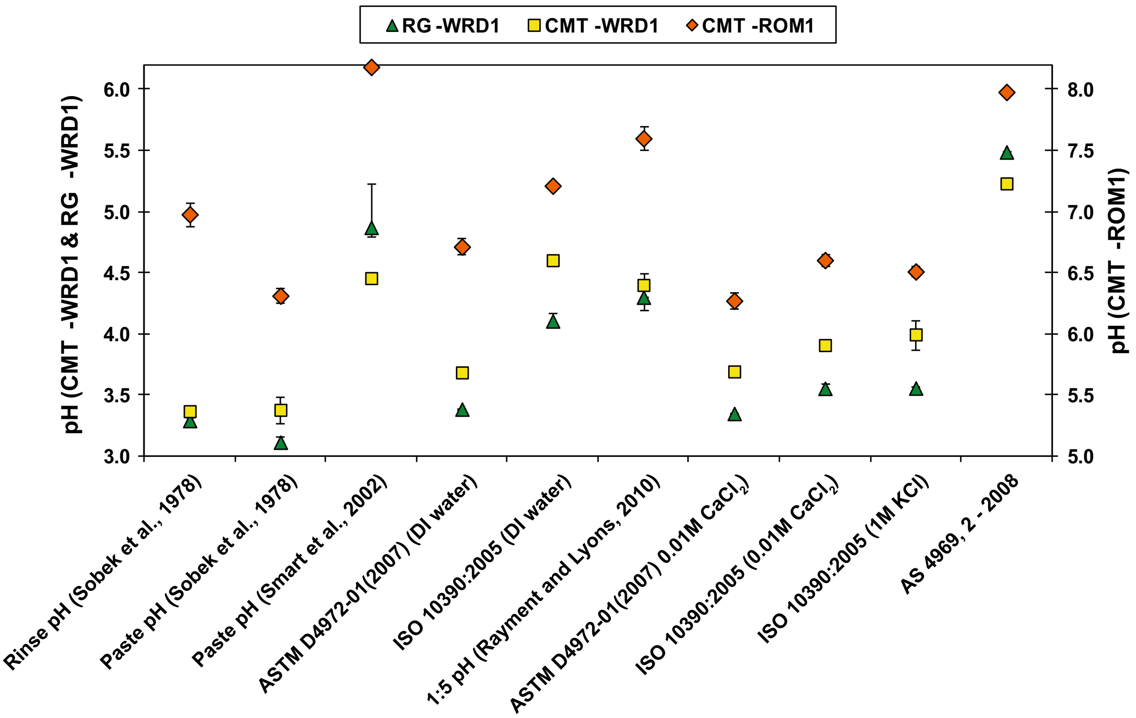

Fig. 2 Mean pH values (n = 5 per analysis) acquired using different test protocols for sulfidic rock samples (i) CMT-ROM1, (ii) CMT-WRD1, and (iii) RG-WRD1. The upper and lower percentiles are plotted for the five replicates. The analyses for the 1:5 pH test (Rayment and Lyons 2010) were carried out by Intertek, Perth on the <2 mm size fraction

samples on the NAPP versus NAG pH waste classification scheme demonstrates that the Mt Lyell and Royal George samples are potentially acid-forming materials.

The likelihood of acid production from the tested materials was further supported by the abundance of sulphide minerals within all samples (Supplemental Table 1).

Pyrite and chalcopyrite were the dominant sulphides in CMT-ROM1 (maximum of 4.6 and 9.1 wt%, respectively) and CMT-WRD1 (maximum of 0.5 and 21.6 wt%, respectively). By contrast, RG-WRD1 contained ≤3.6 wt% pyrite and trace amounts of sphalerite (Supplemental Table 1). Unlike the CMT-ROM1 and CMT-WRD1 samples, RG-WRD1 has trace amounts of jarosite (≤0.3 wt%) and scorodite (≤0.2 wt%), which are indicative of sulphide oxidation and acid generation (cf. Jambor et al. 2000).

pH Testing

The acid–base accounting reference material KZK-1 has a certified paste pH value of 8.8 (±0.21 between laboratories), which has been established using the Sobek et al. (1978) method. The pH values from six different pH test methods using DI water varied by 0.5 pH units from 8.97 to 9.48. The AMIRA paste pH (Smart et al. 2002) and ASTM method D4972-01(2007) (DI water) produced results that were comparable to those of the certified values (Fig. 1). By contrast, pH tests using electrolyte solutions resulted in values that were between 0.5 and 0.6 pH units less than the certified value for 0.01 M $CaCl_2$, and 0.6–0.9 pH units higher for 1 M KCl. The pH testing of the standard was completed using the <74 μm size fraction provided by the supplier, despite the fact that the various pH testing protocols should be performed on different grain sizes (<0.075, <0.25, <2 mm). Thus, the analysis of the standard does not allow conclusive deductions on the analytical accuracy of individual pH test protocols. Regardless, analysis of the KZK-1 standard demonstrates that there was significant variation in measured pH when applying different test protocols.

A wide range of pH and EC values were also measured for CMT-ROM1, CMT-WRD1, and RG-WRD1, according to the different pH test protocols (Fig. 2). The pH assessment of CMT-ROM1 shows circumneutral pH values with a median of 6.85 from all nine pH tests, ranging from 6.27 (±0.05) using ASTM D4972-01(2007)(E) to 8.18 (±0.02), according to the paste pH method of Smart et al. (2002). The pH values observed for CMT-WRD1 showed a median value of 3.91, with a range between pH methods of 3.37 (±0.02) using the rinse pH test of Sobek et al. (1978) to 5.23 (±0.02), according to AS4969.2-2008. Similarly, RG-WRD1 has acidic pH values with a median of 3.55, ranging from 3.11 (±0.02) using the paste pH test (Sobek et al. 1978) to 5.49 (±0.02) using AS4969.2-2008 (Fig. 2). EC measurements ranged from 200 to 118,000 μS cm^{-1}. In general, the lowest EC values were observed in tests using low solid:solution ratios and distilled water as the extracting solution (e.g. ISO 10390:2005). By contrast, the highest EC values were detected in tests using 1 M KCl (e.g. AS4969.2-2008; ISO 10390:2005).

The Croydon waste rock samples had higher pH values in the <0.075 mm fraction for 28 out of the 35 samples than the <2 mm fraction. The pH values were similar for a given size fraction for both ISO 10390:2005(E) and ASTM D4972-01(2007)(E), despite differences in the respective testing procedures, suggesting that grain size was the dominant control on pH (Supplemental Table 2). The pH values of the <2 mm size fraction for ISO 10390:2005(E) and ASTM D4972-01(2007)(E) were within a 2σ error for 57 % of the samples, while for the <0.075 mm size fraction, 46 % of pH values from both tests were consistent within 2σ error.

The results of the modified abrasion pH for selected minerals and their respective XRD analyses are presented in Table 3. Only calcite, malachite, pyrite, chalcopyrite, and sulphur were pure monomineralic specimens, while Iceland spar, galena, and gypsum had a purity of >99 wt% (Table 1). Carbonates such as calcite, malachite, and magnesite gave modified abrasion pH values of 8.33 ± 0.03, 7.71 ± 0.03, and 9.32 ± 0.01, respectively. By contrast, a wide range of pH values was observed for sulphides, which varied from 3.86 ± 0.02 for pyrite to 4.22 ± 0.02 for chalcopyrite. Impurities within the minerals resulted in significantly different pH values. For example, the modified abrasion pH of pure chalcopyrite was 4.22 compared to 6.56 for chalcopyrite containing sphalerite and trace amounts of pyrite and quartz.

Discussion

This study showed that using different pH tests, each with unique experimental protocols and distinct sample requirements, yields significantly different pH values for the same sample. As pH is defined as the negative base-10 logarithm of the hydrogen ion activity in a test solution (Buck et al. 2002), the variations in pH detected by this study equate to large differences in the relative hydrogen ion activity and measurements of rinse and paste pH depends strongly on methodology. Below we discuss how the (a) extracting solution, (b) ionic strength, and (c) grain size all contributed to the variability observed and the implications of this for ARD prediction.

Type of Extracting Solution

The type of extracting solution prescribed in the pH methods had a pronounced effect on the resulting pH. The use of a 0.01 M $CaCl_2$ electrolyte solution resulted in a much smaller range of pH units between methods than those which used DI water. The low ionic strength of DI water (≈10 μS cm^{-1}), combined with low soluble salt contents of samples (200 to <1000 μS cm^{-1}), can bias pH

Table 3 Modified abrasion (MA) pH (median; n = 9) of mineral samples

Mineral	MA pH	Q1	Q3	Abrasion pH	Mineralogy (wt%)
Calcite I	8.33	0.03	0.04	8	99.9 calcite, trace quartz
Calcite II	8.37	0.05	0.01	9, 10	92.5 calcite, 7 dolomite, 0.5 quartz
Iceland spar	8.43	0.04	0.04	N/A	99.8 calcite, trace dolomite
Dolomite	8.87	0.02	0.01	9, 10	97.1 dolomite, 1.8 calcite, trace apatite, quartz
Malachite	7.71	0.03	0.06	7	100 malachite
Azurite	6.91	0.03	0.04	6, 7	97.3 azurite, 2.1 malachite, trace quartz
Siderite	7.79	0.01	0.01	5, 6, 7	85.6 siderite, 5.8 goethite, 4.4 hematite, 4.3 quartz
Magnesite	9.32	0.01	0.01	10, 11	87.3 magnesite, 12 dolomite, trace quartz
Olivine	9.78	0.05	0.01	10, 11	78.9 forsterite, 18 enstatite, 3.1 clinopyroxene
Plagioclase	8.29	0.03	0.03	N/A	82.6 albite, 16.1 muscovite, 1.3 chlorite
K-feldspar	9.26	0.02	0.01	N/A	84.9 microcline, 14.8 albite, trace quartz, ankerite
Pyrite	3.86	0.02	0.10	N/A	100 pyrite
Pyrrhotite	7.38	0.06	0.07	N/A	95.7 pyrrhotite, 1.9 pyrite, 1.1 chalcopyrite, trace calcite, quartz
Chalcopyrite I	4.22	0.02	0.06	N/A	100 chalcopyrite
Chalcopyrite II	6.56	0.12	0.09	N/A	96.3 chalcopyrite, 2.7 sphalerite, trace quartz, pyrite
Sphalerite	8.04	0.01	0.00	6	89.5 sphalerite, 4.4 magnetite, 3.9 calcite, trace pyrite, quartz
Arsenopyrite I	5.34	0.04	0.02	N/A	98.7 arsenopyrite, 1.1 quartz, trace chalcopyrite
Arsenopyrite II	7.73	0.01	0.01	N/A	62.8 arsenopyrite, 23.1 calcite, 11.9 amphibole, 2.2 quartz
Galena	6.70	0.02	0.01	N/A	99.2 galena, trace fluorite, sphalerite, calcite
Celestine	7.92	0.03	0.00	5, 6	97.1 celestite, 2 gypsum, trace quartz, clay
Gypsum	6.94	0.01	0.03	6	99.6 gypsum, trace unidentified
Jarosite	6.28	0.01	0.01	5, 6	84.4 jarosite, 15.6 quartz
Native sulfur	7.29	0.06	0.02	6	100 sulfur

The abrasion pH values of Stevens and Carro (1948) are also shown. Mineralogical composition as determined by QXRD (wt%). The difference between the median, 25th, and 75th percentile values are shown for Q1 and Q3 respectively

N/A not available

readings, as observed in the wide range of pH values reported for DI water in these experiments. The variability in the pH of DI water results from large liquid junction effects, which arise from unequal diffusion of ions across the junction between the measuring solution and the internal reference electrode solution (Illingworth 1981), leading to noisy and imprecise data (Brezinski 1983; Illingworth 1981; Sumner 1994).

The use of $CaCl_2$ is well established in the soil science community to mitigate seasonal fluctuations in soil pH measurements due to variability in anion concentrations, e.g. SO_4^{2-}; NO_3^- (cf. Rayment and Lyons 2010). Generally pH measurements made with $CaCl_2$ solution yield a lower pH (by 0.5–1 pH units) compared to pH values measured in DI water as a result of exchange between Ca^{2+} ions with H^+ and Al^{3+} ions on particle surfaces (Conyers and Davey 1988; Miller and Kissel 2010). We observed a strong linear relationship between the DI water and 0.01 M $CaCl_2$ tests for the reference and sample materials using 1:1 ($y = 0.93\chi$, $R^2 = 0.99$) and 1:5 ($y = 0.88\chi$, $R^2 = 0.99$) solid to solution ratios. For the tests with a 1:1 solid to solution ratio, the pH difference between DI water and 0.01 M $CaCl_2$ decreased with increasing acidity. For example, CMT-ROM1 showed a 0.44 pH-unit difference between the ASTM D4972-01(2007) tests (1:1 solid to solution ratio) with DI water and 0.01 M $CaCl_2$, while the pH difference for the weathered CMT-WRD1 and RG-WRD1 samples was insignificant (<0.04). However, decreasing the solid to solution results in larger pH offsets for all sample types (0.55–0.69 pH-units) following the ISO 10390:2005 (DI water and 0.01 M $CaCl_2$) method.

When comparing pH data for single samples from the various pH test methods, it is apparent that other methodological factors, such as grain size, influence the pH measurements. Hence, the pH values measured with 0.01 M $CaCl_2$ are not systematically lower. For example, the saturated paste pH (Sobek et al. 1978) is within the error range of the pH values reported for ASTM D4972-01(2007; $CaCl_2$) for CMT-ROM1 (Fig. 2). Also, the pH is higher in CMT-WRD1 and RG-WRD1 for ASTM D4972-01(2007; $CaCl_2$) by 0.31 and 0.24 pH-units respectively, compared to the saturated paste pH (Sobek et al. 1978). These discrepancies are likely due to other variables such as the higher solid:solution ratio and smaller grain size (<0.25 mm) used in the Sobek et al. (1978) test. The use of 0.01 M $CaCl_2$ in pH tests for unweathered sulfidic materials (e.g. drill core samples) is favourable as the time it takes for the pH reading to reach the end-point is significantly reduced compared to tests using DI water. The enhanced stability of the InLab®Expert Pro pH electrode when using $CaCl_2$ is due to the increased EC of the measurement solution.

Ionic Strength

The solid:solution ratio controls the ionic conductivity of the solution in which the pH measurement is made, through changes in the dilution of the H^+ ions released into solution. Dilution of the hydrogen ions increases the measured pH as EC decreases (Fig. 3), which results in large junction potentials and greater inaccuracies in pH measurements (cf. Kissel et al. 2009; Sumner 1994). The problem of measuring pH in low EC solutions like DI water is compounded by the fact that the calibration solutions often have a much higher EC (>5000 µS cm^{-1}) than the sample supernatant or paste (Wiesner et al. 2006). Our evaluation of pH test methodologies (Fig. 3) is consistent with previous studies that show an increase in pH with decreasing solid:solution ratios (e.g. Afzal and Yasin 2002; Miller and Kissel 2010). The Sobek et al. (1978) paste pH method has the highest solid:solution ratio of 2:1 compared to the other pH tests, yielding the lowest pH values. By contrast, AS4969.2-2008, which has a solid to solution ratio of 1:40, produced the highest pH values for all three sulfidic samples, despite using an electrolyte (1 M KCl) as the extracting solution.

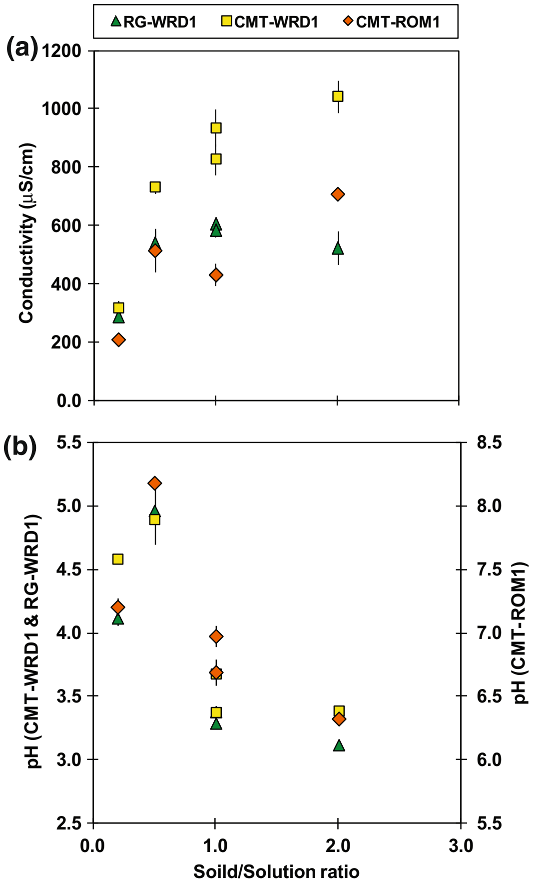

Fig. 3 **a** EC, and **b** pH data for rinse and paste tests that used DI water as the extracting solution. The EC increases as the solid:solution ratio increases (**a**), while the pH decreases as the solid:solution ratio increases (**b**). Similar results for the rinse pH test (Sobek et al. 1978) and ASTM D4972-01(2007) (DI water) method were recorded for CMT-ROM1 (EC) and RG-WRD1 (pH), with both testing methods having a solid:solution ratio of 1

Grain Size

Grain size controls chemical reactions through changes in particle surface area, which can increase rates of sulphide oxidation and weathering (Liu et al. 2008). Mining and mineral processing result in grain size reduction of geological material. Generally, a greater surface area of minerals and rock materials should increase the rate of element release into waters wetting the mineral and rock surfaces (cf. Förstner and Salomons 1980). Acid production and neutralisation are controlled by the exposure of acid-producing and acid-neutralising minerals, which in turn can vary greatly in particle size and surface area. For example, Stromberg and Banwart (1999) demonstrated using column leach tests that ≈80 % of the acid production and dissolution of silicates resulted from the <0.25 mm fraction. In our study, the BET surface area data demonstrated: (a) that the <0.075 mm fraction had a surface area three times larger than the surface area of the <2 mm fraction, with an average of 2.2 compared to 0.7 m^2 g^{-1}, and (b) that the <0.25 mm fraction had an intermediate surface area (Table 2). We observed the highest total trace metal (Ag + As + Bi + Co + Cu + Mo + Ni + Pb + Sb + Se + Tl + Zn) and sulfur content in the <0.25 mm fraction for all three samples (Table 2). However, the ratio of total trace element concentration to sulfur increased with decreasing particle size, which suggests that individual metal-bearing minerals control the detected trace element distribution across the size fractions. This is supported by the XRD data, which shows that for CMT-ROM1 and RG-WRD-1, the <0.25 mm fraction contains the highest proportion of sulphides (13.7 and 3.8 wt%, respectively), while the proportion of sulphides for CMT-WRD1 is similar between the <0.075 and <0.25 mm fractions (22 wt%).

Abrasion pH and the Influence of Mineral Dissolution Kinetics

Rinse, paste, and NAG pH tests are commonly conducted on sulfidic wastes and ores and are part of static testing procedures. Rinse and paste pH measurements provide information on the current state of net acidity, whereas NAG pH analyses provide a preliminary evaluation of future acid generation potential. Weathered sulfidic rock materials are known to have acidic rinse and paste pH values because of the partial or complete oxidation of acid-generating sulphides and the presence of soluble, acid-generating metal sulphates (Lottermoser 2010). However, unweathered sulfidic materials can have a neutral paste and rinse pH, but a significant acid-generating potential. The modified abrasion pH data presented for sulphides was higher by 1–2 pH units than that of sulphide minerals when treated with hydrogen peroxide (e.g. NAG pH). The unexpectedly high pH of sulphide mineral samples such as sphalerite and arsenopyrite II are likely due the presence of minor amounts of calcite (Table 3). However, other sulphides such as pyrrhotite (95.6 wt% purity), gave a modified abrasion pH of 7.38. The acid-forming mineral jarosite also yielded a higher pH value than expected (6.28 ± 0.01; Table 1). Jennings et al. (2000) observed a pH value of 4.12 when jarosite was subjected to oxidation by H_2O_2, and a paste pH value of <2.5 was reported for jarosite-rich tailings by Hammarstrom et al. (2005). Overall, these data highlight that neutral pH values can arise from sulphide minerals at various stages of weathering, such as pyrrhotite (6.70 ± 0.02) or galena (7.38 ± 0.02), with the latter generating much less acidity than pyrite (cf. Plumlee 1999).

Application of Rinse and Paste pH Testing to ARD Prediction

At mine sites, the release of soluble salts from sulfidic rock depends on their degree of weathering, which in turn affects the EC of the solution. Since higher ionic strength solutions favour more stable pH readings (cf. Sumner 1994), the degree of sulphide oxidation can influence the accuracy of rinse and paste pH measurements made in DI water. The influence of weathering on the measured pH of sulfidic samples can be explored using Sobek et al. (1978) rinse and paste pH tests (Table 1). Although these two test protocols differ in their solid:solution ratio and particle size, the pH values for the weathered sulfidic samples were extremely similar (within 0.01 and 0.18 pH units) between test methods for both CMT-WRD1 and RG-WRD1, respectively. By contrast, analysis of the unweathered sample CMT-ROM1 gave a difference of 0.67 pH units between these two tests. This demonstrates that unweathered rock samples are more sensitive to pH test protocol specifications due to their inherently lower EC. However, considering that assessment of environmental risk relative to mining operations commonly concerns unweathered sulfidic materials, more reliable pH assessments can be made using weak electrolyte solutions (e.g. 0.01 M $CaCl_2$). Of the nine pH protocols investigated, the ASTM D4972-01 (2007) (0.01 M $CaCl_2$) method is the favoured pH test method for unweathered sulfidic rocks because pH readings are more stable in high-ionic strength solutions, leading to more rapid, precise, and reproducible results.

NAG pH measurements of the unweathered CMT-ROM1 sample revealed a median NAG pH value of 2.9, while the nine different pH test protocols produced a much higher median pH value of 6.71 ± 0.70 (interquartile range between tests). Clearly, the latter pH value does not reflect the sample's ability to produce acid in the long term, but rather its first flush characteristics. NAG pH measurements of the weathered sulfidic waste rocks revealed a value of 2.2 for both samples (CMT-WRD1, RG-WRD1). Similarly acidic pH values were also found by the nine different pH test protocols, with median pH values of 3.91 (±0.77) and 3.55 (±0.76), respectively. Combining rinse and paste pH data obtained on unweathered sulfidic rocks with parameters such as total S (wt%), metal and metalloid concentrations (e.g. Parbhakar-Fox et al. 2011), or NAG pH (e.g. Weber et al. 2006), can provide a more reliable ARD risk assessment.

This study highlights that the selection of a rinse and paste pH method can affect ARD risk classification, for example, when using a NAG pH-paste pH classification scheme. In particular, the paste pH method of Smart et al. (2002) and the 1:5 method of Rayment and Lyons (2010) shift the ARD classification from high to medium ARD risk (Fig. 4).

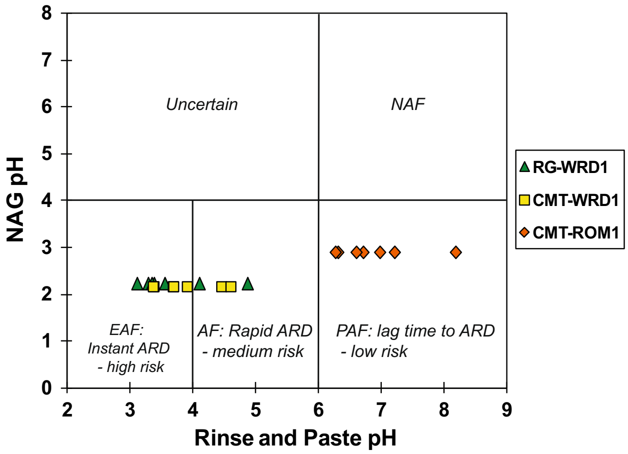

Fig. 4 Classification scheme for bulk sulfidic samples according to rinse and paste pH and NAG pH. Data for rinse and paste pH are plotted by sample type, and include pH measurements from methods that used DI water and 0.01 M $CaCl_2$, but exclude the pH results of tests using 1 M KCl. The samples are classified as extremely acid forming (EAF), acid forming (AF), potentially acid forming (PAF), non-acid forming (NAF), or uncertain

Furthermore, ARD risk assessment based on total metal and metalloid concentrations (Supplemental Figure 1), shows that the level of ARD risk can vary from low to high risk according to the methodology chosen for rinse and paste pH tests. Therefore, ARD risk assessments need to consider the biases in the various pH test methodologies, as observed in this paper, and carefully select and conduct pH analyses.

Example of pH Biases in ARD Risk Classification: Croydon Waste Rocks

The effect of grain size on rinse and paste pH values was determined by carrying out two pH tests (ISO 10390:2005(E) and ASTM D4972-01(2007)(E)), using two grain size fractions of the Croydon waste rock samples (<0.075 and <2 mm; Supplemental Table 2). Despite the methodological differences between these two pH tests (e.g. equilibration time, solid:solution ratio, shaking) the pH values observed were similar for a given grain size fraction (Supplemental Figure 2). Overall, the data suggest that it is grain size and not methodology that controls the rinse and paste pH. We observed more alkaline pH values in the <0.075 mm fraction than in the <2 mm fraction for 80 % of the waste samples analysed. Parbhakar-Fox et al. (2014) also observed an increase in pH with decreasing grain size when performing paste pH measurements on different grain size fractions (<0.075, <5, and <20 mm) of Croydon waste rock samples, using the pH test protocol of Smart et al. (2002). The relationship between pH and grain size is controlled by the mineralogy and abundance of exposed acid-producing or neutralising surfaces, with previous studies recording both increases in pH with decreasing grain size (Shaw et al. 2000), and decreasing pH with decreasing grain size (Lapakko et al. 2006). The rinse pH of the Croydon waste rock may be influenced by silicate mineral dissolution (e.g. muscovite, chlorite), releasing alkalinity and consuming H^+ ions (cf. Bowell et al. 2000). Therefore, as particle size decreased, the surface area available for neutralising reactions increased, resulting in the observed pH-grain size relationship.

The sulfidic waste rock samples from Croydon were studied in detail to characterise the waste rocks into groups based on their mineralogical, textural, and chemical similarities (Parbhakar-Fox et al. 2011). In the classification of these mine waste materials, as presented in Parbhakar-Fox et al. (2014), a cut-off criterion paste pH value of <5.5 was used for potentially acid-forming (PAF) materials. Incorporation of the grain size results presented here, into the ARD classification criteria used by Parbhakar-Fox et al. (2014), showed that a third of the samples ($n = 35$) would have a different classification (NAF vs PAF) based on grain sizes of <0.075 and <2 mm (Supplemental Figure 2). These results demonstrate that grain size is a strong determinant of pH, and can change ARD classification schemes for some samples. However, when it comes to using a different extraction solution, the use of 0.01 M $CaCl_2$ solution compared to distilled water (e.g. paste pH of Smart et al. 2002) had no effect on the classification of samples as NAF versus PAF (Supplemental Figure 2). Consequently, ARD risk assessments should document the details of the water-based testing methods. We recommend using 0.01 M $CaCl_2$ as the extraction solution, and a high solid to solution ratio to mitigate some of the methodological variability of paste pH for the assessment of sulfidic materials. Ideally, pH test work should be pursued on a range of size fractions.

Conclusions

Rinse and paste pH tests are used to assess the environmental risks associated with mining and mineral processing of sulfidic rock materials. This study compared the use of nine different rinse, paste, and soil pH test protocols on three sulfidic rock materials and the international reference material KZK-1. The measured pH values showed significant variability according to the methodology. The most important factors that influenced the measured pH values were: (1) type of extracting solution (DI water, $CaCl_2$, KCl); (2) ionic conductivity; and (3) grain size. The use of DI water as the sole extracting solution results in pH values that are strongly dependent on methodology. This study recommends the use of pH testing methods such as ASTM D4972-01(2007) ($CaCl_2$), which generates a relatively high ionic strength solution, that in turn leads to more rapid measurements and analytical data that are less sensitive to and influenced by methodological factors (e.g. solid:solution ratio). Furthermore, unweathered sulfidic rock materials typically have low EC values of $<1000\ \mu S\ cm^{-1}$, and hence a 0.01 M $CaCl_2$ test solution for such materials leads to ionic conditions that are similar to those of the buffer solutions used to calibrate the pH electrode, and overall provide more rapid, reproducible, and precise analyses.

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