Evaluation of Tests for Predicting Mine Waste Drainage pH

Draft Report to the Western Governor's Association

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SEPARATE VOLUME

1. INTRODUCTION

Tailings, waste rock, and spent heap and dump leach materials, as well as the mine wall rock itself, are wastes which remain after mine abandonment. Some mining wastes are relatively stable chemically and, therefore, environmentally innocuous with respect to release of acid and trace metals. On the other end of the spectrum are wastes at mine sites classified as U. S. Environmental Protection Agency (EPA) Superfund Sites. Some of these sites were abandoned in the 1800's and have generated problematic drainage for roughly a century. Remediation costs for individual sites can range from roughly ten million to over one hundred million dollars (Biggs, 1989).

Metallic mineral mining regulations have been, or are being, written to reduce the potential adverse impact of mine drainages on surface and ground waters. Plans for closure and post-closure care of mine wastes are an important aspect of these rules and must be submitted prior to mine development. In order to design such plans prior to mine development, projected mine wastes must be evaluated for their potential to release acid, trace metals, and other contaminants. Mine waste disposal unit siting, construction, and mitigation design can then be tailored to the potential of the mine waste drainage for adversely impacting the environment.

Existing data on drainage quality from a mine waste of a similar composition, generated by similar mining methods, and exposed to similar environmental conditions for an extended time provide the best indicator of drainage quality. Since these data are rarely available, it is necessary to conduct tests to predict mine waste drainage quality. Several tests have been developed for this purpose. These tests have been applied in coal mining and, to a lesser extent, in metallic mining.

However, little information is available on the comparison of various test predictions, or on the correlation between predictions and actual drainage quality under field conditions. Studies which have been conducted include limited information on the composition of mine wastes examined. To better understand the implications of commonly applied predictive tests, a suite of well-characterized mine waste samples was subjected to a variety of predictive tests. The test results were then compared to each other and to existing field drainage quality data.

2. OBJECTIVES

The objectives of this study are as follows.

1. Enumerate contacts within the WGA states with information on observed relationships between waste composition and water quality.
2. Summarize existing information on the chemistry of mine waste dissolution and its influence on water quality.
3. Enumerate and describe testing methods used for mine waste drainage quality prediction.

4.   Compare various predictive tests to each other and to observed field results by applying tests to well-characterized wastes for which a long-term drainage quality record exists.

The first objective was addressed by the preparation of a directory of contacts within the WGA states (Wessels et al., 1991). The second and third objectives were met by publication of a literature review on the prediction of mine waste drainage pH (Lapakko, 1991). The present report describes the work done to address the fourth objective.

3. BACKGROUND CHEMISTRY

To accurately determine the capacity for acid production it is necessary to measure those and only those components which produce acid. Acid is produced as a result of the oxidation of iron sulfide minerals present in mine waste, as indicated by reaction 1 (Nelson, 1978) and reaction 2 (Stumm and Morgan, 1980). Two moles of acid are produced for each

$$FeS(s) + (3/2)H_2O + (9/4)O_2(g) = FeOOH(s) + 2H^+(aq) + SO_4^{2-}(aq) \qquad [1]$$
$$FeS_2(s) + (5/2)H_2O + (15/4)O_2(g)$$
$$= FeOOH(s) + 4H^+(aq) + 2SO_4^{2-}(aq) \qquad [2]$$
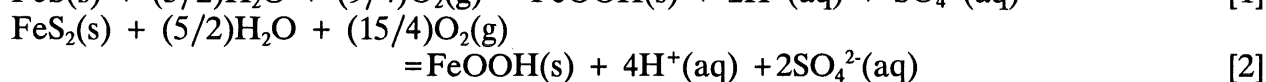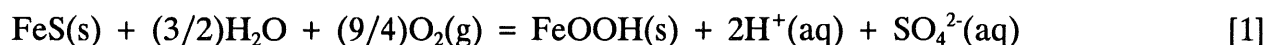
mole of sulfur oxidized. Dissolution of sulfate minerals such as melanterite and jarosite will also produce acid (reactions 3 and 4, respectively). As was the case for the sulfide minerals,

$$FeSO_4 \cdot 7H_2O(s) + (1/4)O_2(g) = FeOOH(s) + SO_4^{2-}(aq) + 2H^+(aq) + (11/2)H_2O \qquad [3]$$

$$KFe_3(SO_4)_2(OH)_6(s) = K^+(aq) + 3FeOOH(s) + 2SO_4^{2-}(aq) + 3H^+(aq) \qquad [4]$$
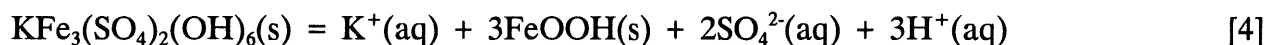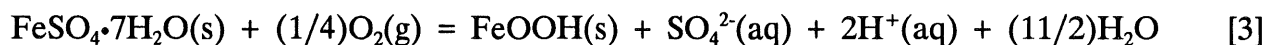
the dissolution of melanterite yields two moles of acid per mole of sulfate dissolved. In contrast, the dissolution of jarosite yields 1.5 moles of acid per mole of sulfate dissolved. The dissolution of sulfate minerals such as anhydrite (reaction 5) or barite ($BaSO_4$) will not produce acid.

$$CaSO_4(s) = Ca^{2+}(aq) + SO_4^{2-}(aq) \qquad [5]$$

The most effective minerals for consuming (neutralizing, buffering) acid are calcium carbonate and magnesium carbonate (reactions 6-9). Reactions 6 and 8 are dominant above

$$CaCO_3(s) + H^+(aq) = HCO_3^-(aq) + Ca^{2+}(aq) \qquad [6]$$

$$CaCO_3(s) + 2H^+(aq) = H_2CO_3(aq) + Ca^{2+}(aq) \qquad [7]$$

$$MgCO_3(s) + H^+(aq) = HCO_3^-(aq) + Mg^{2+}(aq) \qquad [8]$$

$$MgCO_3(s) + 2H^+(aq) = H_2CO_3(aq) + Mg^{2+}(aq) \hspace{4cm} [9]$$
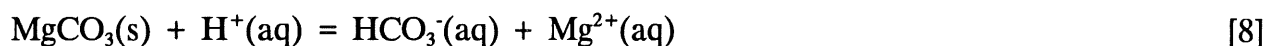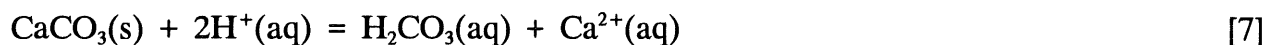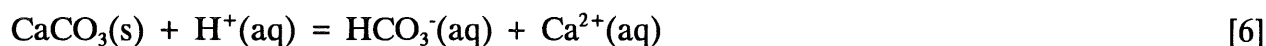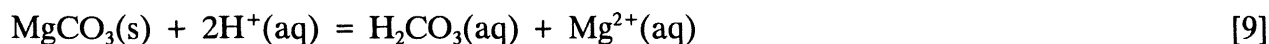
approximately pH 6.3, while reactions 7 and 8 are dominant below this pH. Other minerals, such as anorthite and forsterite, can also consume acid but their dissolution rate (and associated rate of acid consumption) is typically slow in the neutral pH range (reactions 10, Stumm and Morgan, 1981; 11). These minerals dissolve more rapidly as pH decreases and, therefore provide more buffering under acidic conditions.

$$CaAl_2Si_2O_8(s) + 2H^+(aq) + H_2O = Ca^{2+}(aq) + Al_2Si_2O_5(OH)_4(s) \hspace{1.5cm} [10]$$

$$Mg_2SiO_4(s) + 4H^+(aq) = 2Mg^{2+}(aq) + H_4SiO_4(aq) \hspace{3cm} [11]$$
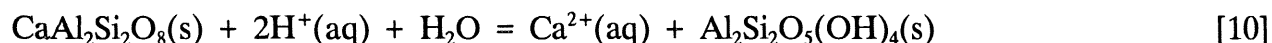
Iron carbonates will provide no net consumption of acid. The initial dissolution of one mole of iron carbonate will consume one or two moles of acid (reactions 12, 13). However, under environmental conditions the one mole of ferrous iron released will oxidize to ferric iron (reaction 14) which will precipitate as ferric oxyhydroxide (reactions 15). The oxidation of ferrous iron is slower than the subsequent ferric oxyhydroxide precipitation, and is reported to be second-order with respect to OH$^-$ concentration (Sung and Morgan, 1980, Eary and Schramke, 1990). The oxidation and precipitation reaction will yield two moles of acid (reaction 16). Thus, iron carbonate will not contribute to acid consumption.

$$FeCO_3(s) + H^+(aq) = HCO_3^-(aq) + Fe^{2+}(aq) \hspace{3.5cm} [12]$$

$$FeCO_3(s) + 2H^+(aq) = H_2CO_3(aq) + Fe^{2+}(aq) \hspace{3.5cm} [13]$$

$$Fe^{2+}(aq) + (1/4)O_2(g) + H^+(aq) = Fe^{3+}(aq) + (1/2)H_2O \hspace{2.5cm} [14]$$

$$Fe^{3+}(aq) + 2H_2O = FeOOH(s) + 3H^+(aq) \hspace{4cm} [15]$$

$$Fe^{2+}(aq) + (1/4)O_2(g) + (3/2)H_2O = FeOOH(s) + 2H^+(aq) \hspace{2.5cm} [16]$$
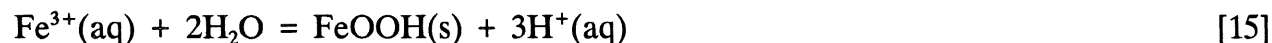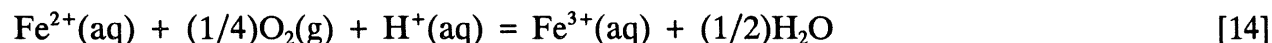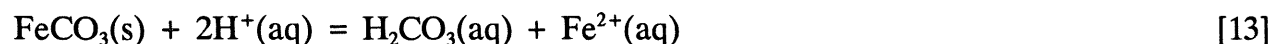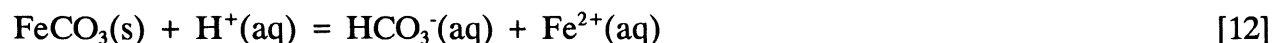
4. METHODS

4.1. Mine Waste Samples

4.1.1. Sample Procurement

A request for participation was sent to the WGA member states. This request solicited

1) a list of contacts with information on observed relationships between mine waste composition and drainage quality within the respective states, and
2) representative samples of mine waste for which drainage quality data were available.

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WGA members provided names of contacts through which mine waste samples could be sought. From July through November 1990, mining companies were contacted by telephone, and those which indicated a potential for participation were sent a written request for samples.

This written request identified the following desireable attributes of mine waste samples for the study. First, samples with field drainage quality data were preferred. Second, samples with a marginal potential for acid production were desireable. (To use only samples with high sulfur to carbonate ratios would be of limited value since all tests would probably predict acid drainage. Similarly, samples with very low sulfur to carbonate ratios would be of limited value since all tests would probably predict alkaline drainage.) Thirdly, a variation in mineralogy and petrology among the samples was viewed as beneficial. In response to these requests 16 tailing samples and 20 rock samples were sent to the Minnesota Department of Natural Resources (MN DNR).

4.1.2. Sample Screening

Of the 36 samples, 16 were of limited value due to lack of field data, similarity with other samples, reportedly extreme sulfur to carbonate ratios, and/or excessive oxidation (appendix 1). The remaining 20 samples, 12 tailings and 8 rock samples, were sent to Lerch Brothers, Inc. where they were analyzed for sulfur, sulfate, and carbon dioxide. These values were used to estimate the Acid Production Potential and Neutralization Potential. Based on these values, 10 samples which exhibited a range of sulfur and carbonate contents were selected for submittal to tests for prediction of mine waste drainage pH (table 1).

The samples distributed for predictive testing were relatively fresh, that is, they were not highly oxidized due to environmental exposure. Samples RK1 and RK4 had been exposed to the environment for less than two months. Sample RK3 had been in a rock pile for two to three years, and RK2 had been stockpiled for about 15 years. However, the rock particles collected were fairly large and were crushed prior to distribution. Consequently, most of the rock surface was relatively fresh.

The ages of tailings TL1, TL4, and TL5 are unknown, but their appearance and chemistry suggests they have not been extensively weathered. Sample TL3 had been in the tailings basin less than two months while for TL6 this period was between zero and two years. Sample TL2 may have been in the basin for up to ten years. However, this sample was collected from a depth of about ten feet and was relatively unoxidized.

Table 1. Samples selected for predictive testing.

SAMPLE	MINE TYPE	HOST ROCK	SULFUR (%S)			CO_2	MOD	NP^3	NET NP^4	FIELD
			TOTAL	AS SO_4	SULFIDE[1]	(%)	APP^2			
RK1	Au	pyritized mudstone	0.46	0.04	0.42	0.11	13	3	-10	NO DATA
RK2	Cu-Ni	troctolite-gabbro	.64	.01	.63	.03	20	0.7	-19	MOD. ACID
RK3	Au	quartz latite	1.63	.03	1.60	1.41	50	32	-18	MOD. ACID
RK4	Au	adularized and pyritized mudstone	2.91	.09	2.82	1.42	88	32	-56	STR. ACID
TL1	Mo	metasomatised aplite/andesite	0.96	0.06	0.90	0.87	28	20	-8	NEUTRAL
TL2	Mo	quartz monzonite w/quartz porphyry	1.49	.04	1.45	.80	45	18	-27	NEUTRAL
TL3	Au	sideroplessite quartz schist (?)	2.19	.07	2.12	4.06	66	92	26	NEUTRAL
TL4	Cu		2.30	.20	2.10	.25	66	6	-60	NEUTRAL
TL5	Au	latite	5.05	.20	4.85	.65	152	15	-137	STR. ACID
TL6	Au	(pyrrhotite) skarn	5.81	.63	5.18	2.01	162	46	-116	NEUTRAL

[1] Determined as difference between total S and SO_4
[2] Acid Producing Potential in tons $CaCO_3$/1000 tons rock = 31.25 x Sulfide
[3] Neutralization Potential in tons $CaCO_3$/1000 tons rock = 22.73 x CO_2
[4] Net NP in tons $CaCO_3$/1000 tons rock = NP - MOD APP

TL: tailing
RK: rock

ls\kl43alt

4.1.3. Sample Preparation and Analysis

The mine waste samples were split into different subsamples by Lerch Brothers (Hibbing, MN). The splitting procedure was tested by analyzing the sulfur and carbon dioxide content of three sample splits, to ensure uniformity of the samples generated. The waste rock samples, as received, were all fairly coarse (appendix 1), and these samples were crushed to obtain a homogeneous sample from which splits could be taken for the various tests. The TL4 sample was crushed to eliminate clumps and the consequent sample inhomogeneity. For the remaining tailings samples, the particle size distributions for tailings were determined on the samples as received.

The various splits were for particle size analysis (Lerch Brothers), chemical analysis (Bondar-Clegg, Ottawa, Ontario), mineralogical analysis (Hanna Research, Nashwauk, MN), as well as predictive tests by B. C. Research (Vancouver, B. C.), of the University of South Carolina (Columbia, SC), Lawrence Consultants Ltd. (Vancouver, B. C.), and the Minnesota Department of Natural Resources (MN DNR).

Samples were analyzed by Bondar-Clegg for sulfur, sulfate, carbon dioxide, silicon, major metal components (Al, Ca, Fe, K, Mg, Mn, Na, P, Ti), trace metals of regulatory interest (Ag, As, Ba, Cd, Cr, Cu, Mo, Ni, Pb, Zn), and a set of miscellaneous trace metals included in the ICP analytical package (Bi, Co, Ga, La, Li, Nb, Sc, Sn, Sr, Ta, Te, V, W, Y, Zr). Sulfur was analyzed by LECO induction furnace and sulfate was analyzed following a sodium carbonate leach. Carbon dioxide was analyzed using a Coolermetrics carbon dioxide analyzer. Silica and the major metal components were extracted using borate fusion and analyzed using DC Plasma. The remaining metals were extracted using a solution of HF, $HClO_4$, HNO_3, and HCl and analyzed by ICP.

Mineralogical analyses were conducted by Louis Mattson of the Hanna Research Center in Nashwauk, MN. X-ray diffraction (XRD) was used for mineral identification as well as for determination of the approximate modal composition. This analysis was applied to the bulk sample and to a heavy mineral concentrate. The heavy mineral concentrate was analyzed to more accurately identify the sulfides and other heavy minerals present. This was necessary since the sulfide content of some samples was quite low.

The chemical analyses were used in conjunction with XRD data to more accurately determine the mineral composition. The formula for dolomite used by Hanna was 30% CaO, 22% MgO, and 48% carbon dioxide, which represents equal molar amounts of calcium carbonate and magnesium carbonate. The corresponding contents for ankerite were 30%, 15%, and 45%, with the remaining 10% composed of iron oxide. The values for dolomite composition are theoretical while those for ankerite are "typical" values. The extent of sulfide and carbonate mineral liberation was determined by wet screening on 100, 270, and 500 mesh sieves, and using optical microscopy to examine the fractions separated. The coarse waste rock fragments were examined macroscopically to qualitatively assess the surface area of sulfide and carbonate minerals available for reaction in the large particles.

4.2. Predictive Test Methods

Based on the literature review the following predictive tests were chosen for examination.

Static tests
>Acid-Base Accounting (Sobek et al., 1978)
>Modified Acid-Base Accounting (Lawrence, 1990)
>B. C. Research Initial Test (Duncan and Bruynesteyn, 1979)
>Net Acid Production Test (Lawrence et al., 1988)

Kinetic tests
>Wet-Dry Cycle Test (Lapakko, 1988)
>Standard Humidity Cell Test (Sobek et al., 1978)
>Modified Humidity Cell Test (Lawrence, 1990, conducted on waste rock samples only)
>Elevated Temperature Test (Renton et al., 1985)
>Soxhlet Extraction Test (Singleton and Lavkulich, 1978)
>Shake Flask Test (a common batch reactor test)

The following presentation identifies the laboratory which conducted the test and summarizes the methods used. Additional detail on testing procedures is available in the publications cited.

4.2.1. Static Tests

Acid-Base Accounting (Sobek et al., 1978) was conducted by Lawrence Consultants Ltd. Total sulfur was analyzed by LECO furnace, and the Acid Production Potential (APP in kg $CaCO_3$/t) was calculated as the product of percent total sulfur and 31.25. To determine Neutralization Potential (NP), samples were crushed to -60 mesh. Approximately 0.5 g of sample was placed on a piece of aluminum foil, and one or two drops of 1:3 hydrochloric acid (HCl) is added to the sample. Based on the extent of "fizzing" in this test, a volume and concentration of HCl were selected and added to 2 g of -60 mesh mine waste in a flask. The mixture of acid and mine waste was then boiled until the reaction ceased, as indicated by the termination of the production of bubbles. Distilled water was added to attain a total volume of 125 mL and the contents of the flask were boiled for one minute, then cooled to room temperature. The mixture was then titrated to pH 7.0 with sodium hydroxide.

Modified Acid-Base Accounting (Lawrence, 1990) was conducted by Lawrence Consultants Ltd., under the direction of Dr. Richard Lawrence. The APP was calculated as the product of 31.25 and the sulfide sulfur content. (Lawrence used the term acid potential, but APP will be used to maintain consistency in the terminology among methods.) Sulfide sulfur was determined by LECO furnace after a non-oxidative digestion of the sample with hydrochloric acid.

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As with the method of Sobek et al. (1978), the fizz test was used to determine the volume and strength of HCl addition to a 2 g sample (-60 mesh). The acid/mine waste mixture was digested for 24 hours at room temperature, at which time pH was measured. If pH was not in the range of 1.5 to 2.0, the digestion was rerun with an acid addition adjusted based on the observed pH. After the pH criterion was met, the acid/mine waste mixture was titrated with NaOH until a pH of 8.3 was maintained for at least 30 seconds.

The **B. C. Research Initial Test (Duncan and Bruynesteyn, 1979)** was conducted by B. C. Research, under the direction of Rik Vos. Although this method uses different terminology and different units of quantification, the terminology and units are translated to be consistent with those of the ABA method for ease of presentation in this report. APP was calculated based on the total sulfur content as analyzed using a Leybold-Heraeus carbon sulfur analyzer. The NP was determined by titrating, with 1.0 N sulfuric acid, a stirred mixture of 10 g mine waste (70 percent minus 325 mesh) and 100 mL distilled water. The titration was continued until pH 3.5 was reached and less than 0.1 mL of acid was added over a period of four hours. As requested by the MN DNR, Neutralization Potentials at pH endpoints of 6.0 and 5.0 were also determined. Type 45 AR Chemtrix pH controllers with Cole Parmer electrodes were used for the titration.

A **modification of the Net Acid Production Test (NAP, Coastech Research Inc., 1989)** was conducted by Lawrence Consulting Ltd., under the direction of Dr. Richard Lawrence. The MN DNR suggested that recent advancements by O'Shay et al. (1990) be considered for the test method. After conducting some preliminary experiments, Lawrence conducted the NAP Test as follows. To a 1.00 g mine waste sample (80% minus 200 mesh) 100 mL of hydrogen peroxide (at least 30% v/v with distilled) was added incrementally (since the reaction of hydrogen peroxide and sulfide can be violent), and the mixture was heated to near boiling for one hour. If the peroxide was depleted after one hour, 50 mL of peroxide was added and heated for 30 minutes. The flask was cooled for 10 to 15 minutes and 1 mL of 0.0157 M copper solution was added and the mixture was boiled for 10 minutes. The solids were removed by filtration and washed with 1 M $CaCl_2$. A sample of the filtrate was then titrated to pH 7.0. Four samples were analyzed for sulfur before and after the NAP test (RK4, TL1, TL3, TL6).

4.2.2. Kinetic Tests

The **Wet-Dry Cycle Test (Lapakko, 1988)** was conducted by the Minnesota Department of Natural Resources (MN DNR) under the direction of Kim Lapakko. Tailing samples were run as received and rock samples were crushed to -100 mesh (appendix 2). ABA analyses (Sobek et al., 1978), using LECO furnace for sulfur analyses, were conducted on all samples before and after the test.

Samples, run in duplicate, were placed into the upper segment, or reactor, of a two-stage filter unit. Prior to the inception of the experiment all samples were rinsed with three

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distilled water volumes of 200 mL, to remove products which accumulated from oxidation during sample storage. To each reactor, 200 mL of distilled water was added and allowed to drain overnight through the mine waste sample. This rinsing was repeated weekly for 20 weeks. Between rinses the solids were retained in the reactors and stored in a box to further oxidize. A thermostatically controlled heating pad was placed beneath the box to to control temperature. The box was stored in a small room equipped with an automatic humidifier and dehumidifier, to maintain a stable range of humidity. Temperature and relative humidity were monitored two to three times a week. The temperature ranged from 23.9 to 30.0°C, with an average of 27.6°C and a standard deviation of 1.4°C (n=54). The relative humidity ranged from 48 to 67%, with an average of 57.7% and a standard deviation of 4.0% (n=52).

Some experimental modifications were necessary for some of the samples, due to accretion of the solids and/or low flow through the solids bed. These problems were apparently due to both particle size and mineralogical factors. During the drying cycle the grains of sample RK1 tended to cement and, consequently, it was necessary to remove the consolidated solid from the reactor and break it up prior to rinsing. Samples RK3 and RK4 accreted to a lesser extent and cracks formed in the solid bed. To enhance uniform flow through the solids, the samples were mixed with a stainless steel spatula in the reactor prior to rinsing. Despite these preparations there were times when all of the rinse water did not pass through the solids, and it was necessary to decant from the top of the bed. The volume decanted from RK3 and RK4 was quite small, around 2% of the total sample volume, while the corresponding value for RK1 was about 15%. Although sample TL4 did not accrete, flow did not readily pass through the bed and about 21% of the total sample volume was contributed by decanting.

The volume of rinse water, or drainage, was determined and pH was analyzed directly in the lower stage of the reactor. Samples were then filtered and analyzed on site for alkalinity, acidity, and specific conductance. Samples were also taken for subsequent analysis of metals and sulfate. Samples taken for metal analyses were acidified with 0.2 mL AR Select nitric acid (Mallinckrodt) per 50 mL sample. An Orion SA 72 pH meter, with a Ross combination pH electrode (8165), was used for pH analysis and a Myron L conductivity meter was used to determine specific conductance. Alkalinity and acidity were analyzed using standard titration techniques (APHA et al., 1989). Sulfate was analyzed using an HF Scientific DRT-100 nephelometer for the barium sulfate turbidimetric method (APHA et al., 1989). Metals were analyzed by X-Ray Assay Laboratory (Don Mills, Ontario) using ICP.

The **Standard Humidity Cell Test** was conducted by the University of South Carolina Environmental Hydrogeology Laboratory, under the direction of Dr. Frank Caruccio. ABA analyses were conducted on all mine waste samples before and after the Humidity Cell Test. The Acid Production Potential was based on the pyritic sulfur content which was determined using the method of Burns (1970), at the suggestion of the contractor.

Sample masses of 210 to 365 grams were placed into plastic weathering cells (18.5 cm diameter, 6 cm height), which were constructed with underdrains for sample collection and to eliminate air-locks in the cell. The samples were all rinsed with 450 mL of deionized water prior to the start of the test. Subsequently, 100 mL of deionized water was added to each cell weekly, stirred, and allowed to sit for 15 to 60 minutes. The standing water was then decanted and the remaining water was allowed to drip from the sample for two to three hours. The volume of drainage was determined, and drainage from the cells was analyzed using procedures outlined in Standard Methods (e.g. APHA et al., 1989) for specific conductance, pH, acidity, alkalinity, iron, and manganese. Humidified air was pumped into the cell continuously over the course of the experiment, and some samples remained wet over the course of this cycle. At the suggestion of the contractor, the cells were inoculated with 1 mL of 9K medium during the seventh week of the study.

The **Modified Humidity Cell Test (Lawrence, 1990)** was conducted on the four waste rock samples in the study by Lawrence Consulting Ltd., under the direction of Dr. Richard Lawrence. Modified Acid-Base Accounting analyses, using LECO furnace for sulfur analyses, were conducted on the samples before and after the kinetic test. A sample mass of 1 kg was added to the humidity cell. A deionized water volume of 1.5 L was added to each cell and after one hour the drainage valve at the bottom of the cell was opened.

Following this initial rinse, dry air was passed up through the sample for three days, humid air for three days, and on the seventh day 500 mL of deionized water was added to the cell. After one hour the drainage valve at the bottom of the cell was opened and the drainage collected was filtered (0.45 micron). Little water passed through samples RK1 and RK3 in the first leach cycle. Due to the limited permeabilty of these samples it was necessary to introduce air above the samples, as well as collect drainage both from the bottom of the sample and by decanting from the top.

After the fourteenth leach cycle each cell was inoculated with 1 mL of 9K medium which was supplied by Dr. Frank Caruccio and prepared according to his instructions. However, microscopic examination indicated that the bacterial presence was not significant. Lawrence (1991) speculated that the effect of the inoculation was probably negligible.

The volume of drainage was determined and drainages were analyzed for pH, conductivity, alkalinity, acidity (free and total), sulfate, calcium, magnesium, iron, arsenic, cadmium, cobalt, copper, nickel, lead, and zinc. Nitric acid was added to samples collected for analysis of metals. Minen Laboratories performed all analyses "using standard procedures" (Lawrence, 1991).

The **Elevated Temperature Test (modified from Renton, 1983; Renton et al., 1985; 1988)** was conducted by the MN DNR under the direction of Kim Lapakko. Tailing samples were run as received and rock samples were crushed to -100 mesh (appendix 5). ABA analyses (Sobek et al., 1978), using a LECO furnace for sulfur analyses, were conducted on all samples before and after the test.

Samples, run in duplicate, were placed into the upper segment, or reactor, of a two-stage filter unit. Prior to the inception of the experiment all samples were rinsed with three distilled water volumes of 200 mL, to remove products which accumulated from oxidation during sample storage. The solids were retained in the reactors and stored in a Thelco Precision Scientific oven in which temperature averaged 100.9°C, with a standard deviation of 3.5°C (n=75). The solids were subsequently rinsed every two weeks for 20 weeks. To each reactor 200 mL of distilled water, heated to 85°C, was added and allowed to drain overnight through the mine waste sample, and this procedure was repeated on the following day.

The volume of drainage and specific conductance were determined for each of the two samples. The two samples were composited, filtered, and analyzed on site for alkalinity, acidity, and specific conductance. Samples were also taken for subsequent analysis of metals and sulfate. Samples taken for metal analyses were acidified with 0.2 mL AR Select nitric acid (Mallinckrodt) per 50 mL sample. An Orion SA 72 pH meter, with a Ross combination pH electrode (8165), was used for pH analysis and a Myron L conductivity meter was used to determine specific conductance. Alkalinity and acidity were analyzed using standard titration techniques (APHA et al., 1989). Sulfate was analyzed using an HF Scientific DRT-100 nephelometer for the barium sulfate turbidimetric method (APHA et al., 1989). Calcium and magnesium were analyzed at the MN DNR Minerals Office in Hibbing using a Perkin Elmer 603 Atomic Absorption Spectrophotometer in the flame mode.

During the drying cycle the grains of sample RK1 tended to cement and, consequently, it was necessary to remove the consolidated solid from the reactor and break it up prior to rinsing. Samples RK3 and RK4 accreted to a lesser extent and cracks formed in the solid bed. To enhance uniform flow through the solids, the samples were mixed with a stainless steel spatula in the reactor prior to rinsing. Despite these preparations there were times when all of the rinse water did not pass through the solids, and it was necessary to decant from the top of the bed. The volume decanted from RK3 and RK4 was less than 3.5% of the total sample volume collected. Although grains of sample TL4 did not cement, the sample had a low permeability. Decanting contributed about 25% of the total sample volume.

The **Soxhlet Extraction Test (Singleton and Lavkulich, 1978)** was conducted by B. C. Research under the direction of Rik Vos. Modification A was used, in which half of the waste sample was submerged. The volume of drainage was determined and the drainage was analyzed for pH, acidity, alkalinity, sulfate, calcium, magnesium, potassium, iron, aluminum, and silicon. pH was analyzed with a Fisher Accumet pH meter (610A) with a Cole Parmer electrode. Acidity, alkalinity, and sulfate (turbidimetric method) were analyzed according to Standard Methods (APHA, 1989). Calcium, magnesium, silicon, and aluminum were analyzed by sequential inductively coupled plasma emission spectroscopy using a Perkin Elmer 40 emission spectrometer. Potassium and iron were analyzed using a Perkin-Elmer Zeeman 5100 atomic absorption spectrophotometer in the flame mode. B. C.

Research Initial Tests, using a Leybold-Heraeus carbon/sulfur analyzer for sulfur analyses, were conducted on all samples before and after the kinetic test.

The **Shake Flask Test (a common batch reactor test)** was conducted by the MN DNR under the direction of Kim Lapakko. Tailings samples were run as received and rock samples were crushed to minus 100 mesh. ABA analyses were conducted on the samples before and after the kinetic test. Each 75 g mass of solids to be used in the experiment was rinsed three times with distilled water to remove reaction products which accumulated during sample storage. Three flasks were run for each solid.

After drying, the 75 g mass of solids and 200 mL of distilled water were placed into a 250-mL erlenmeyer flask. The flask was covered with a perforated plastic cap to prevent loss of water while permitting air to enter the flask. The flasks were placed on an Eberbach model 1481 shaker table which was set at high speed. For weekly analyses of pH and conductivity, the shaker table was shut off for two to three hours to allow settling of the solids. pH was analyzed directly in the flask. About 15 mL of sample was removed for analysis of specific conductance and subsequently returned to the flask. The flask was then capped and the shaker table was turned on. For each mine waste sample a flask was permanently removed from the shaker table after 7, 14, and 21 weeks.

After settling for two to three hours, pH and specific conductance were analyzed and the aqueous fraction was decanted and filtered. The filtrate was analyzed on site for alkalinity and acidity, and samples were taken for subsequent analysis of sulfate, calcium, and magnesium. The flasks were then left uncovered to allow the sample to dry for subsequent weighing and ABA analysis. The analytical methods were the same as those used in the Elevated Temperature Test.

5.   Results and Discussion

5.1. Mine Waste Analysis

The splitting procedure yielded consistent sulfur and carbon dioxide contents for the samples generated, indicating that samples distributed for analysis and predictive testing were of uniform composition (appendix 1). The particle size distributions of the various samples submitted for predictive tests are presented in table 2. The sulfur content of the samples, most of which occurred as sulfide, ranged from 0.46% to 5.81%. Carbon dioxide concentrations, which reflect the carbonate mineral content, ranged from virtually zero to about 4% (table 3). The major components of the rocks, in a general order of decreasing abundance, were silicon, aluminum, iron, potassium, magnesium, and calcium (table 3). Concentrations of series of trace elements, including those of regulatory concern, were also determined (appendix 1).

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Table 2. Particle size distribution of mine waste samples distributed for predictive tests.

Waste Rock Samples

Screen	mesh	RK1	RK2	RK3	RK4
	+6	1.52	8.57	1.55	16.82
-6	+16	31.92	44.83	28.65	53.38
-16	+35	26.32	18.63	31.47	14.33
-35	+61	10.99	7.65	13.46	4.37
-61	+100	7.52	6.69	9.85	3.06
-100	+140	4.96	4.10	4.66	1.71
-140	+200	2.95	3.23	3.24	1.18
-200	+325	5.24	3.83	3.45	1.74
-325		8.58	2.47	3.67	3.41

Tailing Samples

Screen	mesh	TL1	TL2	TL3	TL4	TL5	TL6
	+100	75.49	27.57	0.59	27.10	31.08	22.57
-100	+270	11.69	26.65	31.22	23.16	21.10	31.41
-270	+500	4.14	14.61	29.90	12.08	12.10	18.31
-500		8.68	31.17	38.24	37.66	35.72	27.71

Table 3. Chemical analysis for sulfur, carbon dioxide, and major components in mine waste samples.

Concentrations in PCT

	S_{TOT}	SO_4-S	S^{-2}-S	CO_2	Al_2O_3	CaO	Fe_2O_3	K_2O	MgO	MnO	Na_2O	P_2O_5	SiO_2	TiO_2	LCI	Total
RK-1	0.46	0.04	0.42	0.11	15.20	0.51	6.27	3.24	3.61	0.03	1.19	0.04	60.50	0.73	6.63	97.96
RK-2	.64	.01	.63	.03	17.20	7.79	14.52	0.61	7.90	0.15	2.59	0.23	45.73	1.54	0.15	98.42
RK-3	1.63	.03	1.60	1.41	12.80	0.28	4.59	5.84	0.53	0.71	0.10	0.17	69.30	0.21	4.01	98.54
RK-4	2.91	.09	2.82	1.42	11.10	1.27	5.67	5.46	1.57	0.07	0.06	0.25	66.40	0.55	5.73	98.13
TL-1	0.96	.06	.90	.87	11.30	2.05	2.87	5.98	1.47	0.07	1.35	0.25	69.80	0.52	2.40	98.06
TL-2	1.49	.04	1.45	.80	9.91	1.66	4.17	4.53	1.11	0.08	0.34	0.21	74.98	0.26	2.70	99.96
TL-3	2.19	.07	2.12	4.06	5.28	1.60	21.94	0.95	4.13	0.57	0.19	0.06	56.65	0.24	7.59	99.19
TL-4	2.30	.20	2.10	.25	14.40	0.35	4.12	4.84	0.67	0.04	0.29	0.11	68.80	0.35	4.24	98.21
TL-5	5.05	.20	4.85	.65	13.60	0.33	7.35	6.70	0.78	0.01	1.84	<0.01	62.40	0.29	5.09	98.40
TL-6	5.81	.63	5.18	2.01	4.59	14.90	22.30	1.31	4.92	0.27	0.27	0.21	47.60	0.30	2.63	99.30

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The predominant sulfur-bearing minerals in the samples were pyrite and pyrrhotite, and marcasite was detected in four samples (table 4A). Lesser amounts of trace metal sulfides were detected in all samples. The most frequently encountered carbonate minerals were calcite, dolomite, and siderite (table 4B). Ankerite, magnesite, and possibly rhodochrosite were each detected in one sample. Quartz, feldspar, and mica were the major rock-forming minerals (table 4C).

Visual inspection of the waste rock samples for assessing the availability of sulfide and carbonate mineral surfaces indicated that RK1 was partially oxidized. Most of the sulfides occurred on fracture surfaces and would, therefore, be readily available for oxidation even in relatively large rock particles. The sulfide minerals in RK2 were reported as "fine grained and occur included in or interstitial to relatively coarse grained rock forming minerals." The sulfide minerals on the surface of larger rock particles would be available for oxidation, but those within the rock matrix would oxidize very slowly.

RK3 was reported to be "generally friable", that is the rock is amenable to physical breakdown. The occurrence of both coarse and fine grained sulfide minerals was both disseminated and in veinlets. The physical breakdown of this rock would leave the sulfide minerals available for oxidation. Both the sulfide and carbonate minerals in RK4 occurred with quartz in veinlets. However, the sulfide veinlets were "relatively open and porous" as opposed to the "tight" veinlets containing carbonate minerals. This suggests that in larger rock particles, the sulfide minerals would be accessible to air and water, and therefore available for oxidation. In contrast, the tight structure of the carbonate veinlets would limit the reactivity of the carbonate minerals present in larger rock particles. The sulfide and carbonate minerals in the tailings were all well liberated due to the small particle size.

5.2. Static Tests

5.2.1. Introduction

Several static tests have been developed to quickly and inexpensively estimate if a mine waste will produce acidic drainage. In the present study, 10 mine waste samples were subjected to the following static tests:

> Acid-Base Accounting Test (ABA, Sobek et al., 1978)
> Modified Acid-Base Accounting Test (Lawrence, 1990)
> B. C. Research Initial Test (Duncan and Bruynesteyn, 1979)
> Net Acid Production Test (NAP, Lawrence et al., 1988).

The objective of the first three tests is to determine the maximum potentials for acid production (Acid Production Potential, APP) and acid neutralization (Neutralization Potential, NP). Whether or not a mine waste will produce acidic drainage is determined by the difference (Net NP) or ratio of these values (NP/APP). The NAP Test uses

Table 4A. Sulfur-bearing mineral content in weight percent (analysis by Hanna Research).

Regulatory Element-Bearing Minerals		RK-1	RK-2	RK-3	RK-4	TL-1	TL-2	TL-3	TL-4	TL-5	TL-6
Pyrite	S	0.74	-	2.43	5.16	1.58	2.60	1.08	3.68	8.17	1.93
Marcasite	S	0.02	-	-	0.16	-	0.08	-	-	0.95	-
Pyrrhotite	S	0.03	0.64	-	-	-	-	4.30	-	-	10.92
Pentlandite	Ni,S	-	0.18	-	-	-	-	-	-	-	-
Mackinawite	Ni,S	-	<0.0	-	-	-	-	-	-	-	-
Arsenopyrite	As,S	?	1	0.01	0.02?	-	0.01?	0.05	<0.01?	-	0.08?
Maucherite	Ni,As,A	-	-	-	-	-	-	-	-	-	-
Tennantite	g	0.02?	0.01	-	?	-	-	-	-	0.02	-
Proustite	Cu,As,S	-	-	-	-	-	-	-	0.07	-	<0.01
Chalcopyrite	Ag,As,S	?	-	0.04	<0.0	0.04	0.02	0.02	?	0.02	?
Cubanite	Cu,S	-	0.27	-	1	-	-	-	?	-	0.23
Bornite	Cu,S	-	0.67	-	-	-	-	-	0.13	<0.0	-
Chalcocite	Cu,S	?	0.04	-	-	?	0.03	-	-	1	-
Covellite	Cu,S	?	-	-	0.01	?	-	-	-	-	-
Stibnite	Cu,S	?	-	-	<0.0	-	-	-	-	<0.0	0.18
Tetrahedrite	Sb,S	<0.01	-	<0.0	1	-	-	?	<0.01	1	-
Molybdenite	Cu,Sb,S	?	-	1	0.01	0.06	0.02	-	-	-	-
Ferrimolybdite	Mo,S	-	-	<0.0	?	?	-	-	0.02	-	<0.01
Galena	Mo	-	-	1	-	<0.0	<0.0	<0.0	0.04	<0.0	-
Sphalerite	Pb,S	<0.01	-	-	-	1	1	1	-	1	0.02
Acanthite	Zn,Cd,S	?	-	0.25	<0.0	0.01	0.04	0.01	-	-	0.03
Gypsum	Ag,S	0.02	-	0.79	1	-	-	-	-	0.01	-
Anhydrite	SO_4	-	-	<0.0	0.02	0.4	-	0.3	-	0.02	-
Barite	SO_4	-	-	1	-	-	-	0.1	?	-	-
Jarosite	Ba,SO_4	-	-	-	0.5	-	0.4	-	?	-	-
Melanterite	SO_4	?	-	-	-	?	-	-	-	-	-
	SO_4	0.1?	0.1?	0.3	?	-	-	-		0.1	5.4?
		0.2		-	-					-	
				-	0.2?					0.2?	

"?" indicates the mineral was possibly present but not positively identified by XRD.

Table 4B. Carbonate mineral content in weight percent (analysis by Hanna Research).

Carbonate Minerals	RK-1	RK-2	RK-3	RK-4	TL-1	TL-2[1]	TL-3	TL-4	TL-5	TL-6
Calcite	?	0.1	0.5	-	1.5	0.7	0.2	0.6	-	4.6
Dolomite	?	-	-	3.0	0.4	0.8	-	-	1.10	-
Ankerite	-	-	-	-	-	-	1.9	-	-	-
Siderite	0.3	-	3.2	-	-	0.2	8.3	-	-	-
Rhodochrosite	-	-	?	-	<0.1	-	-	-	-	-
Magnesite	-	-	-	-	-	-	-	-	0.23	-

[1] Trace amounts of copper carbonates were noted in TL-2.
"?" indicates the mineral was probably present but not positively identified by XRD.

Table 4C. Rock forming mineral content in weight percent (analysis by Hanna Research)[1].

	RK-1	RK-2	RK-3	RK-4	TL-1	TL-2	TL-3	TL-4	TL-5	TL-6
Quartz	24	-	41	34	38	53	42	45	21	12
Feldspar	24	54	29	29	39	30	12	13	52	5
Mica	6	4	12	4	14	10	10	30	10	2
Chlorite	14	2	2	2	1	-	14	-	-	-
Amphibole	-	4	-	-	-	-	3	-	-	3
Pyroxene	-	18	-	-	-	-	-	-	-	55
Olivine	-	11	-	-	-	-	-	-	-	-
Stilpnomelane	-	-	-	-	-	-	2	-	-	-
Serpentine	-	<1	-	-	-	-	-	-	-	-
Kaolinite	2	-	8?	2	-	-	-	6	6?	-
Clay (15 angstroms)	29	-	-	19	-	-	-	-	-	-
Iron Oxides/ Ilmenite	<1	4	?	1	2	2	-	1	1	-

[1] Samples may also contain accessory to trace amounts of one or more of the following minerals: rutile, sphene, garnet, epidote, graphite, tourmaline, scheelite, topaz, apatite, fluorite.

hydrogen peroxide to accelerate the oxidation of sulfide minerals present in the mine waste, and the acid generated then reacts with other host rock minerals. The acid production and acid consumption reactions are assumed to be complete, and the resultant solution acid condition represents the difference between acid production and acid consumption. The value determined is therefore analogous to the Net NP.

These tests are, of course, simplifications of mine waste dissolution under environmental conditions. They assumes complete reaction of acid producing and acid consuming components, and equal rates of acid production and consumption. The extent of reaction of either acid-producing or acid-consuming components may be less than the total capacity. The dissolution of a given mineral may be limited if it is "shielded" within the rock matrix, for example occuring as an inclusion within another mineral. Mineral dissolution may also be inhibited if exposed mineral surfaces become coated with products of other reactions. For example, the formation of iron oxyhydroxide and/or calcium sulfate coatings on limestone, with a consequent inhibition of limestone dissolution, has been reported. Iron oxyhydroxide coatings may also form on the surface of sulfide minerals, with a resultant retardation of their oxidation.

Secondly, evaluation of static tests by the difference between the potentials for neutralization and acid production, assumes that the rate of acid neutralization will equal the rate of acid production. If the rate of acid production exceeds the rate of acid consumption, the resultant drainage will be acidic. This occurrence has been reported for laboratory dissolution tests in which the limestone particles were larger than the sulfide particles (Lapakko and Antonson, 1991). If the dissolution of neutralizing minerals exceeds that of acid producing minerals, some of the NP will be depleted without neutralizing acid produced by iron sulfide oxidation. Indeed, in any neutral to basic drainage some excess alkalinity will be released.

Assumptions regarding the extent of reaction and relative rates of acid production and acid consumption are presently necessary for static tests. Information on the extent and relative rates of reaction is limited, and static tests cannot be evaluated without assigning a value to these variables. Recognizing that such assumptions are necessary, the following discussion addresses the agreement among and accuracy of Acid Production Potential (APP) and Neutralization Potential (NP) measurements determined by the first three tests. The Net NP determined by all four tests are compared among themselves and to available drainage quality data.

5.2.2. Accuracy of Acid Production Potential Measurements

The Acid-Base Accounting and B. C. Research Initial Tests base the APP on the total sulfur content of the sample while the Modified ABA bases the APP on the sulfide-sulfur content of the sample. Since most of the sulfur in the mine waste samples examined was present as sulfide, the APP values determined for the ten samples were in fairly close agreement

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(figure 1). With the exception of sample TL6, the APP values for a given sample were within 4 to 9.7 kg $CaCO_3$/t of the mean of the three values. The values determined for sample TL6 were more disparate since the sulfide-sulfur content of this samples was less than the total sulfur content. That is, a substantial amount of the sulfur present in this sample occurred as sulfate (table 3). As a result, the APP determined by the Modified ABA technique was lower than the values determined by the other two techniques.

The Modified ABA assumes that only sulfide-sulfur contributes to acid production, while the other two methods assume all sulfur present in the samples contributes to acid production. In the case of TL6 the sulfate-sulfur is apparently present as melanterite ($FeSO_4 \cdot H_2O$, table 4A). Since the dissolution of one mole of melanterite will yield two moles of acid, the Modified ABA method underestimates the actual Acid Production Potential of sample TL6. The Modified ABA method is clearly more accurate than the ABA and B. C. Initial Test if sulfate is present in minerals such as gypsum ($CaSO_4 \cdot 2H_2O$) and/or barite ($BaSO_4$), the dissolution of which does not produce acid.

The methods of sulfur analysis must be considered in quantifying the sulfur species present. For example, one contractor used pyritic sulfur to determine APP, and this underestimated the APP of mine wastes containing significant amounts of pyrrhotite. The pyritic sulfur content was close to the sulfide sulfur content for six of the samples, but was considerable lower in samples RK2, RK3, TL3, and TL6. The difference in values was due to elevated pyrrhotite in samples RK2, TL3, and TL6, and due to the presence of galena and sphalerite in sample RK3. Since pyrrhotite will oxidize and produce acid, the APP of the first three samples was underestimated by about 10 to 130 kg $CaCO_3$/t. The pyritic sulfur APP for sample RK3 may be slightly more accurate than the sulfide-sulfur APP, since galena and sphalerite will not produce much acid upon dissolution. Certain aspects of sulfur analysis are presented by Mirza et al. (1992).

In summary, the accuracy of a given method of determining the Acid Production Potential (APP) of a given mine waste is dependent on the sulfur species present in the mine waste. Consequently, the sulfur speciation for a given mine waste will determine the simplest technique for accurately quantifying the APP. All methods assume that the trace metal sulfide content of the mine waste is negligible. In the most complex case sulfur may be present as iron sulfides (e.g., pyrite), acid producing sulfate minerals (e.g., jarosite), and non-acid producing sulfide minerals (e.g., anhydrite). In such a case, analyses for all sulfur species would be necessary to accurately assess the APP. Although none of the three aforementioned methods involve such detailed speciation, the method of Reclamation Research Unit and Schafer and Associates (1987) does analyze for iron sulfides, acid producing sulfate minerals such as jarosite, and non-acid producing sulfate minerals. It is unclear whether this method would accurately assess the acid contribution of melanterite.

If iron sulfide and non-acid producing sulfate minerals are the only sulfur-bearing minerals present, the Modified ABA adequately quantifies APP. If all sulfur is present as iron sulfides, the ABA technique will accurately quantify the APP. For other mine wastes it will
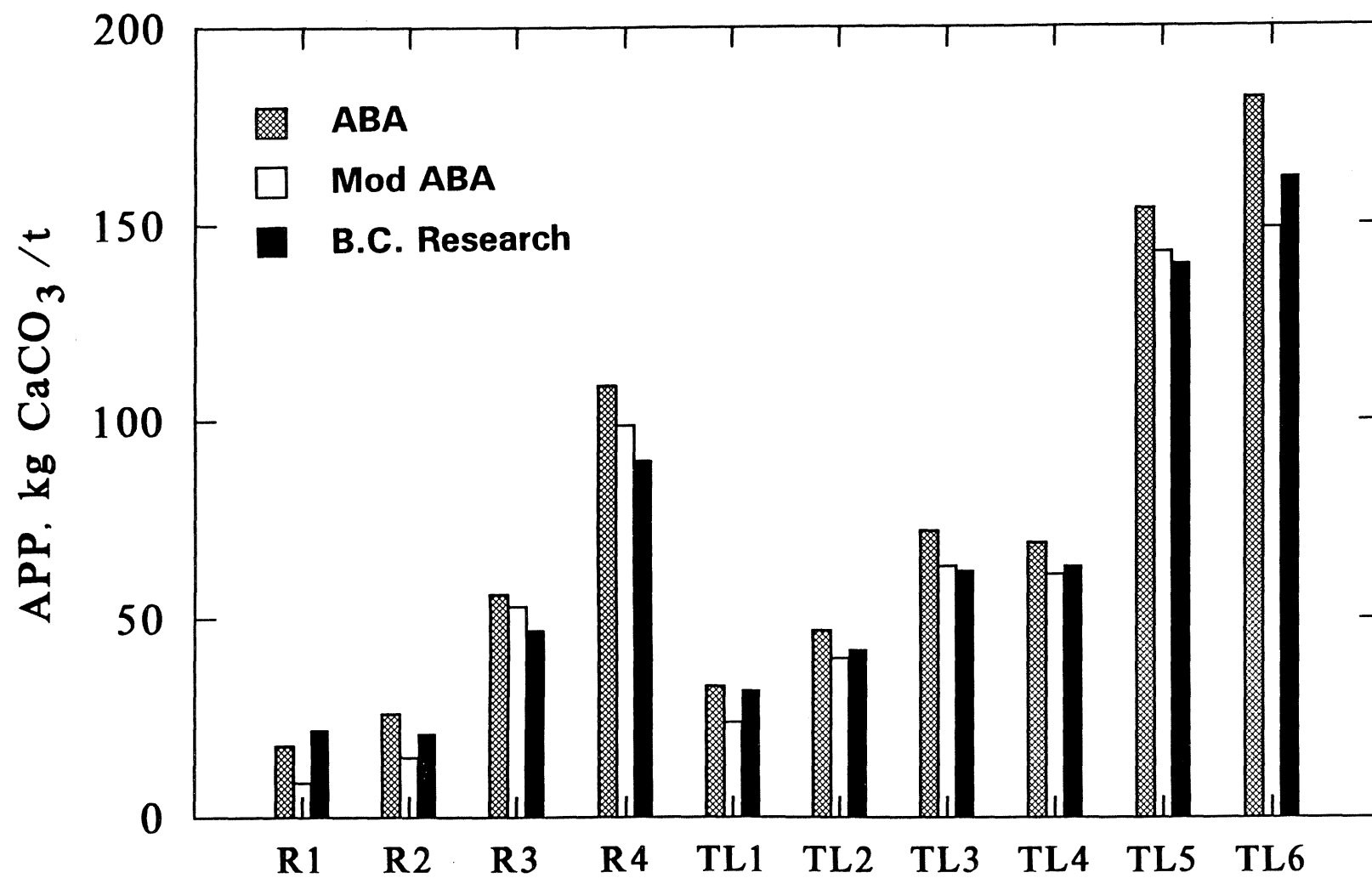
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Figure 1. Acid Production Potential using three methods.

provide the maximum possible value for acid production. The use of the pyritic sulfur content to determine APP will underestimate the actual APP of mine wastes containing pyrrhotite.

5.2.3. Neutralization Potential Agreement and Accuracy

For all samples except TL3 and TL6, there was good agreement between NP values determined by the ABA and the Modified ABA methods. These were also in agreement with the B. C. Research Initial Test NP for samples RK1, RK4, TL1, and TL2. Of the six remaining samples, the B. C. Research Initial Test yielded the highest NP for four samples (RK3, TL3, TL4, TL5) and the ABA NP was highest for two samples (RK2 and TL6). For samples RK3, TL4, and TL5 the the B. C. Research Initial Test values were roughly 10 to 15 kg $CaCO_3$/t higher than the ABA and Modified ABA values. The variation among the three methods was greatest for samples RK2, TL3, and TL6, with no consistent trend in the relative magnitudes of the three values (figure 2).

Assessment of the accuracy of NP values is complicated by the fact that acid consumption is a function of solution pH. Calcium carbonate will dissolve and neutralize acid not only at low pH, but also when solution pH is above 6.0. For other minerals this dissolution and neutralization will be significant only at lower pH values. Since the ABA, Modified ABA, and B. C. Research Initial Tests all subject mine waste samples to solutions with pH in the range of about 1 to 3.5, they measure contributions to NP which occur below pH 6.0. Whereas these reactions do neutralize acid, they may not maintain drainage pH in an environmentally acceptable range. Thus, some of the NP measured by these techniques may not be "effective" NP with respect to maintaining acceptable drainage pH.

For example, the NP (Sobek et al., 1978) of a Duluth Complex rock sample was measured as 11 kg $CaCO_3$/t, and the sample was subjected to a laboratory dissolution test (Lapakko, 1990). After the depletion of only 0.5 kg $CaCO_3$/t the drainage pH decreased below 6.0. In this lower pH range, dissolution of the plagioclase, pyroxenes, and olivine present in the host rock continued to neutralize acid, but the rate of neutralization was inadequate to maintain a drainage pH above 6.0.

To provide a meaningful value for prediction of acid drainage, tests must quantify the NP available to maintain a drainage pH of at least 6.0. In order to assess the accuracy of the static test NP values, the NP available to maintain a pH above 6.0 was calculated based on sample mineralogy and measured directly in the laboratory. The mineralogical calculation assumed that the calcium carbonate and magnesium carbonate present in the mine waste samples (table 4B), and only these minerals, would buffer pH to at least pH 6.0. These minerals will dissolve and neutralize acid most readily when in contact with a solution of pH above 6.0.
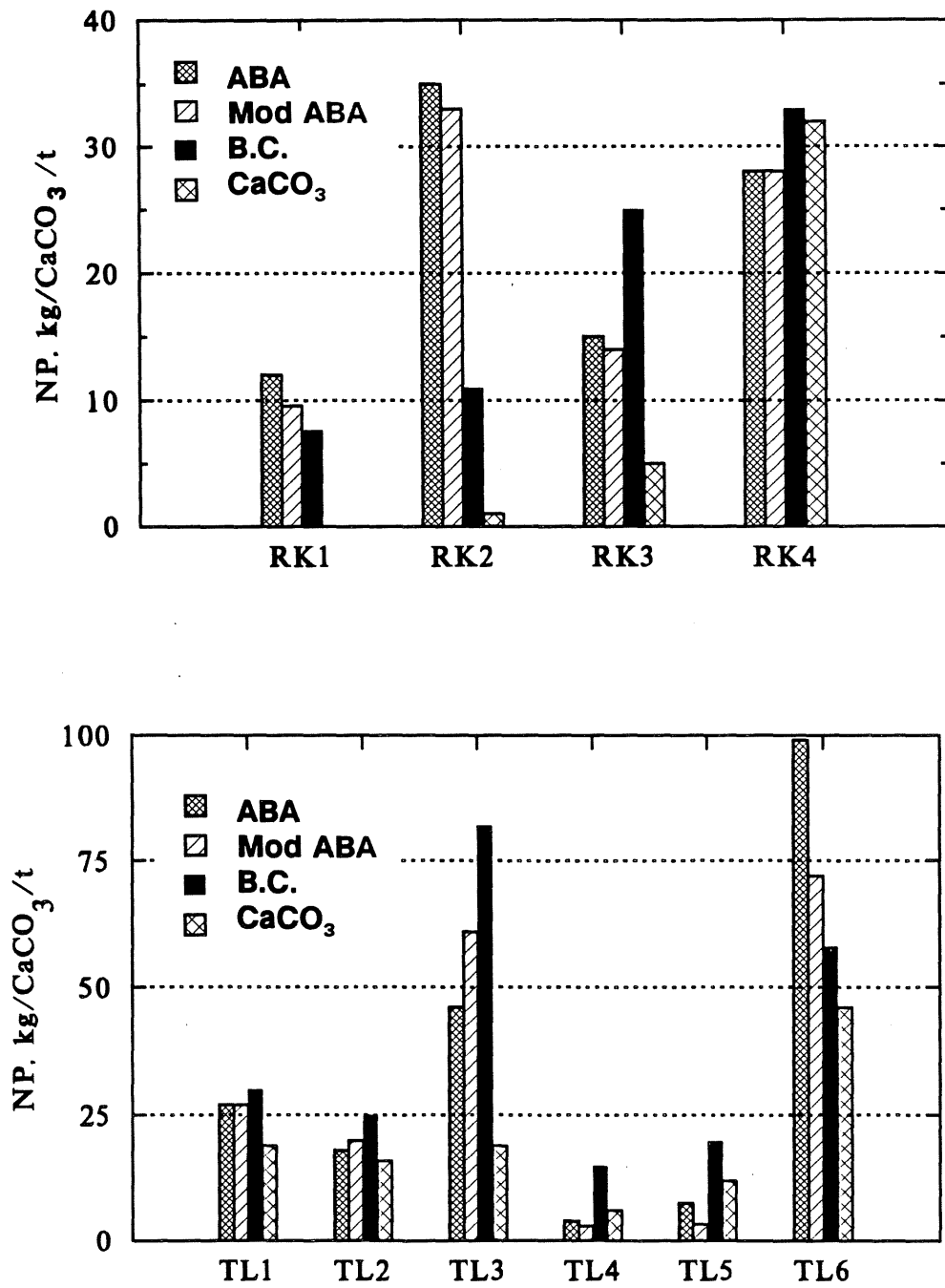
Figure 2. Neutralization Potential using four methods.

Secondly, the NP available as a function of pH was measured directly. This was done by modifiying the B. C. Research Initial Test to measure the NP at pH 6.0 and 5.0 in addition to the standard endpoint of pH 3.5. Acid was added to a mine waste/water mixture and the acid consumption (NP) was measured when the pH of the mixture reached 6.0, 5.0, and 3.5. The first value yields a direct measurement of the amount of NP available to maintain a pH above 6.0, or the "effective" NP. For all samples the NP at the pH 6.0 endpoint was less than that at the pH 3.5 endpoint, with this difference being the greatest for samples RK3 and TL3 (figure 3).

The NP available above pH 6.0 was in good agreement with the NP calculated based on the calcium carbonate and magnesium carbonate content (figure 4). The discrepancy between the two values was greatest for sample TL3, and this difference was the equivalent of roughly one percent calcium carbonate. The apparently elevated value determined by the titration may have been due to buffering contributions by other host rock components, "false" buffering by iron carbonate dissolution, or error in the carbonate mineral analysis. Nonetheless, the agreement between the two measurements was quite good.

The accuracy of the static test NP was determined based on their agreement with the NP based on the calcium carbonate and magnesium carbonate content of the sample. This agreement was quantified as the difference (Δ) between the static NP and the NP based on the carbonate content (static test NP - ($CaCO_3$ + $MgCO_3$ NP) = Δ). Based on this difference the accuracy of the static tests was classified as good (-9 < Δ < 4 kg $CaCO_3$/t), moderate (8 < Δ < 12 kg $CaCO_3$/t), or poor (20 < Δ < 65 kg $CaCO_3$/t).

The accuracies of the ABA and Modified ABA NP were in the same category for all samples and were equally divided among the three classifications (table 5). These tests were most accurate for samples RK4, TL2, TL4, and TL5. The major rock forming minerals in these samples were quartz, feldspar, and mica, although sample RK4 did contain a substantial amount of clay. Examination of the sample chemistry (table 3) suggests that the feldspar was largely potassium feldspar. The presence of these minerals apparently has little influence on the accuracy of the ABA and Modified ABA NP determination.

These two tests were moderately accurate in quantifying the NP of samples RK1, RK3, and TL1. Once again the major rock forming minerals present in these samples were quartz, feldspar, and mica, with substantial chlorite and clay also present in sample RK1. The major difference between these samples and the samples mentioned above is that the feldspar is largely calcium feldspar (as implied by the chemical data presented in table 3). Apparently the 24 to 39 percent calcium feldspar present contributed about 10 kg $CaCO_3$/t to the NP value.

The ABA and Modified ABA NP values were least accurate for samples RK2, TL3, and TL6, exceeding the carbonate NP values by 26 to 53 kg $CaCO_3$/t. Samples RK2 and TL6 both contained pyroxene (18 and 55%, respectively) and sample RK2 also contained 11% olivine. No other samples contained these minerals. In addition, sample RK2 had the
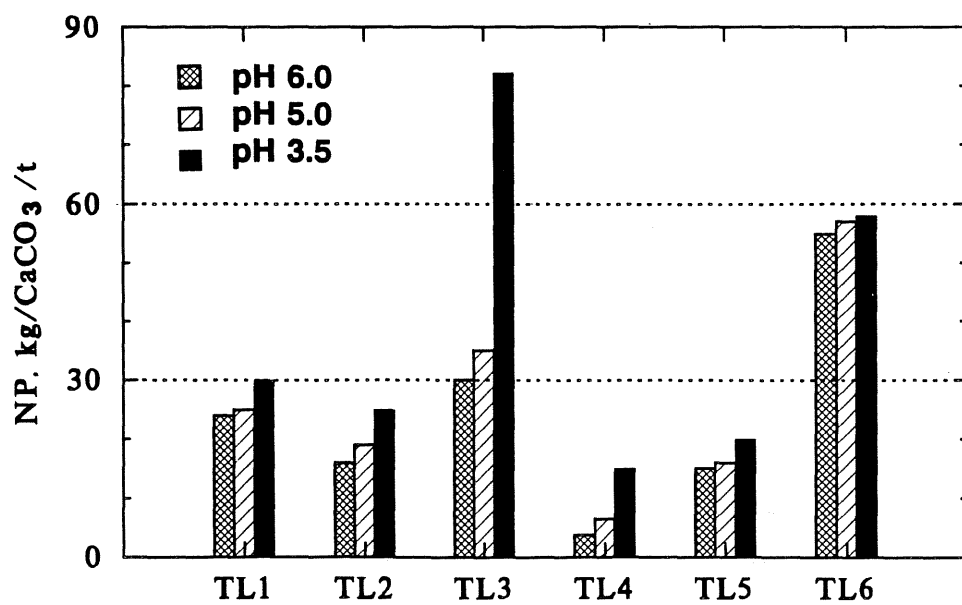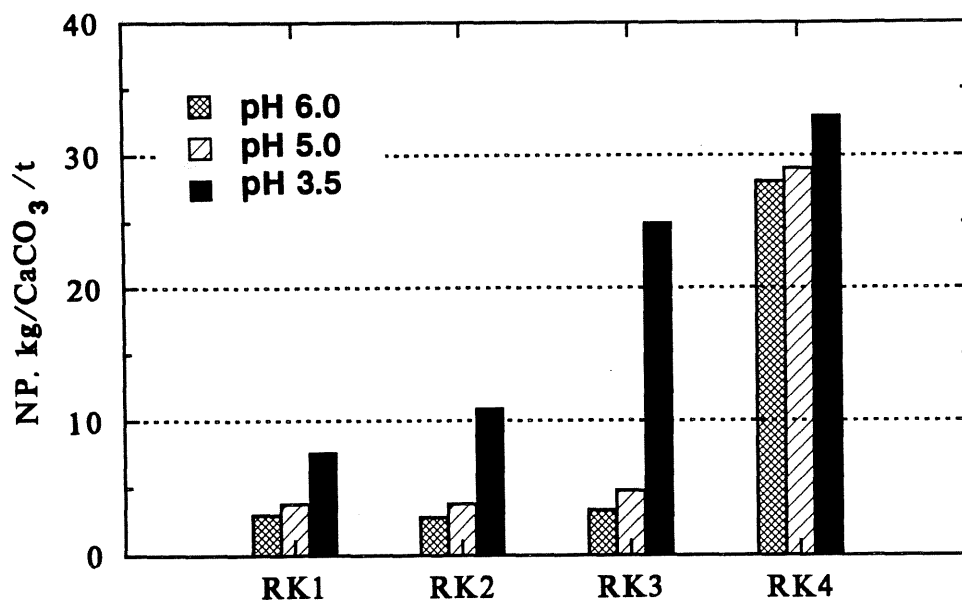
Figure 3. B.C. Research Neutralization Potential using three
endpoint pH values.
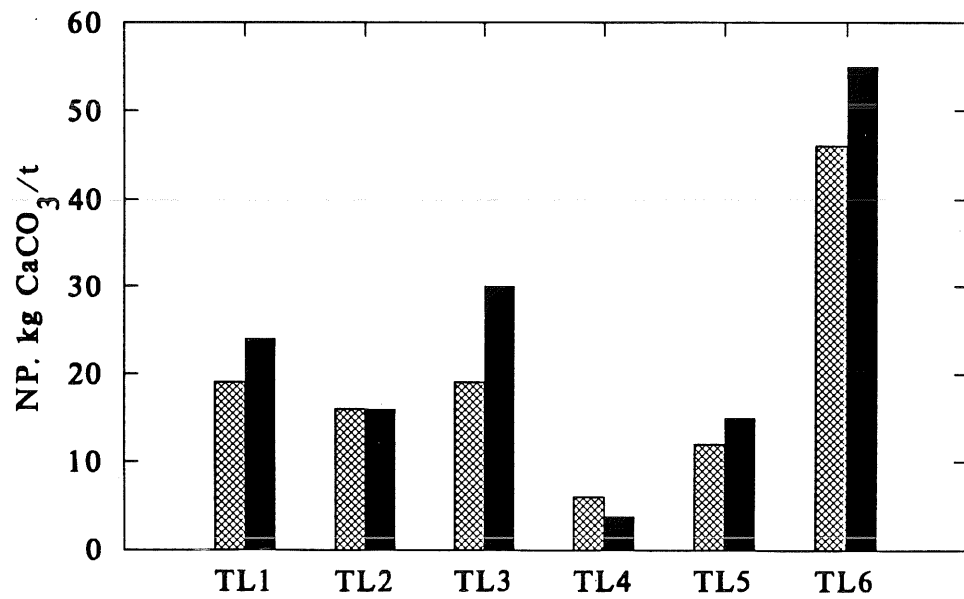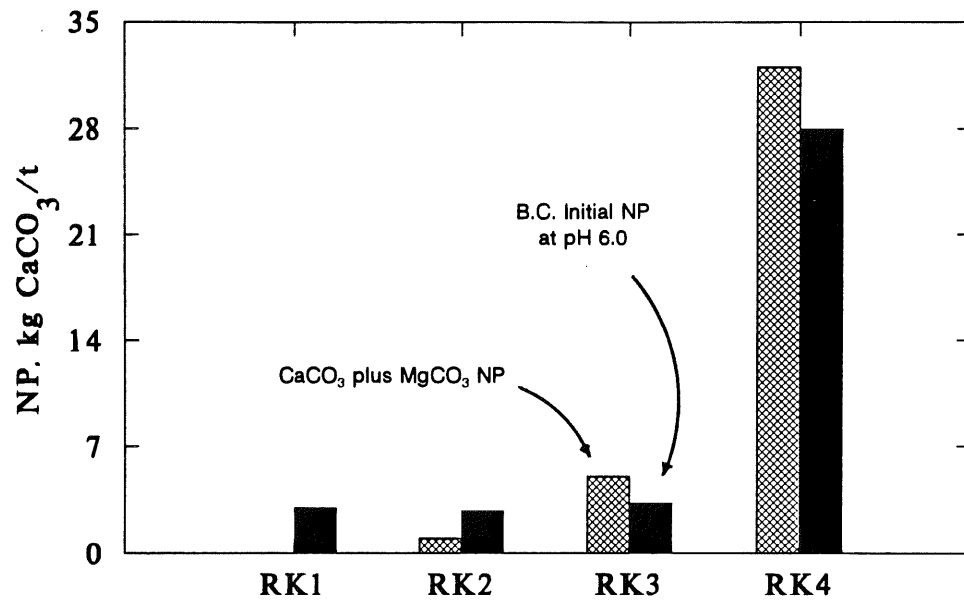
Figure 4. B.C. Research Initial N.P. at pH 6.0 compared to total
calcium and magnesium carbonate N.P.

Table 5.   Accuracy of static test NP values.

Accuracy	ABA	Mod. ABA	B.C.Initial
Good[1]	RK4 TL2 TL4 TL5	RK4 TL2 TL4 TL5	RK4
Moderate[2]	RK1 RK3 TL1	RK1 RK3 TL1	RK1 RK2 TL1 TL2 TL4 TL5 TL6
Poor[3]	RK2 TL3 TL6	RK2 TL3 TL6	RK3 TL3

[1] $-9 \le$ NP - carbonate NP ≤ 4 kg $CaCO_{3/t}$

[2] $8 \le$ NP - carbonate NP ≤ 12 kg $CaCO_{3/t}$

[3] $20 \le$ NP - carbonate NP ≤ 63 kg $CaCO_{3/t}$

Carbonate NP = 10 ($CaCO_3$) + 18.6 ($MgCO_3$) where $CaCO_3$ and $MgCO_3$ are the calcium carbonate and magnesium carbonate contents, respectively, in weight percent.

highest feldspar content, most of which was calcium feldspar, of the samples. Apparently the pyroxene, olivine, and calcium feldspar consumed acid under the low pH conditions in the NP tests. However, as illustrated in laboratory dissolution experiments (Lapakko, 1990), it is unlikely their dissolution would contribute significantly to maintaining a drainage pH above 6.0.

As discussed for the B. C. Initial titration to pH 6.0, the large discrepancy observed for TL3 may have been influenced by buffering of other host rock components or error in the carbonate mineral analysis. The influence of these factors are unlikely to account for the large differences observed. The major rock forming minerals present in sample TL3 are similar to those present in samples in the good and fair classifications. However this sample contained ankerite and siderite which yielded a total iron carbonate content of 9.3 weight percent (table 4B). The iron carbonate may have contributed to an NP value which was excessive by about 25 to 50 kg $CaCO_3$/t.

The initial dissolution of one mole of iron carbonate will consume one or two moles of acid. However, under environmental conditions the one mole of ferrous iron released will oxidize to ferric iron which will precipitate as ferric oxyhydroxide. The oxidation and precipitation reaction will yield two moles of acid. Thus, iron carbonate will not contribute to acid consumption. (See reactions 12-16 and the associated discussion in section 3.) The ABA and Modified ABA NP tests may not have allowed adequate time for the oxidation and precipitation reactions to occur completely and, consequently, yield excessively high NP values for samples with elevated iron carbonate contents.

Such error is more likely to occur with the ABA Test than the Modified ABA Test. The Modified ABA Test titrates to pH 8.3 as opposed to the pH 7.0 value in the ABA Test. The higher titration pH allows more time for ferrous iron oxidation to occur. More importantly, ferrous iron oxidation is reported to be second-order with respect to hydroxide concentration (Sung and Morgan, 1980; Eary and Schramke, 1990). This indicates that the oxidation at pH 8.3 would be two orders of magnitude higher than that at pH 7.0. Thus the Modified ABA would be more likely to account for the acid generated by precipitation of iron released from iron carbonate minerals. Consequently, the Modified ABA would be less subject to error due to the presence of iron carbonates. The reason for the elevated Modified NP for sample TL3 may be due to lesser contributions from iron carbonates and a greater degree of dissolution and buffering by other host rock minerals.

As was the case for the ABA and Modified ABA NP values, the accuracy of the B. C. Initial Test NP for sample RK4 was good. This further indicates the absence of minerals in this sample which consume acid at the lower pH values produced during the NP determinations. However, on samples TL2, TL4, and TL5 (samples for which the ABA and Modified ABA NP accuracy was good) the B. C. NP values were about 5 to 15 kg $CaCO_3$/t higher than the corresponding values for the ABA and Modified ABA Tests.

The elevated B. C. Initial Test NP values for these samples is apparently the result of particle size differences in the tests. The potassium feldspar dissolution in the B. C. Research Initial Test may have been enhanced due to the smaller particle size used (-300 mesh) as opposed to the "as received" particle size used for the ABA and Modified ABA NP determinations (which require a particle size of -60 mesh). Roughly 50% of the "as received" samples were in the +300 mesh fraction (table 2). The smaller particle size used in the B. C. NP Test, and consequent increased specific surface area, enhances the initial rapid ion exchange reaction of feldspar dissolution. This ion exchange involves acid consumption by the sample. Based on this hypothesis the reduction of particle size for NP determinations appears unwise.

The B. C. Initial NP accuracy was also fair for samples RK1, RK2, TL1, and TL6. Thus, the accuracy for samples RK1 and TL1 was similar for that for the ABA and Modified Tests, while the B. C. Initial values were more accurate for samples RK2 and TL6. This indicates that the pyroxene and olivine present in these samples (and calcium feldspar in RK2) did not dissolve as extensively as in the ABA and Modified ABA NP Tests. The lower pH conditions of the latter tests apparently resulted in the more extensive dissolution of these minerals.

The accuracy of the B. C. Research Initial NP Test was poor for samples RK3 and TL3, which had iron carbonate contents of 3.2 and 8.7 weight percent, respectively. The B. C. Initial NP values exceeded the actual NP values by 20 and 63 kg $CaCO_3$/t, respectively. Thus, the B. C. Initial NP was less accurate than the ABA and Modified ABA NP Tests for samples with elevated iron carbonate contents. This is most likely due to a lesser extent of the iron oxidation and precipitation reactions in the B. C. Research Initial Test. The B. C. Initial NP determination involves only an acid addition, as opposed to an acid addition followed by a titration with a base. Consequently, iron released during the acid addition of the B. C. Initial Tests has less time to react. Furthermore, the oxidation of iron will be slower under the acidic conditions of the B. C. Research Test as opposed to the higher pH conditions during the base titration in the ABA and Modified ABA Tests. (See discussion above, as well as reactions 12-16 and associated discussion in section 3.)

In summary, the ABA and Modified ABA NP values were in fairly good agreement, and the B. C. Research Initial NP was typically higher than these values. All three of the static tests tended to overestimate the NP available as calcium carbonate and magnesium carbonate. This suggests that the static test NP values overestimate the NP available to maintain a drainage pH above 6.0. This overestimation was typically about 10 kg $CaCO_3$/t, and was apparently due to the presence of calcium feldspar in the samples. For the ABA and Modified ABA methods the overestimation was higher yet for samples containing pyroxene, olivine, or iron carbonate minerals. The extent of overestimation for the B. C. Research Initial NP was greatest for samples containing iron carbonate.

Acid titration of a mixture of a mine waste sample and distilled water down to pH 6.0 yielded NP values consistent with those determined based on the calcium carbonate and

magnesium carbonate content. For the 10 samples examined, this titration appears to be a reasonable and, generally more conservative, method of determining the neutralization potential available for maintaining drainage pH above 6.0. The titration also overestimated the Neutralization Potential based on calcium carbonate and magnesium carbonate content for a sample with an elevated iron carbonate content. However, the magnitude of this overestimation was less than that for the static tests.

5.2.4. Net Neutralization Potential

The Net Neutralization Potential is the difference between the Neutralization Potential and the Acid Production Potential (Net NP = NP - APP). There is presently no agreement on the critical value of Net NP, below which drainage will be acidic and above which drainage will be neutral or alkaline. Sobek et al. (1978) indicated that coal waste would produce acidic drainage if the ABA Net NP were less than -5 kg $CaCO_3$/t. This value was "based mainly on agronomic considerations" (Perry, 1985). Day (1989) suggested that a Net NP value of +10 kg $CaCO_3$/t be used as the threshold for acid production, while Morin (1989) observed values of -15, +10, and +20 kg $CaCO_3$/t for a modified procedure. Ferguson (1989) indicated that it was difficult to determine the acid generating character of samples with Net NP values of -20 to +20 kg $CaCO_3$/t due to poor agreement among methods in this range. For simplification of data presentation, a critical Net NP value of zero will be used. Thus, if Net NP exceeds zero it has an excess of NP, and implies that the waste will not produce acid. This value is not endorsed, but rather used as a tool for data presentation.

In addition to the ABA (Sobek et al., 1978), Modified ABA (Lawrence, 1990), and B. C. Research Initial (Duncan and Bruynesteyn, 1979) Tests discussed above, the Net NP was also determined using the Net Acid Production Test (NAP). In the NAP test the oxidation of the mine waste sample is accelerated by exposure to hydrogen peroxide. (Since this test involves the oxidation of sulfide minerals and the consequent dissolution of buffering minerals, it is similar to a kinetic test.) The resultant excess or deficiency of acid in solution is used to quantify the Net Acid Production of the waste (Net AP). For ease of comparison with other tests, the results from this test will be expressed as Net NP, which is determined as Net NP = -Net AP.

The Net NP values for the ABA, Modified ABA, B. C. Research Initial, and NAP Tests agreed on the acid-producing character of seven of the samples (figure 5). There were, however, differences in the magnitudes of the Net NP values for these samples. The range of the four Net NP values for a given sample varied from 10 to 61 kg $CaCO_3$/t, although for seven of the ten samples the Net NP range was between 10 and 30 kg $CaCO_3$/t. The range tended to increase as Net NP decreased from 0 to -150 kg $CaCO_3$/t.

The differences among Net NP values for the ABA, Modified ABA, B. C. Initial Tests were largely the result of differences among the NP values for the tests. That is, if the NP of a
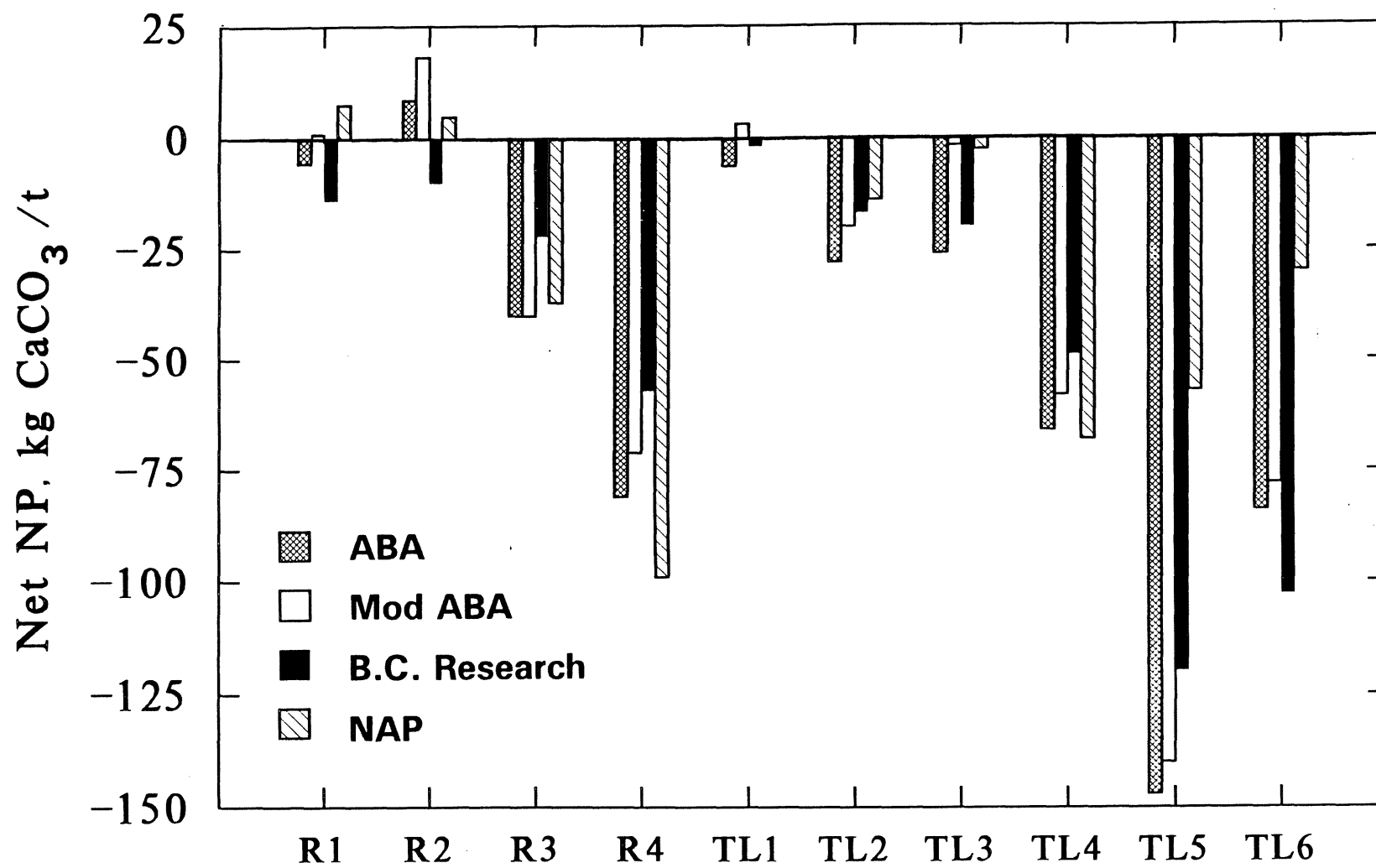
Figure 5.   Net Neutralization Potential using four methods.

sample were relatively low, the Net NP value would be similarly low. Differences in the sulfur analysis used for APP determination also contributed to differences in the Net NP, but these differences were relatively small. That is, the use of sulfide-sulfur content of these particular samples (Modified ABA) was only slightly less than the total sulfur content.

The Net NP values for the ABA, Modified ABA, B. C. Research Initial, and NAP Tests did not agree on the acid-producing character of samples RK1, RK2, and TL1. The Net NP values for these three samples were closer to zero than the other samples. Thus, small differences in the APP or NP values among the three methods would lead to a change in the sign of the Net NP value.

Although the NAP Net NP was often higher than the other Net NP values, the disparity was not generally large (figure 5). Indeed the contractor for the ABA, Modified ABA, and Net NP tests, indicated "the Net Acid Production test results correlate extremely well with the Acid Base Accounting procedures" (Lawrence Consulting Ltd., 1991). Lawrence (1992) indicated that the NAP values more closely approximated those from the ABA and Modified ABA than in previous experiences.

Modifications of the previous method, such as the greater dosage of hydrogen peroxide and longer reaction time, may have contributed to this improved agreement. The modified method used sequential doses of 100 mL and 50 mL of hydrogen peroxide (30% strength) per gram waste, and allowed 90 minutes of reaction. The previous method used 100 mL of 15% hydrogen peroxide with a five gram sample of waste, and allowed a reaction time of either five minutes or one hour (Coastech, 1989). The $CaCl_2$ rinse of the solids in the modified method may also have released additional acid from the solids and, thereby, improved the accuracy of the technique.

However, on samples TL5 and TL6 the NAP Net NP was considerably higher than the values from the other static tests. This suggests that for these samples the acid production in the NAP was less than the APP values for the other static tests, or the acid consumption in the NAP test exceeded the NP of the static tests. Three occurrences could lead to underestimation of APP and a resultant NP elevation for samples TL5 and TL6. First, incomplete oxidation of the iron sulfide minerals in these samples would contribute to the higher Net NP values for the NAP test. Incomplete oxidation of coal, coal pyrite, and ore pyrite by hydrogen peroxide has been observed, (Mirza et al., 1992), although test methods were different. Samples TL5 and TL6 had the highest sulfur contents, 5.0% and 5.8%, respectively. Sulfur analyses of four samples, before and after the peroxide oxidation, indicated that the fraction of sulfur oxidized decreased as sulfur content increased. Nonetheless, even for TL6 (5.84% S) over 95% of the sulfur present was oxidized (table 6). If the residual sulfur occurred as an acid-producing mineral, such as pyrite or pyrrhotite, the actual APP of the sample would be about 5% less than the true value.

Second, incomplete oxidation of ferrous iron and and the subsequent precipitation of iron oxyhydroxide may have contributed to elevated Net NP values. The presence of dissolved

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Table 6.   Extent of sulfide oxidation in the Net Acid Production (NAP) Test

Sample	Head Percent	Residue Percent	Percent Oxidized
RK4	3.48	0.07	98
TL1	1.06	0.01	99
TL3	2.30	0.04	98
TL6	5.84	0.27	95

iron after titration would produce acid which was not accounted for by the Net NP test. This test used a titration to pH 7.0 rather than 8.3, and this lower pH end point would tend to magnify the potential for this error. (See reactions 12 - 16 and the related discussion in sections 3 and 5.2.3.) Thirdly, incomplete oxidation of sulfide may have contributed to underestimation of acid production and the consequent elevated Net NP. For example, oxidation of sulfide to elemental sulfur consumes acid. However, when sulfide is oxidized to sulfate there is no net acid consumption or production.

Overestimation of NP may also have contributed to the elevated Net NP of TL5 and TL6. The oxidation of iron sulfides present in the solids produced an acidic solution in the test. The host rock components were subjected to this solution at near boiling temperatures for one to two hours. This may have resulted in attack of host rock components and consequent buffering by their dissolution. Such acid consumption would overestimate the actual NP and, consequently, result in an elevated Net NP. Despite the differences between the NAP and other static test results it was concluded that the NAP test "could provide a useful alternative field and laboratory static test procedure and has the advantage that no sulfur analyses are required" (Lawrence Consulting Ltd., 1991). It was noted that "further work is required to verify these observations" (Lawrence Consulting Ltd., 1991).

5.2.5. Comparison with Field Drainage Quality

All but five of the Net NP values were less than or equal to zero and, for the purpose of discussion and not recommendation, it is assumed that this implies the waste will produce acidic drainage. Two of the three rock samples were correctly identified as acid producers by all tests (table 7). The ABA, Modified ABA, NAP tests identified RK2 as non-acid producing, while in this rock produced mildly acidic drainage in the field (approximate pH range 4.7-5.3). This error was likely due to overestimation of the neutralization potential available above pH 6.0 for this rock. (See the discussion of Neutralization Potential.)

The validity of predictive tests for the long-term drainage from tailings can not be verified conclusively based on tailings basin water quality during operation. All static tests identified the tailings samples TL2 through TL6 as acid producers, although the operational tailings basin water associated with all these tailings was basic. The pH in operational systems is likely to be alkaline irrespective of the tailing composition due to "the continuous alkaline addition and flooded nature of the waste" (Ferguson, 1991). Mineral processing often adds alkaline chemicals to the basin, and the submerged environment inhibits oxidation of the sulfide minerals (Ritcey, 1991).

Consequently, the water quality from operational tailings basins does not necessarily represent the drainage quality after closure. After closure there will be no alkaline mineral processing inputs, and the basin may be drained thereby exposing the tailings to the atmosphere. For example, the water in the basin containing the TL5 tailings had a pH of around 10 and the drainage pH from the tailings was near seven. However, after one to two

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Table 7. Static Test Predictions vs. Field Drainage Quality.

Sample	Net NP in $kgCaCO_3/t$						Field Drainage Quality	Source of Field Data
	ABA[1]	MOD ABA[1]	B.C. Initial[2]	NAP[1]	Alternative A[3]	B[4]		
RK1	-5.7	0.8	-14	-7.7	-8.8	-5.8	No data	No data
RK2	8.5	18	-10	5.1	-14	-12	pH 4.7-5.3	1000-ton rock piles in field
RK3	-40	-40	-22	-39	-48	-50	Acid	Small water volumes in field
RK4	-81	-71	-57	-103	-67	-71	Approximate pH 3 at 40 wks.	Column test on large particles
TL1	-6.2	3.3	-1.8	0.0	-5	0	Basic	Operational tailings basin water
TL2	-29	-20	-17	-14	-24	-24	Basic	Operational tailings basin water
TL3	-26	-1.7	-20	-2.6	-44	-33	Basic	Operational tailings basin water
TL4	-66	-58	-49	-71	-55	-57	Basic	Operational tailings basin water
TL5	-147	-140	-120	-86	-131	-128	pH 2.5-3.0	Test plot in field
TL6	-84	-78	-103	-59	-136	-127	Basic	Operational tailings basin water

[1] Method of Sobek et al. (1978) conducted by Lawrence Consulting Ltd.
[2] Method of Bruynesteyn and Duncan (1979) conducted by B.C. Research.
[3] APP based on sulfide sulfur plus acid generating sulfate mineral content, NP based on calcium carbonate plus magnesium carbonate content.
[4] APP determine as in footnote 3, NP based on B.C. Research Initial Test titration to pH 6.0.

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years in a non-submerged field test plot receiving no operational inputs, the pH of pore water in the tailings dropped below 3.0.

5.3. Kinetic Tests

5.3.1. Introduction

Kinetic tests are more expensive and time consuming than static tests. In these tests, mine waste samples are dissolved and the resultant water quality has been assumed to be representative of that generated by the waste in the field. The tests are typically run on a small mass of relatively fine particles. Tailings need not be modified for these tests but the size of waste rock samples must be reduced.

This reduction in particle size may change the relative amounts of acid producing and acid consuming minerals available for reaction. For example, in large rocks sulfide grains may be contained within relatively unreactive silicate grains and be largely unavailable for reaction. By reducing particle size these grains will be liberated and become more available for reaction than in the large rock. Thus, the particle size reduction would enhance the tendency to produce acid. Similarly, calcium and magnesium carbonate minerals may be fairly tightly bound in relatively large "limestone" particles. In this form the surface area available for reaction will be small relative to particles crushed to 0.2 mm or smaller. As a result the ability of the sample to consume acid would be overestimated.

The drainage from sulfidic rock (or tailings) will become acidic if the rate of acid production exceeds the rate of acid consumption. Drainage generated in a kinetic test may be acidic immediately or within the test duration, and the sample can be identified as an acid producer. If the drainage is not acidic during the duration of the test, it may remain so until (and therefore beyond the point at which) all acid producing minerals were depleted. It is also possible that it would become acidic if the test were continued for a longer period. Consequently, a kinetic test on a sample which produces drainage which is not acidic does not necessarily indicate that the sample will not produce acid during the decades and centuries following mine closure.

If a rock contains at least a moderate amount of NP its initial drainage will probably be neutral, since the buffering minerals present will neutralize the acid produced by iron sulfide oxidation. As acid production continues (e.g., iron sulfide oxidation continues) the NP of the rock may be depleted. Factors which contribute to this condition include depletion of the buffering minerals and coating the surface of buffering minerals. If the NP is depleted while a significant amount of sulfide minerals remain, the drainage will become acidic. The period between the initiation of dissolution and acidification of drainage has been referred to as the lag period.

Detection of an initial lag period requires an extended period of experimentation (Hedin and Erickson, 1988; Miller and Murray, 1988). Neutral drainage could be generated over the relatively short duration of a test but, over a longer period, the neutralization potential could be depleted with resultant drainage acidification. Thus the rates of acid production and consumption can be determined from kinetic tests, but it may be time consuming to experimentally determine if the acid neutralizing capacity will be depleted before the acid producing capacity.

5.3.2. Data Presentation for Individual Tests: Drainage pH, sulfur and NP depletion, relative rates of acid production and consumption
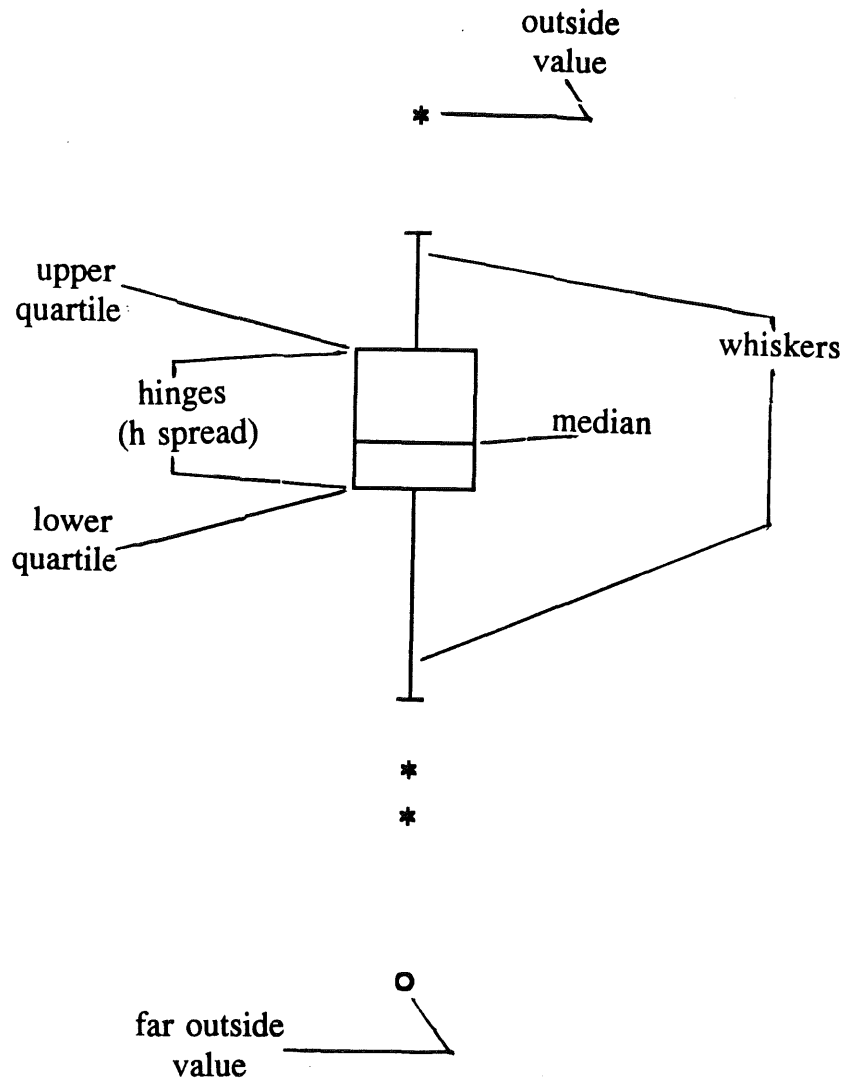
The following discussion addresses

1) the observed drainage pH in the kinetic tests,
2) the extent of sulfate, calcium, and magnesium release to solution, and
3) the rate of carbonate mineral dissolution relative to that of sulfide oxidation.

The observed drainage pH is used as an indicator of the drainage pH in the field. Mine waste drainage quality predictions have typically been based solely on the drainage pH during the test. The pH data for each test are presented in a boxplot format (figure 6), which concisely describes the frequency distribution of the drainage pH values observed. The temporal pH variation of pH, as well as other drainage quality parameters, are presented in the appendix associated with each test.

Discussion of the extent of mine waste dissolution is presented based on the sulfate, calcium, and magnesium concentrations observed in the kinetic tests. The oxidation of iron sulfide minerals releases sulfate to solution and leads to acid production (reactions 1, 2). The acid produced can react with calcium carbonate, magnesium carbonates, and/or other minerals present in the mine waste to release calcium and/or magnesium (reactions 6-11). The sulfate, calcium, and magnesium released will remain in solution unless concentrations increase beyond the solubility of a secondary solid phase. For example, if the concentrations of calcium and sulfate exceed the solubility of gypsum, $CaSO_4(s)$, may precipitate.

If sulfate, calcium, and magnesium are conserved in solution (that is, no precipitation of $CaSO_4$, $MgSO_4$, or other sulfate, calcium, or magnesium solids and no adsorption of these components), the rate of their appearance in solution equals their rate of release from the solid phase. Thus, the rate of sulfate appearance in solution equals the rate of sulfide mineral oxidation, and the sum of calcium and magnesium appearance in solution equals the rate of neutralizing mineral dissolution. Furthermore, these values can be used to determine the mass of sulfide and neutralizing minerals dissolved.

The extent of dissolution is expressed as the percent of the sulfide minerals and NP (Sobek et al., 1978) initially present in the rock which was released during the test. This provides

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outside
value

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*
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upper
quartile

hinges
(h spread)

median

whiskers

lower
quartile

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*
*
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O
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far outside
value

Values at a distance x from the hinges, where
   $1.5H < x < 3H$, are designated by "*" and
   $3H \leq x$ are designated by a "o".

The whiskers show the range of values which fall
   within 1.5 Hspreads of the hinges. They do
   not necessarily extend to the inner fences.

Figure 6. Interpretation of box plot figures.

an assessment of the degree of mine waste dissolution in the tests relative to that which might occur over the long term in the field. If the extent of dissolution is small, there is a large degree of uncertainty in the use of the laboratory drainage pH as an indicator of drainage quality from an abandoned mine waste over a period of decades.

Third, the rate of carbonate mineral dissolution relative to that of sulfide mineral oxidation is approximated as the molar ratio of the sum of calcium and magnesium release to sulfate release. This ratio indicates if the conditions of a test preferentially accelerate either carbonate mineral dissolution or sulfide oxidation. A ratio of one implies that one mole of calcium or magnesium carbonate dissolves per mole of iron sulfide oxidized. This in turn indicates that two moles of acid are consumed by each mole of carbonate mineral dissolved (reactions 7, 9). A ratio lower than one indicates that the calcium and magnesium carbonate dissolution is less than the sulfide oxidation and consequent acid production. This condition suggests that the drainage is acidic or that components other than calcium and magnesium carbonate are contributing to acid neutralization. A ratio of two indicates that one mole of acid is consumed per mole of carbonate mineral dissolved (reactions 6, 8). Ratios in excess of two indicate that some calcium and magnesium is being release without consuming acid.

In the **Wet-Dry Cycle Test (Lapakko, 1988)**, TL5 was the only sample which generated drainage pH values below 6.0 (figure 7). The pH of drainage from TL5 was above 6.0 for the week 0 rinses and decreased to about 2.8 at week 20. This pH trend alone indicates that the sample is an acid producer if subjected to alternate wet and dry conditions. Of the remaining nine samples the drainage pH for samples RK1, RK2, and RK3 was in the approximate range of 7.0 to 7.5. These samples had the lowest calcium carbonate and magnesium carbonate content (table 4B). The drainage pH for the remaining six samples was typically in the range of 7.5 to 8.0.

With the exception of sample TL6, less than nine percent of the sulfur present in the samples which produced nonacidic drainage (table 8). This includes sulfate released in the three rinses at week 0. The percentage of the Neutralization Potential released from these nine samples ranged from 3.5 to 42 percent. The fact that both iron sulfide and carbonate minerals remained upon the test completion indicates that the drainage pH observed during the test may not be indicative of the long-term drainage quality. That is, if the rate of acid consumption continued to equal or exceed the rate of acid production, the drainage would remain non-acidic. However, if the rate of acid consumption were to decrease below that of acid production, the drainage would become acidic. Two factors leading to the latter condition are the depletion of buffering minerals available for neutralization and, second, the coating of buffering minerals, with an attendant decrease in their dissolution rate.

The molar ratio of calcium plus magnesium release to sulfate release was between one and two for most of the samples. The ratio was below one for sample TL5, reflecting the acidic conditions of the drainage. The ratio was excessively high for samples TL1 and TL2, and may have been influenced by error in the ICP analyses of calcium and magnesium.

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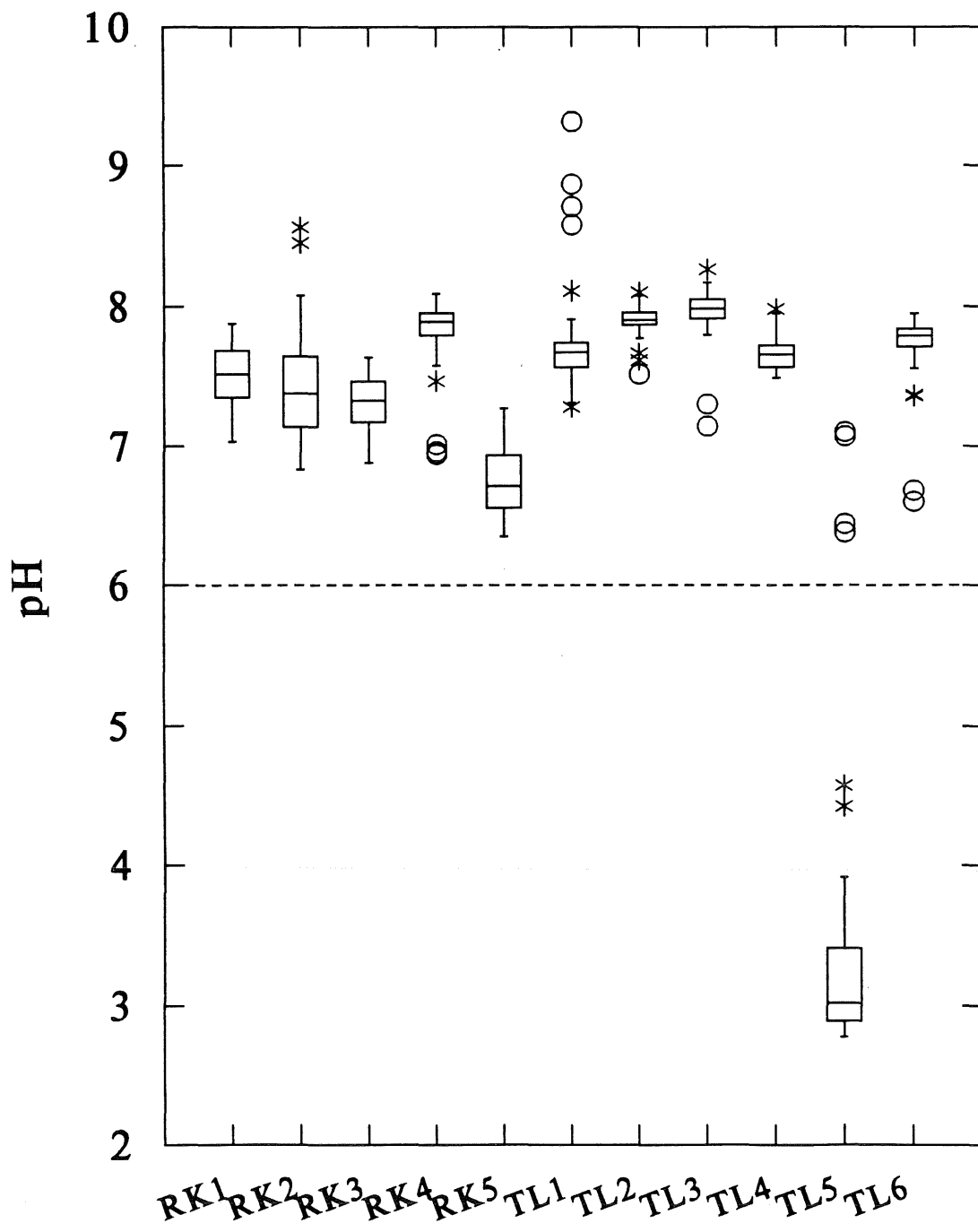
Figure 7. pH box plot for Wet-Dry Cycle Test.

Table 8. Wet-Dry Cycle Test: percent sulfur and NP release, and molar ratio of calcium plus magnesium release to sulfate release[1].

Parameter, units	RK1	RK2	RK3	RK4	TL1	TL2	TL3	TL4	TL5	TL6
% sulfur[2]	8.496	7.858	4.324	5.471	3.737	2.924	7.533	2.897	13.488	15.052
% NP[3]	14.75	4.11	16.27	22.25	8.37	25.17	15.74	79.74	169.33	35.46
$(Ca+Mg)/SO_4$[4]	2.10	0.984	1.36	1.59	3.03	4.75	1.59	2.02	0.432	1.31

[1] MN DNR
[2] Percentage of total sulfur initially present in mine waste which was released from week 0 to week 20.
[3] Percentage of total NP initially present in mine waste which was released from week 0 to week 20.
[4] For weeks 1 - 20 (excluding rinse prior to test).

In the **Standard Humidity Cell Test** the only sample to produce strongly acidic drainage was TL5 (figure 8). Drainage pH from this sample was 7.2 at week 0 and decreased to the range of 2.2 to 2.4 after week 15. Based on the observed drainage pH alone, TL5 was identified as a strong acid producer. Of the remaining samples, only RK2 produced more than a single pH reading below 6.0. About 40 percent of the drainage pH readings for this sample were in the approximate range of 5.4 to 5.8. Most of the low pH values occurred from weeks five to twelve. For samples RK1 and TL6, one drainage pH value below 6.0, but virtually all of the remaining values were above 7.0.

The contractor summarized the character of the samples, identifying sample TL5 as "by far the most problematic". It was noted that the calcium release from sample TL6 was elevated, and the "leaching test was terminated before the calcium content of this sample was completely removed". He further stated that calcium depletion would render "the sample pyrite-enriched and acid-prone" and that the waste rock samples were "non-problematic".

The percentage of sulfide minerals oxidized ranged from 2.8% to 6%, except for samples RK1 and TL5 for which this value was about 10%. With the exception of samples TL4 and TL5, the percentage of Neutralization Potential depleted was less than 20% (table 9). The percentage of NP release from sample T5 exceeded 100%, indicating that all of the NP was depleted. This is consistent with the acidic drainage generated by this sample. About 70% of the NP initially present in sample TL4 was depleted during the test, suggesting that the drainage from this sample would have become acidic had the oxidation of iron sulfides continued at a similar rate for an additional ten to twenty weeks. Since the sulfate release was decreasing near the end of the test, it is difficult to predict the ultimate pH from this sample. The other eight samples contained substantial amounts of sulfur and NP at the end of the test, suggesting that neutral drainage observed in the test may not be indicative of the drainage generated over the long term.

The molar ratio reflecting the relative rates of carbonate and sulfide minerals was typically in the expected range of one to two. The ratios for TL5 and RK3 were below this range, reflecting the more acidic drainage generated by these samples.

The **Modified Humidity Cell Test** was conducted only on the four waste rock samples. The majority of drainage pH values observed for each of the samples was below pH 6.0. For RK1, RK2, and RK3 the majority of drainage pH values were in the range of 5.0 to 6.0, while most values for RK4 were lower (figure 9). These values are qualitatively consistent with the acidic drainage observed in large scale tests on RK2 and RK3, and with observed field water quality for RK4 (table 1). (No verification data are available for RK1.) It should be noted that the minimum drainage pH value for each sample occurred in week 4, which is somewhat unusual. It is possible that excessively low values were obtained be due to an irregularity in analysis or test conditions for this week.

The drainage pH values for this test were lower than those for most of the other tests. This was a reflection of decreased acid neutralization by buffering minerals. Particle size was
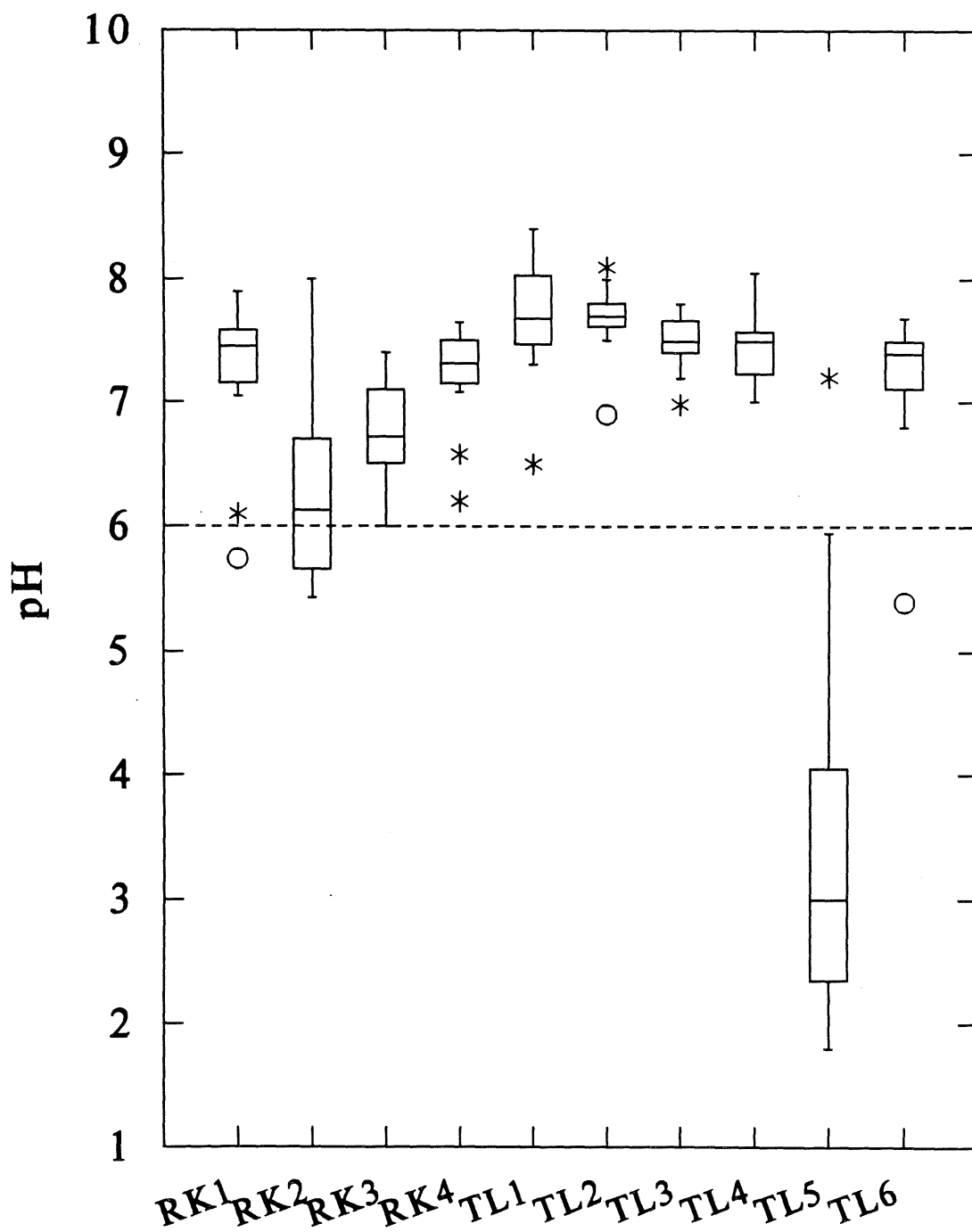
Figure 8. pH box plot for Standard Humidity Cell Test.

Table 9.   Standard Humidity Cell Test: percent sulfur and NP release, and molar ratio of calcium plus magnesium release to sulfate release[1].

Parameter, units	RK1	RK2	RK3	RK4	TL1	TL2	TL3	TL4	TL5	TL6
% sulfur[2]	9.540	3.859	3.085	5.097	5.572	2.795	9.259	3.357	10.783	5.955
% NP[3]	15.17	1.77	7.80	19.18	8.19	10.56	15.17	71.05	130.27	11.41
$(Ca+Mg)/SO_4$[4]	1.42	0.797	0.853	1.14	1.52	1.66	1.10	1.30	0.531	1.06

[1] University of South Carolina.
[2] Percentage of total sulfur initially present in mine waste which was released from week 0 to week 20.
[3] Percentage of total NP initially present in mine waste which was released from week 0 to week 20.
[4] For weeks 1 - 20 (excluding rinse prior to test).
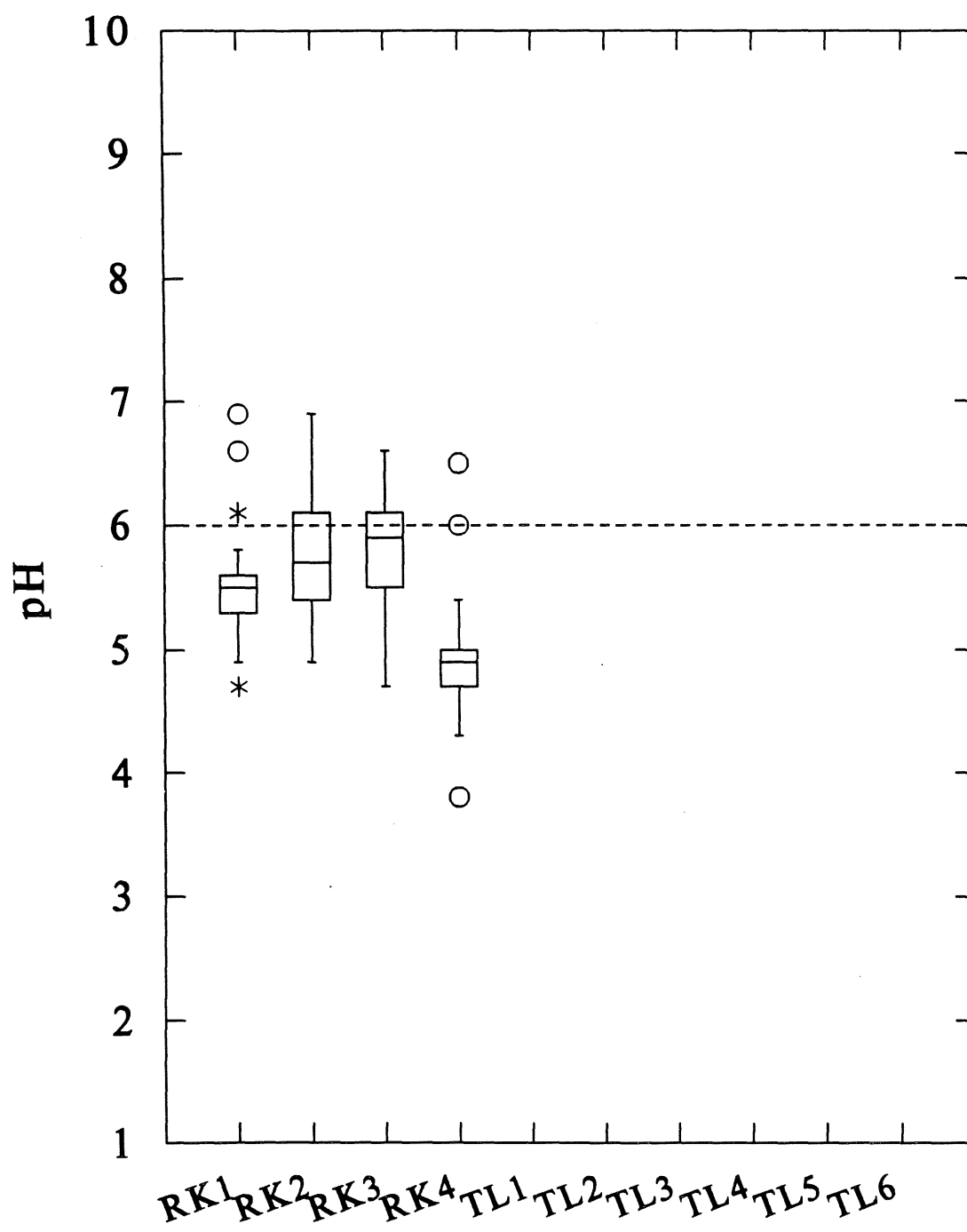
Figure 9. pH box plot for Modified Humidity Cell Test.

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reduced in the Wet-Dry Cycle, Elevated Temperature, and Shake Flask Tests. The buffering mineral dissolution rate in these experiments was consequently enhanced. The buffering mineral dissolution in the Standard Humidity Cell and Soxhlet Tests was enhanced by a longer period of contact between the mine waste samples and drainage.

Less than ten percent of the sulfides and less than 15 percent of the NP initially present in the sample were depleted during the experiment (table 10). This indicates that the pH of the drainage could decrease if the samples were subjected to additional dissolution. The contractor addressed this possibility as follows.

> (The) test results did not generally confirm the static test indications that 3 of the 4 waste rock samples are potentially acid producing (note that the NAP method only indicated 2 samples to be potentially acid producing). The most probable explanation for the lack of confirmation is that the tests were not run for sufficient time to overcome the moderate NP values of the samples. The indications are that the sample RK3 might have been starting to demonstrate acid producing activity and a few more weeks testing might have confirmed this indication. This illustrates the need to be flexible in designing the duration of a kinetic test program, although budget considerations are, of course, important in most programs. It should be recognized, however, that for the remaining two samples, an unreasonable time period might be required to confirm the acid producing potential and develop water quality predictions.

> It should also be noted that despite the lack of evidence for acid generating activity in the .... tests on samples RK2, RK3, and RK4, the pH of leachates remained below 6, indicating the inability of the alkaline components of the samples to modify the pH of the incoming water to satisfactory values.

These comments address two noteworthy points. First, the degree to which the reactive NP (and iron sulfide) has been depleted determines the degree to which a kinetic test reflects the "long term" quality of drainage from a mine waste. Thus, the sulfur content and NP of a mine waste must be considered in the design and interpretation of kinetic tests. Second, drainage pH below 6.0 is unsatisfactory. Considerable discussion has been directed at acidic drainage as that which has pH in the region of about 3.5 and lower. Indeed, static tests determine Neutralization Potential based on the buffering available in titrating to this pH region. However, as noted by the contractor, drainage pH in the region of 3.5 to 6.0 is unsatisfactory. While, the conventionally tacitly accepted pH range (roughly pH < 3.5) represents a more severe drainage quality problem, the range of 3.5 to 6.0 is also problematic.

The molar ratio of calcium plus magnesium release to sulfate release in this test were all below 1.0. This indicates that the rate of sulfide oxidation exceeded the rate of carbonate mineral dissolution, as is supported by the mildly acidic drainages generated.

Table 10. Modified Humidity Cell Test: percent sulfur and NP
release, and molar ratio of calcium plus magnesium
release to sulfate release[1].

Parameter, units	RK1	RK2	RK3	RK4
% sulfur[2]	9.123	2.423	2.496	7.607
% NP[3]	7.26	0.931	4.05	13.7
$(Ca+Mg)/SO_4$[4]	0.919	0.666	0.823	0.655

[1] Lawrence

[2] Percentage of total sulfur initially present in mine waste which was
released from week 0 to week 20.

[3] Percentage of total NP initially present in mine waste which was
released from week 0 to week 20.

[4] For weeks 1 - 20 (excluding rinse prior to test).

Elevated Temperature Test, as with the previously discussed tests, sample TL5 produced the most highly acidic drainage and the remaining tailings produced neutral to alkaline drainage. Some drainage pH values below 6.0 were observed for each of the waste rock samples, RK1 - RK4 (figure 10). Although the weekly replication for the duplicate reactors in this test was erratic, the overall distribution of drainage pH values was reproducible between the duplicate reactors.

Of these four samples RK4 generated the most highly acidic drainage, followed by RK1, RK3, and RK1, respectively. The pH of drainage from RK4 was initially above 7.0 and decreased below 4.0 at the end of the test, identifying sample RK4 as a strong acid producer. After week 6 all of the drainage pH values from sample RK1 were less than or equal to 6.0, and most of these values were less than 5.0 (figure 10). These data suggest than RK1 would produce an acidic drainage less severe than RK4. About 40 percent of the drainage pH values from sample RK3 were less than pH 6.0, and the minimum values for both reactors were observed at week 12. Only two drainage pH values below 6.0 were observed for RK2, the mildest drainage pH of the four waste rock samples.

The percent of sulfide minerals oxidized was highest for RK1 followed by RK4, TL5, and TL6, respectively (table 11). The extent of sulfide oxidation in this test was greater than that in any of the others. The extent of sulfides oxidized in the other solids was roughly three to ten percent.

The percent of NP (ABA method) released from both TL5 and RK4 exceeded 100%, which is consistent with the acidic drainages from these solids. The fraction of NP released for TL4 was also quite high, suggesting that the NP might be depleted from this sample, with consequent drainage acidification, if the test were continued for a relatively short time. Less than half of the NP initially present in samples RK1 and RK3 was depleted, which is inconsistent with the acidic drainages observed from these samples. This apparent inconsistency is due to overestimation of the ability of the sample to maintain drainage pH above 6.0 by the ABA NP (see section 5.2.3). The mineralogic data indicate the total calcium carbonate and magnesium carbonate content is considerably less than the NP measured by the ABA technique (figure 2), and these minerals may have been depleted based on the observed extent of calcium and magnesium release.

The molar ratios reflecting the amount of carbonate minerals dissolved relative to sulfide minerals dissolved generally ranged from around 1.0 to 2.3. The ratio for TL5 was exceptionally low, reflecting the low drainage pH. The ratios for RK1, RK3, and RK4 were on the lower end of the typical range, which is qualitatively consistent with the more acidic drainage generated by these samples. The ratio for TL4 was exceptionally high, suggesting that calcium and magnesium were release without neutralizing acid.

Sample TL5 generated a drainage pH of about 6 in the **Soxhlet Test**, the lowest value observed for the test. The drainage pH for RK2 was 5.99, and the remaining samples generated neutral to basic drainage (figure 11). Based on these data alone, TL5 would be
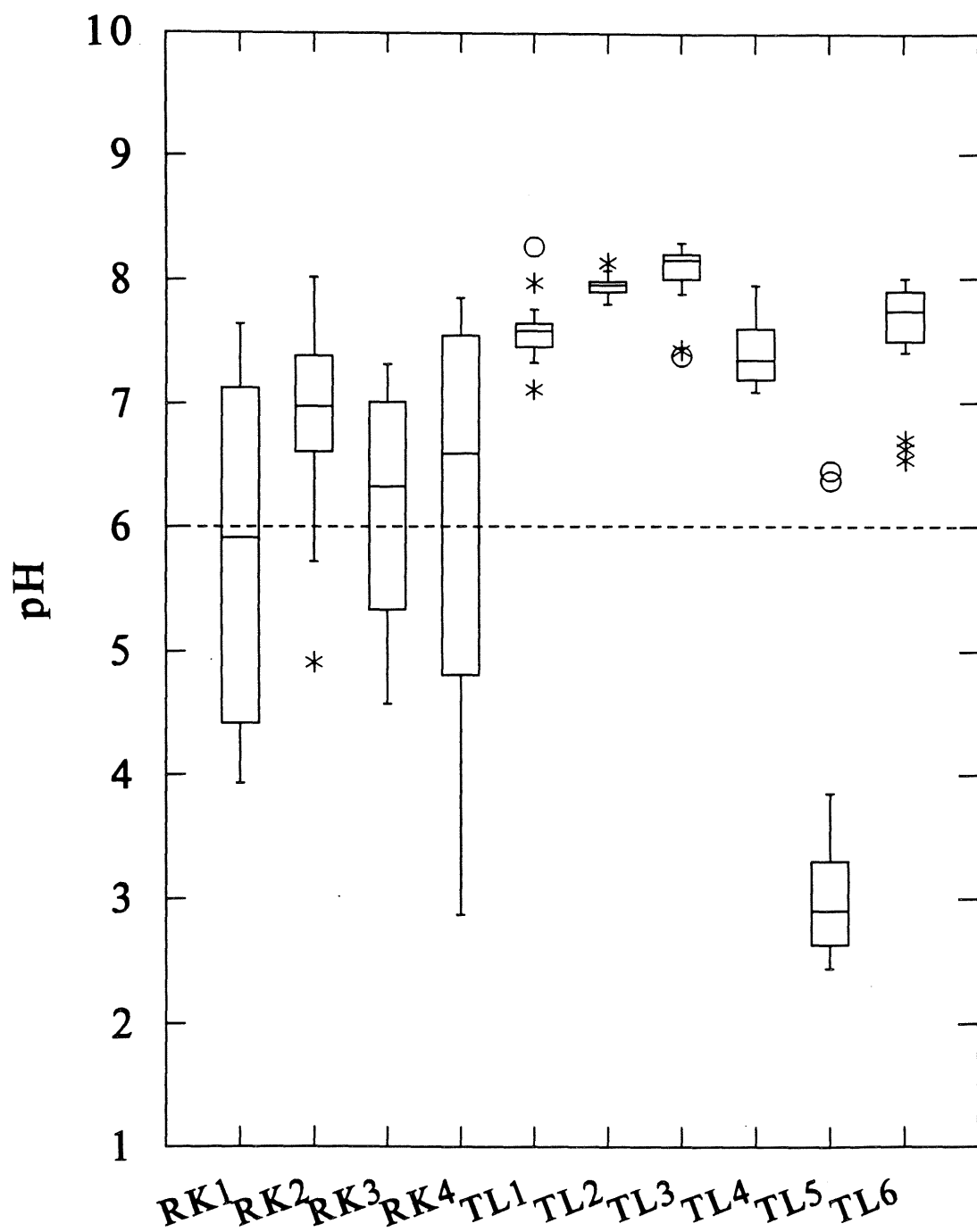
Figure 10. pH box plot for Elevated Temperature Test.

Table 11.   Elevated Temperature Test: percent sulfur and NP release, and molar ratio of calcium plus magnesium release to sulfate release[1].

Parameter, units	RK1	RK2	RK3	RK4	TL1	TL2	TL3	TL4	TL5	TL6
% sulfur[2]	38.788	5.005	10.475	28.181	6.774	9.352	9.727	2.855	22.011	16.375
% NP[3]	41.33	5.63	33.80	101.79	14.82	48.4	24.13	91.58	164.0	40.0
$(Ca+Mg)/SO_4$[4]	1.01	2.38	0.982	1.14	2.29	2.25	1.91	2.62	0.237	1.40

[1] MN DNR
[2] Percentage of total sulfur initially present in mine waste which was released from week 0 to week 20.
[3] Percentage of total NP initially present in mine waste which was released from week 0 to week 20.
[4] For weeks 1 - 20 (excluding rinse prior to test).

Figure 11. pH box plot for Soxhlet Test.

classified as a strong acid producer and RK2 as a mild acid producer. The remaining samples would not be identified as acid producing based on drainage pH alone.
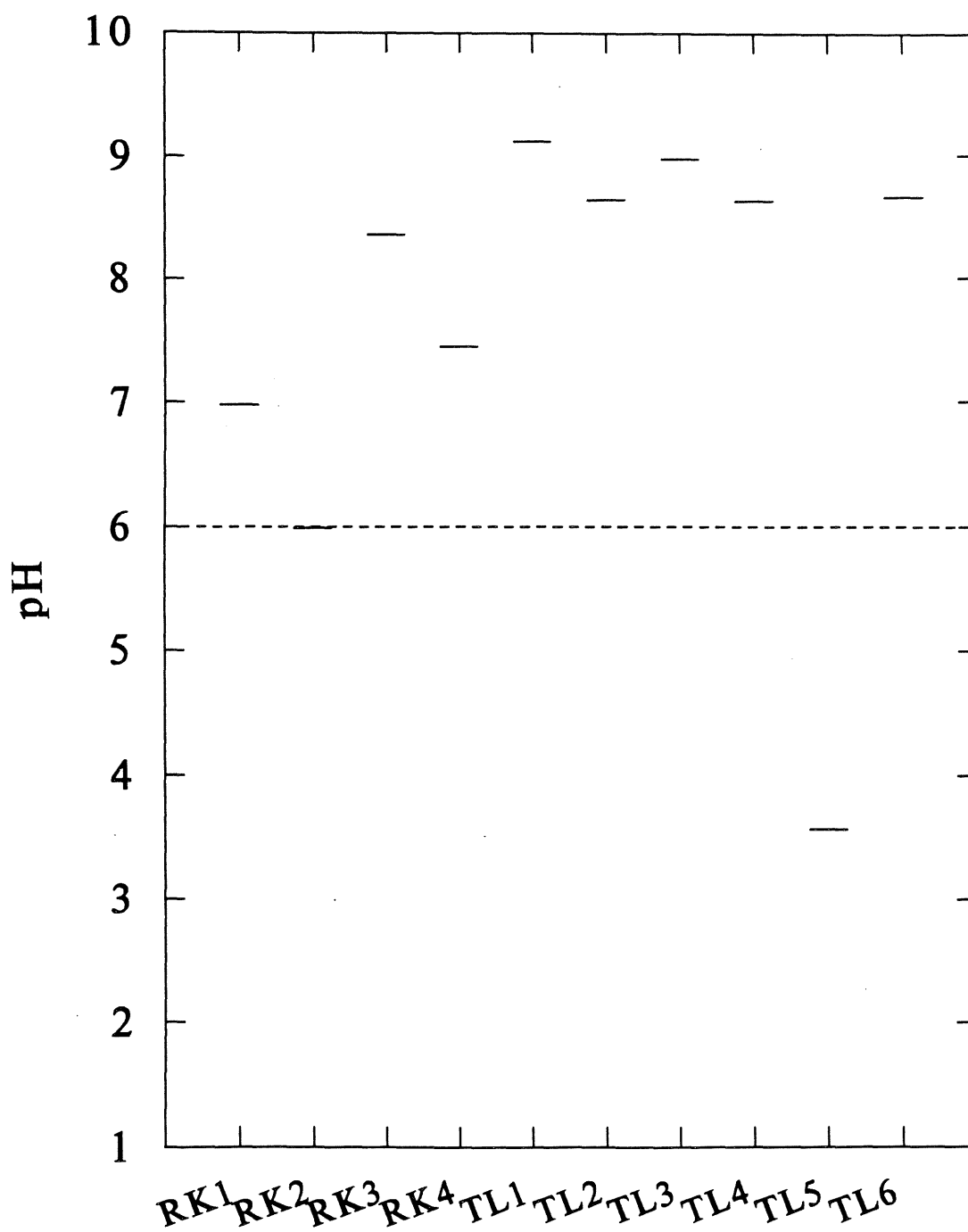
The actual sulfide oxidation and carbonate mineral dissolution in the Soxhlet Test may have been higher than that indicated by the sulfate, calcium, and magnesium observed in the drainage. In this test the components release from the samples accumulate in solution, as opposed to being removed with regular rinses. In particular, sulfate and calcium concentrations may increase to the point at which calcium sulfate precipitates. The probability of calcium sulfate precipitation increased with the rate of sulfide oxidation. If calcium sulfate precipitates from the drainage, some of the sulfate and calcium released from the solid is not accounted for by drainage analysis for these parameters.

The sulfate observed in the drainage from RK1 represented 16 percent of the sulfur initially present in the rock, while the associated values for the other samples ranged from one to five percent (table 12). The contractor commented that "test results suggest that the soxhlet procedure does not allow sufficient oxygen for rapid sulfur oxidation, necessary to generate acid." The calcium and magnesium concentrations in the drainages from TL5 and TL4 represented 55 and 47 percent, respectively, of the NP (ABA method) initially present in these samples. The associated values for the remaining samples ranged from one to five percent of the initial NP.

The precipition of calcium sulfate from the TL5 drainage is highly likely. The drainage was strongly acidic, indicating the NP had been depleted, yet the concentrations of sulfate, calcium, and magnesium indicated only 55 percent NP depletion. Furthermore, the release of magnesium from TL5 was about 1.3 times that of calcium on a molar basis. In the previously discussed tests the release of these parameters was roughly equal. The higher relative magnesium release in this test is consistent with the precipitation of calcium sulfate from the drainage.

The molar ratios in this test were generally between 0.7 and 1.2. The potential for precipitation of calcium sulfate, as well as the release of significant amounts of other cations and anions, in this test makes interpretation of these ratios difficult.

The only acidic pH values in the **Shake Flask Test** were generated by TL5, for which pH was initially around 5.0 and decreased to approximately 3.2 after week 13. The pH values associated with the remaining samples were all in the neutral to basic range (figure 12).

As with the Soxhlet Test, the sulfate and calcium in solution may have been less that that released from the mine wastes, due to precipitation of calcium sulfate. In particular, the calcium and sulfate concentrations associated with TL6 appeared to be controlled by calcium sulfate precipitation. The sulfate and calcium concentrations were fairly stable at about 1600 and 700 mg/L, respectively. (Assuming these values represent equilibrium conditions, and ignoring ionic strength influences yields log k_{so} = -3.54.)

Table 12. Soxhlet Test: percent sulfur and NP release, and molar ratio of calcium plus magnesium release to sulfate release[1].

Parameter, units	RK1	RK2	RK3	RK4	TL1	TL2	TL3	TL4	TL5	TL6
% sulfur[2]	16.017	5.155	3.184	4.238	4.905	5.052	4.271	2.702	3.260	1.290
% NP[3]	14.08	1.63	9.47	14.89	6.50	11.72	4.57	46.58	54.8	4.66
$(Ca+Mg)/SO_4$[4]	0.734	0.555	0.878	1.08	1.20	0.898	0.719	0.912	0.8	1.97

[1] BC Research
[2] Percentage of total sulfur initially present in mine waste which was released from week 0 to week 6.
[3] Percentage of total NP initially present in mine waste which was released from week 0 to week 6.
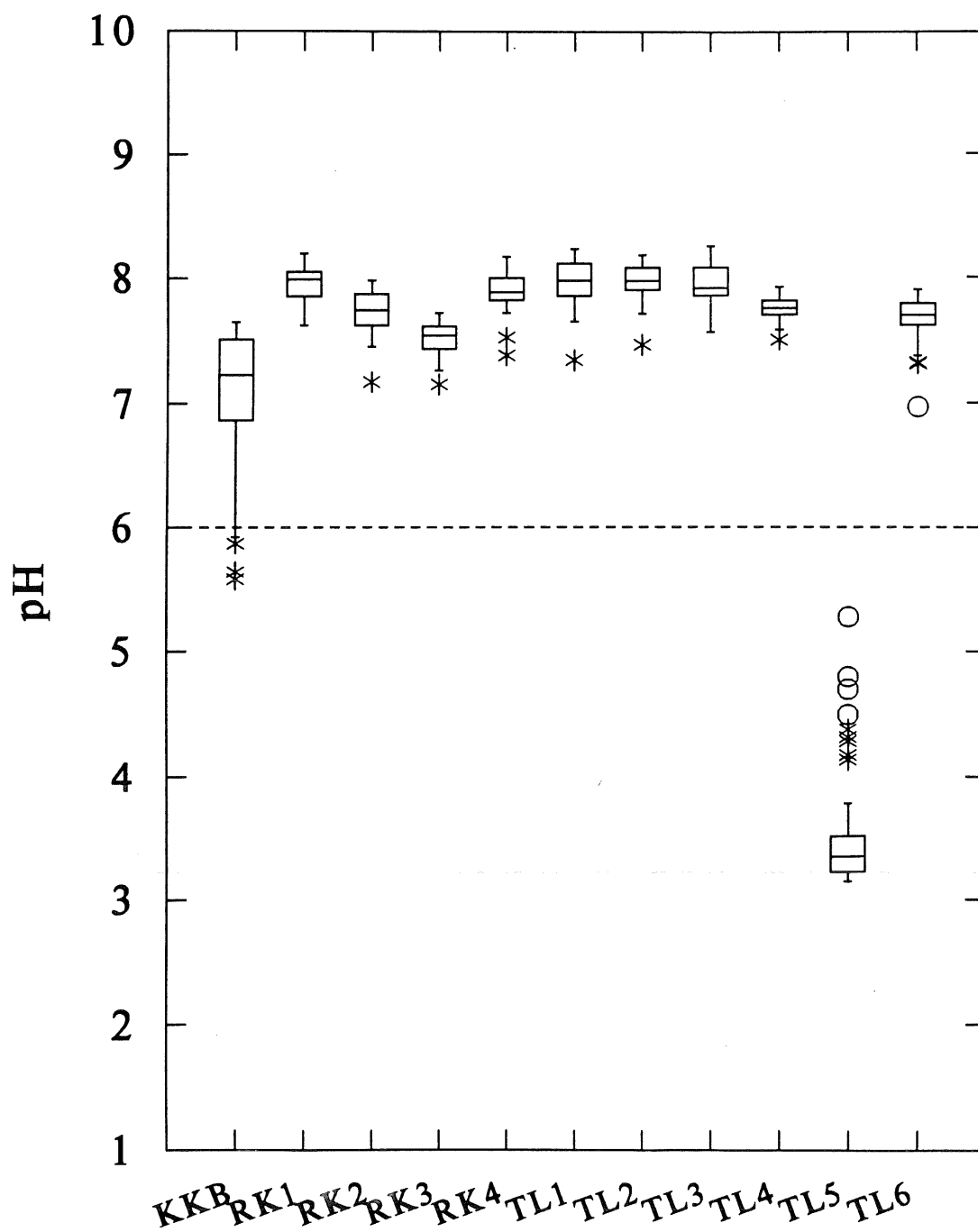[4] For weeks 0 - 6 (samples were not rinsed prior to test).

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Figure 12. pH box plot for Shake Flask Test.

The sulfate observed in solution represented three to nine percent of the sulfur present in the mine waste samples. The actual range for the extent of sulfide oxidation was probably slighly higher, since calcium sulfate precipitation most likely occurred from the solution associated with TL6. The calcium and magnesium observed in solution represented 130 percent of the NP initially present in TL5, which is consistent with the acidic solution generated by this sample. The apparent NP release from TL4 was approximately 65 percent of that initially present, while the associated value for the remaining samples was less than 20 percent (table 13).

The molar ratios in this test were generally between 0.7 and 1.1, roughly similar to those in the Soxhlet Test. For reasons cited for the Soxhlet Test, interpretation of these ratios difficult.

5.3.3. Comparison of Kinetic Tests with Verification Data

The drainage pH values for the five **tests on tailings** were in general agreement. (The Modified Humidity Cell Test was not conducted on the tailings samples.) All tests identified sample TL5 as a strong acid producer. The water associated with these tailings was neutral during during mine operation, but drainage from a test plot dropped to the range of 2.5-3.0 after a year or two. The Soxhlet and Shake Flask Tests provided values slighly higher than this range while the Standard Humidity Cell produced some drainage pH values below this range (figure 13). Despite these quantitative differences, the drainage pH data from all tests would identify this sample as a strong acid producer.

With the exception of a single value from the Standard Humidity Cell Test, the remaining tailings generated drainage pH values above pH 6.0. The typical drainage pH range was 7.5 to 8.0, although the Soxhlet Test values were higher (figure 13). This was in general agreement with the basic pH values reported for these tailings in the field.

However, the validity of predictive tests for the long-term drainage from tailings can not be verified conclusively based on tailings basin water quality during operation. The pH in operational systems is likely to be alkaline irrespective of the tailing composition due to "the continuous alkaline addition and flooded nature of the waste" (Ferguson, 1991). Mineral processing often adds alkaline chemicals to the basin, and the submerged environment inhibits oxidation of the sulfide minerals (Ritcey, 1991).

Consequently, the water quality from operational tailings basins does not necessarily represent the drainage quality after closure. After closure there will be no alkaline mineral processing inputs, and the basin may be drained thereby exposing the tailings to the atmosphere. For example, the water in the basin containing the TL5 tailings had a pH of around 10 and the drainage pH from the tailings was near seven. However, after one to two years in a non-submerged field test plot receiving no operational inputs, the pH of pore water in the tailings dropped below 3.0.

Table 13.   Shake Flask Test: percent sulfur and NP release, and molar ratio of calcium plus magnesium release to sulfate release[1].

Parameter, units	RK1	RK2	RK3	RK4	TL1	TL2	TL3	TL4	TL5	TL6
% sulfur[2]	7.451	5.906	3.007	4.502	4.204	2.924	6.246	3.301	5.677	8.987
% NP[3]	8.33	2.64	8.00	10.86	5.96	10.17	10.37	65.0	132.27	19.8
$(Ca+Mg)/SO_4$[4]	0.973	0.775	0.732	0.589	1.15	1.12	1.10	0.945	0.924	1.12

[1] MN DNR
[2] Percentage of total sulfur initially present in mine waste which was released from week 0 to week 20.
[3] Percentage of total NP initially present in mine waste which was released from week 0 to week 20.
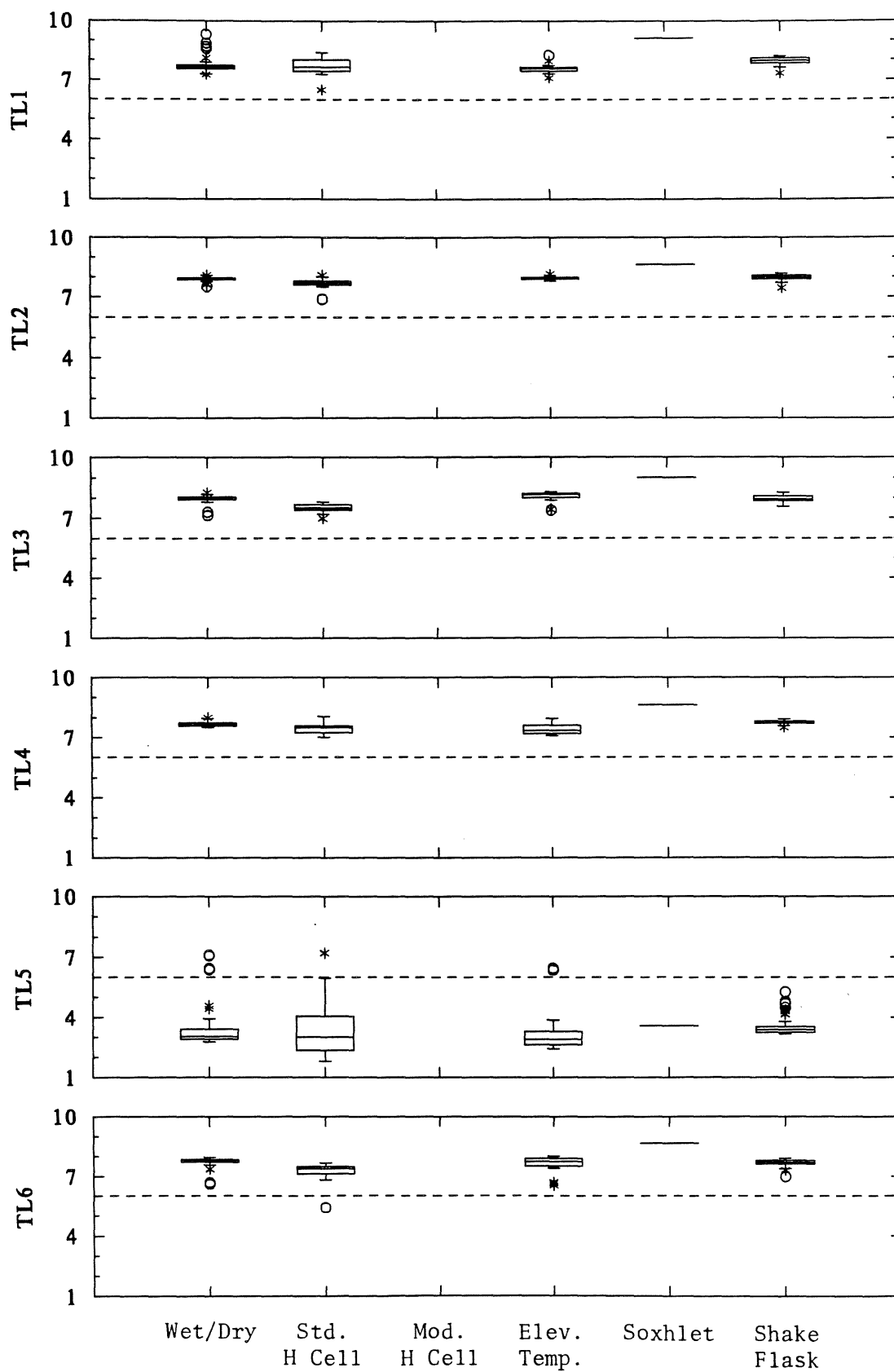[4] For weeks 1 - 20 (excluding rinse prior to test).

Figure 13. pH box plots for tailings samples.

Secondly, the extent of mineral dissolution in the kinetic tests was low, indicating that the samples could produce additional acid. Typically less than ten percent of the sulfur present in these five tailings was oxidized during the kinetic tests (table 14). On an average, about 94 percent of the sulfur originally in these tailings was present at the end of the test. The percentage of NP released during the tests was considerably higher. If the test durations had been longer, sulfide oxidation and the consequent acid production would most likely have continued. Such additional acid production may have depleted the remnant NP with a consequent acidification of the drainage. This appears most likely for sample TL4, for which the NP depletion ranged from about 45 to over 90 percent (table 15), while over 96 percent of the sulfur remained at the end of the test (table 14). However, the slow sulfide oxidation associated with TL4 lends uncertainty to this speculation.

The Elevated Temperature Test produced the greatest degree of sulfide oxidation for all tailings except for TL4, for which all tests oxidized about three percent of the sulfur present. Similarly, the Elevated Temperature Test provided the greatest degree of NP release for all solids. The extent of sulfide oxidation in the remaining test was similar for samples TL1 - TL4. However, for the samples with higher sulfur contents the Wet-Dry Cycle Tests produced a greater degree of sulfide oxidation than the other three tests. This may have been partly due to the method of calculating sulfide release based on the observed release of sulfate to solution. The precipitation of calcium sulfate may have limited the observed sulfate concentrations, and underestimated the actual rate of sulfide oxidation in the Soxhlet and Shake Flask Tests. Sulfur analyses of the fresh and leached solids from these tests were in fairly good agreement with the calculations based on sulfate release to solution.

The accelerated sulfide oxidation observed for most of the tailings in the Elevated Temperature Test is a positive feature. However, this test may also disproportionately accelerate carbonate mineral dissolution. For most of the tailings which generated neutral drainage (all samples except TL5), the molar ratio of calcium plus magnesium release to sulfate release was quite high (table 16). This indicates that the conditions of this test may unrealisticly accerlerate carbonate mineral dissolution as suggested by Bradham and Caruccio (1990). However, the benefit of reducing the time required for predictive testing may outweigh the degree to which carbonate mineral dissolution is biased.

For the waste rock samples, verification data were available only for three of the samples. RK2 produced a drainage pH in the range of 4.7 to 5.3. A pH of 4.9 was measured for a single sample of surface drainage from pile containing RK3, while sample RK4 generated drainage of pH 3 in large scale column tests.

The Wet-Dry Cycle and the Shake Flask Tests typically produced the highest drainage pH values, while the Modified Humidity Cell and the Elevated Temperature Test produced the lowest values (figure 14). Using the observed drainage pH alone as a predictor, the Wet-Dry Cycle and the Shake Flask Tests would have concluded all four rocks would not produce acidic drainage. The Soxhlet Extraction Test yielded a final drainage pH of 5.99 for sample RK2, suggesting a mild tendency for acid production. Although samples RK1

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Table 14.   Percent sulfur release, weeks 0 - 20.

Sample	Wet-Dry[1]	Standard Humidity Cell[2]	Modified Humidity Cell[3]	Elevated Temperature[4]	Soxhlet[5]	Shake Flask[6]
RK1	8.496	9.540	9.123	38.788	16.017	7.451
RK2	7.858	3.859	2.423	5.005	5.155	5.906
RK3	4.324	3.085	2.496	10.475	3.184	3.007
RK4	5.471	5.097	7.607	28.181	4.238	4.502
TL1	3.737	5.572	NT[7]	6.774	4.905	4.204
TL2	2.924	2.795	NT	9.352	5.052	2.924
TL3	7.533	9.259	NT	9.727	4.271	6.246
TL4	2.897	3.357	NT	2.855	2.702	3.301
TL5	13.488	10.783	NT	22.011	3.260	5.677
TL6	15.052	5.955	NT	16.375	1.290	8.987

[1] MN DNR
[2] University of South Carolina
[3] Lawrence
[4] MN DNR
[5] B.C. Research. Test duration was 6 weeks with no initial rinse.
[6] MN DNR. Test duration was 21 weeks.
[7] NT = Not Tested

Table 15.   Percent NP released, weeks 0 - 20.

Sample	Wet-Dry[1]	Standard Humidity Cell[2]	Modified Humidity Cell[3]	Elevated Temperature[4]	Soxhlet[5]	Shake Flask[6]
RK1	14.75	15.17	7.26	41.33	14.08	8.33
RK2	4.11	1.77	0.931	5.63	1.63	2.64
RK3	16.27	7.80	4.05	33.80	9.47	8.00
RK4	22.25	19.18	13.7	101.79	14.89	10.86
TL1	8.37	8.19	NT[7]	14.82	6.50	5.96
TL2	25.17	10.56	NT	48.4	11.72	10.17
TL3	15.74	15.17	NT	24.13	4.57	10.37
TL4	79.74	71.05	NT	91.58	46.58	65.0
TL5	169.33	130.27	NT	164.0	54.8	132.27
TL6	35.46	11.41	NT	40.0	4.66	19.8

[1] MN DNR
[2] University of South Carolina
[3] Lawrence (Lawrence data for Ca and Mg).
[4] MN DNR
[5] B.C. Research. Test duration was 6 weeks with no initial rinse.
[6] MN DNR. Test duration was 21 weeks.
[7] NT = Not Tested

Table 16.   Ratio of calcium and magnesium to sulfate release (mmole) weeks 1 - 20.

Sample	Wet-Dry[1]	Standard Humidity Cell[2]	Modified Humidity Cell[3]	Elevated Temperature[4]	Soxhlet[5]	Shake Flask[6]
RK1	2.10	1.42	0.919	1.01	0.734	0.973
RK2	0.984	0.797	0.666	2.38	0.555	0.775
RK3	1.36	0.853	0.823	0.982	0.878	0.732
RK4	1.59	1.14	0.655	1.14	1.08	0.589
TL1	3.03	1.52	NT[7]	2.29	1.20	1.15
TL2	4.75	1.66	NT	2.25	0.898	1.12
TL3	1.59	1.10	NT	1.91	0.719	1.10
TL4	2.02	1.30	NT	2.62	0.912	0.945
TL5	0.432	0.531	NT	0.237	0.800	0.924
TL6	1.31	1.06	NT	1.40	1.97	1.12

[1] MN DNR
[2] University of South Carolina
[3] Lawrence
[4] MN DNR
[5] B.C. Research. Weeks 0 -6. Test duration was 6 weeks with no initial rinse.
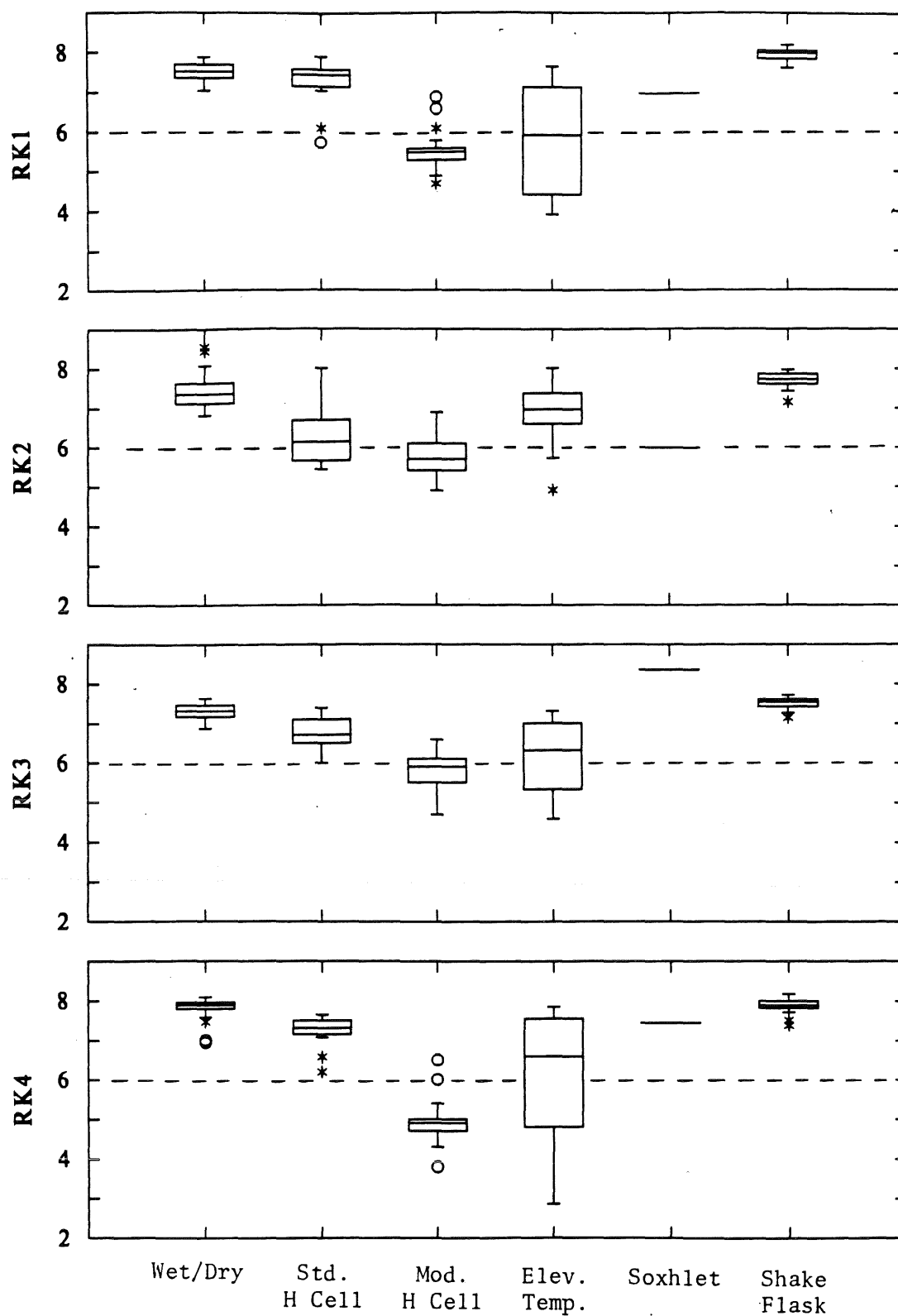[6] MN DNR. Test duration was 21 weeks.
[7] NT = Not Tested

Figure 14. pH box plots for waste rock samples.

and RK2 produced some mildly acidic drainage in the Standard Humidity Cell the contracter described these samples as "non-problematic". Nontheless the Standard Humidity Cell Test did indicate that these samples had the potential to produce some mildly acidic drainage.

All four samples produced some acidic drainage in both the Modified Humidity Cell and the Elevated Temperature Tests, and these two tests most closely approximated the verification pH data. The reason for low pH drainage can be either elevated acid production or decreased acid consumption.

With the Modified Humidity Cell Test the low drainage pH values were the result of decreased acid consumption. The sulfide oxidation rate in the Modified Humidity Cell was roughly equal to or less than that in the Wet-Dry Cycle Test (table 14), however the associated NP release was 25 to 50 percent of that in the Wet-Dry Cycle Test (table 15). These differentials were related to the influence of particle size reduction on the relative rates of acid production and acid consumption. The one kilogram rock samples used in the Modified Humidity Cell were used as received from the MN DNR, with the particle size indicated in table 2. In the Wet-Dry Cycle Test (as well as the Elevated Temperature Test and Shake Flask Test), which uses only 75 g, the samples were crushed to minus 100 mesh. More than 50 percent of each rock sample was finer than 0.053 mm (appendix 2).

Mineralogical analyses indicated that the sulfide minerals present in the larger particles of RK1, RK3, and RK4 were exposed and, therefore, available for oxidation reactions (section 5.1). Reducing the particle size of these samples did not enhance the oxidation of sulfides in these samples, as indicated by comparison of the sulfate release in the Modified Humidity Cell and the Wet-Dry Cycle Test (table 14). However, the NP release was increased by the particle size reduction in the Wet-Dry Cycle Test (tables 15, 16). The reduction in particle size increased the surface area of carbonates, and apparently silicates, such that their dissolution was substantially enhanced. The Modified Humidity Cell more realistically simulated the occurrence of the carbonates in the larger rock particles. Consequently, the buffering mineral dissolution was slower and the drainage pH more closely simulated that observed in the verification tests. Such results emphasize the importance of determining the mode of sulfide mineral and carbonate mineral occurrence when selecting the particle size of waste rock samples to be tested.

The minimum drainage pH values in Elevated Temperature Test were lower than those for the Modified Humidity Cell Test for all waste rock samples except RK2. For these three samples the sulfate release in the Elevated Temperature Test was about four times that in the Modified Humidity Cell Test. This indicates that accelerated acid production depressed the pH of drainage in the Elevated Temperature Test (table 14).

The accelerated oxidation of sulfides present in RK1, RK3, and RK4 was largely the result of the reaction temperature of 100°C in this test. The particles used in the Elevated Temperature Test were -100 mesh and this enhance sulfide oxidation. However, particles

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of similar size were used in the Wet-Dry Cycle Test, and the sulfate release in this test was similar to that in the Modified Humidity Cell Test (table 14). Thus, the majority of the acceleration of sulfide oxidation was the result of the high temperature.

The higher temperature reaction conditions did not accelerate the oxidation of all mine waste samples, as indicated by the comparison of sulfide oxidation rates in the Wet-Dry Cycle Test and the Elevated Temperature Test (table 17). For samples RK1 and RK4 the sulfide oxidation rate at the higher temperature was roughly eight times that at the lower temperature. However, for RK2 the oxidation was actually higher at the lower temperature.

The reason for the variable effect of temperature on sulfide oxidation is probably related to the composition of sulfide minerals in the tailings. The acceleration was highest for samples containing marcasite, and generally lowest for sample in which pyrrhotite was the dominant sulfide. (The influence of temperature on the oxidation rate of sulfides present in TL5 is difficult to assess. This sample generated low pH drainage in both tests, and the low pH may have been the dominant influence on the sulfide oxidation rate at low and high temperature.) The influence of temperature on the sulfide oxidation rate may also be influenced by other sulfide compositional variables, such as the temperature of sulfide crystalization. Additional study would be required to more accurately describe the effect of temperature on the oxidation of sulfides of different compositions.

It is somewhat unusual that the apparent rate of sulfide oxidation did not increase with temperature for all samples. It is possible that while sulfide oxidation was enhanced at higher temperatures, reactions inhibiting this oxidation may have been similarly accelerated. For example, the formation of iron oxyhydroxide coatings on the pyrrhotite mineral surfaces may have been accelerated and contributed to the reduced pyrrhotite oxidation rate. Iron precipitates may be more likely to form on pyrrhotite surfaces than on pyrite surfaces due to a higher pH at the mineral surface. With pyrrhotite oxidation the acid produced per mole of iron oxidized is half that for pyrite (reactions 1, 2).

It is clear that the Elevated Temperature Test can substantially accelerate the weathering of some mine wastes, however, previously identified concerns (Bradham and Caruccio, 1990) were also encountered with this test. The test may disproportionately accelerate carbonate mineral dissolution, as indicated by the ratio of carbonate mineral dissolution to iron sulfide oxidation. Second, problems with inhibited flow were encountered. Third, although the overall pH values between duplicate reactors was similar, the pH values for a given week were not highly reproducible. These are all questions which must be addressed but by no means indicate that this is not a viable predictive test.

Table 17. Influence of elevated temperature on the apparent rate of iron sulfide oxidation.

Sample	Factor[1]	S %	SO$_4$ %	Pyrite %	Marcasite %	Pyrrhotite %	Formation T °C	Type
RK4	8.7	2.82	0.09	5.16	0.16	0	150-180	Hydrothermal
RK1	8.6	0.42	0.04	0.74	0.02	0.03	Ambient	Sedimentary
TL2	5.0	1.45	0.04	2.60	0.08	0	>800	Hydrothermal
RK3	3.6	1.60	0.03	2.43	0	0	170-330	Hydrothermal
TL1	3.1	0.90	0.06	1.58	0	0	>800	Hydrothermal
TL5[2]	1.8	4.85	0.20	8.17	0.95	0	100-300	Hydrothermal (Epithermal)
TL3	1.5	2.12	0.07	1.08	0	4.30	100-300	Hydrothermal
TL6	1.2	5.18	0.63	1.93	0	10.9	220-550	Hydrothermal
TL4	.98	2.10	0.20	3.68	0	0	250-550	Hydrothermal
RK2	.51	0.63	0.01	0	0	0.64	800-1000	Intrusive

[1] Ratio of sulfate release rate in Elevated Temperature Test to that in Wet-Dry Cycle Test, dimensionless.
[2] This sample generated acidic drainage in both Elevated Temperature and Wet-Dry Cycle Test.

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6. SUMMARY

Ten mine waste samples were subjected to four static tests and six kinetic tests to evaluate the ability of the tests to predict mine waste drainage pH. The particle size distribution, chemistry, and mineralogy of the samples were analyzed to improve interpretation of predictive test results. Static tests base drainage quality prediction on measurements of the maximum capacity of a mine waste to produce acid (Acid Production Potential) and consume acid (Neutralization Potential). To predict drainage quality based on these values it is necessary to assume relative rates of acid production and extents to which acid producing and acid consuming minerals will dissolve. As mentioned in previous publications by Ferguson and others, these test should not be used alone for prediction unless there is a large difference between the APP and NP.

Accepting the aforementioned assumptions as necessary for static tests, this study addressed the accuracy of Acid Base Accounting, Modified Acid Base Accounting, and the B. C. Research Initial Tests for quantifying APP and NP. The maximum potential acid production by a mine waste is dependent on the sulfur species present, and accurate analyses of the sulfur species present will allow determination of this value. Analytical tools are available for such analyses. The sulfur species present will vary among mine wastes and less rigorous analytical techniques are adequate if the sulfide mineralogy of a waste is simple. Similarly, less rigorous analyses are adequate if the improved accuracy in APP measurement does not greatly influence the static test evaluation. That is, the improved accuracy does not affect the conclusion based on the Net NP or NP to APP ratio.

The ABA and Modified ABA NP values were in fairly close agreement, and the B. C. Research Initial NP was typically higher than these values. The NP measurements in these tests all measure the amount of acid a sample can consume and maintain a pH of 3.5 or less. All three of the static tests tended to overestimate the NP available as calcium carbonate and magnesium carbonate. This suggests that the static test NP values overestimate the NP available to maintain a drainage pH above 6.0. This overestimation was typically about 10 kg $CaCO_3$/t, and was apparently due to the presence of calcium feldspar in the samples. For the ABA and Modified ABA methods the overestimation was higher yet for samples containing pyroxene, olivine, or iron carbonate minerals. The extent of overestimation for the B. C. Research Initial NP was greatest for samples containing iron carbonate.

Acid titration of a mixture of a mine waste sample and distilled water down to pH 6.0 yielded NP values consistent with those determined based on the calcium carbonate and magnesium carbonate content. For the 10 samples examined, this titration appears to be a reasonable and, generally more conservative, method of determining the neutralization potential available for maintaining drainage pH above 6.0. The titration also overestimated the Neutralization Potential based on calcium carbonate and magnesium carbonate content for a sample with an elevated iron carbonate content. However, the magnitude of this overestimation was less than that for the static tests. This potential error could be reduced

by following the titration to pH 6.0 with filtration, and titrating the filtrate to pH 8.3. This would greatly reduce or eliminate false contributions to NP by iron bearing minerals, particularly iron carbonates. Additional data on this technique will better assess its accuracy.

A modification of the Net Acid Production Test compared favorable with the Net NP values determined by the aforementioned static tests. Increase peroxide addition oxidized at least 95 percent of the sulfur present in the four samples examined. The method would be further improved by titrating the resultant solution to pH 8.3 rather than pH 7.0, to reduce the aforementioned interference from iron carbonates. This modification may be highly beneficial for analyzing mine wastes in the field, although additional study is needed.

The Modified Humidity Cell (Lawrence, 1990) and Elevated Temperature Test (modified from Renton, 1983; Renton et al., 1985; 1988) most closely simulated the available verification pH data. The Modified Humidity Cell test was conducted only on waste rock samples, and its accuracy was attributed to the larger particle size used in the test. The accuracy of the Elevated Temperature Test was due to the acceleration of sulfide oxidation and the attendant acid production.

All tests simulated the field drainage pH from a sample with a reasonably high sulfur content and an NP near zero. In general, the sulfide oxidation and attendant acid production during most tests was not adequate to overcome the buffering available in samples with a moderate amount of NP. This concern has been raised previously by Ferguson. Indeed, less than ten percent of the sulfide present in the samples was oxidized over the course of the tests. This underlines the importance of considering the solid phase characteristics, particularly the NP, of samples when designing kinetic test programs. This applies to the Modified Humidity Cell and the Elevated Temperature Tests as well as the less accurate tests in this study.

The Modified Humidity Cell Test has the benefit of accounting to some degree for the particle size of waste rock. The results for the samples examined were quite good. The actual size distribution of field wastes in general and the mode of occurrence of sulfide and carbonate minerals must be considered to accurately simulate field drainage from waste rock.

The accelerated sulfide oxidation provided by the Elevated Temperature Test yields the benefit of potentially reducing the time required for predictive tests. Some problems with flow through samples and drainage pH reproducibility were encountered with this test. Dissolution of carbonate minerals may also have been disproportionately accelerated. These concerns require additional examination.

The pH of drainage in the Standard Humidity Cell test were somewhat indicative of verification drainage pH data for two of the waste rock samples. The influence of the

continual humid condition of this test, as opposed to the partial drying of samples in the Modified Humidity Cell Test, warrants consideration. The Soxhlet Test results might be improved by limiting the accumulation of reaction products in the drainage. This could be done by draining the leachate more frequently and replacing it with fresh distilled water. This would improve the ability to quantify dissolution rates sulfide and carbonate minerals.

The Shake Flask and Wet-Dry Cycle test accuracy was limited in part by the small particles used in the experiment. The high degree of very fine material artificially enhance the NP of the solids. The use of coarser material in these tests would tend to improve results.

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