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Long Term Dissolution Testing of Mine Waste

Report to the United States
Environmental Protection Agency

Minnesota Department of Natural Resources
Division of Minerals

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1. INTRODUCTION

Kinetic testing is one tool used for the prediction of mine waste drainage quality. In these tests mine waste samples are subjected to dissolution in the laboratory, and drainage quality observed is used to predict the quality of drainage from mine wastes in the field. This concept has been likened to metallurgical testing of drill core samples to predict metal recovery from an ore body (Lapakko 1990a). However, mine waste drainage quality prediction may be more complicated than metallurgical testing due to, among other factors, the long time over which mine waste drainage quality is of concern (Lapakko 1990a). Lawrence et al. (1989) recognized the difficulty in using short duration tests to predict drainage quality over a longer time period, stating "The prediction of long term weathering characteristics of a tailing or waste rock will always have some uncertainty factor if the prediction test is carried out on a practical time scale in the laboratory."

The drainage from sulfidic rock (or tailings) will become acidic if the rate of acid production exceeds the rate of acid neutralization. Drainage generated in a kinetic test may be acidic immediately or within the test duration, and the sample can be classified as an acid producer. If the drainage is not acidic for a specific test duration (e.g. 12 weeks, 20 weeks, 40 weeks, etc.), it might remain so if the test were continued indefinitely. That is, the drainage would remain neutral until all the acid-producing minerals were depleted. However, drainage could become acidic if the test were continued for a longer period. This would occur if the acid-neutralizing minerals were depleted while acid-producing minerals remained and oxidized. Consequently, a kinetic test on a sample that produces non-acidic drainage 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 potential to neutralize acid (neutralization potential or NP) its initial drainage will probably be neutral, since the dissolution of minerals contributing to NP will neutralize the acid produced by iron sulfide oxidation. As acid production continues (i.e., iron sulfide oxidation continues) the rate of acid neutralization may decrease with an attendant decrease in drainage pH. The period between the initiation of dissolution and acidification of drainage has been referred to as the lag period. The rate of acid neutralization will decrease if the effective acid-neutralizing minerals approach depletion, or if coatings form on the surface of these minerals. If the NP is depleted or rendered unreactive while a significant amount of reactive iron sulfide minerals remains, the drainage will become acidic. In contrast, if coatings form on the iron sulfide minerals and the rate of iron sulfide oxidation is adequately inhibited, the drainage will not acidify.

Empirical demonstration of a lag period may require 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 neutralization 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.

The time required to deplete the acid production potential (APP) and the NP has been estimated using the APP and NP of the mine waste and the rates of acid production and acid neutralization observed in kinetic tests (Lapakko 1990b). This estimation was used to predict the acidification of drainage under laboratory conditions. The estimation neglected the effects of coating formation on acid-producing and acid-neutralizing minerals, since it is presently not possible to quantitatively model this formation with the accuracy required to predict the effects on drainage quality. Consequently, the quality of drainage from some abandoned mine wastes over the long term can be assessed only through extended dissolution studies.

The present study employed long term laboratory studies to examine the dissolution of abandoned mine wastes and the consequent drainage quality. Two dissolution experiments conducted under a previous grant (Agreement #CX-816270-01-0) were continued beyond the 20-week time frame initially funded to obtain a test duration of 132 weeks. The Wet-Dry Cycle Test was conducted under approximately ambient indoor conditions, and the Elevated Temperature Test was conducted in an oven maintained at 100°C. The present study also examined the effects of waste rock particle size on drainage quality.

Additional information on the four waste rock (RK1 - RK4) and six tailings (TL1 - TL6) samples examined in this study is presented in Lapakko (1993). In addition to the results of the initial testing, the reader is referred to Lapakko (1993) for information on mine waste dissolution chemistry which may facilitate the uninitiated reader's understanding of the present report. Selected information from the earlier report is reiterated for the convenience of the reader. A literature review on predictive testing for mine waste drainage quality is also available (Lapakko 1991).

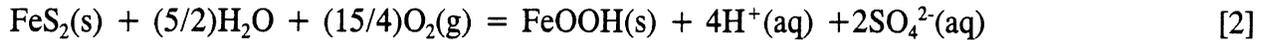
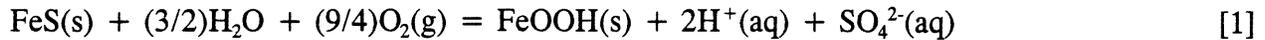
2. OBJECTIVES

The objectives of this study were as follows.

1. Provide a description of longer term dissolution of mine wastes,
2. Provide data which will facilitate interpretation of shorter term predictive tests,
3. Examine the extent to which acid-producing and acid-consuming components of mine waste will dissolve in the laboratory, and
4. Examine the effect of particle size on the dissolution of the mine waste.

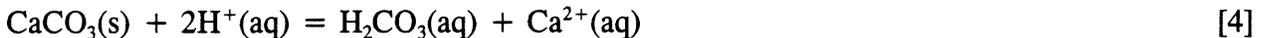
3. BACKGROUND CHEMISTRY

The majority of acid production by mine wastes is due to oxidation of iron sulfide minerals. As indicated by reaction 1 (Nelson 1978) and reaction 2 (Stumm and Morgan 1981). Two moles of acid are produced for each mole of sulfur oxidized.

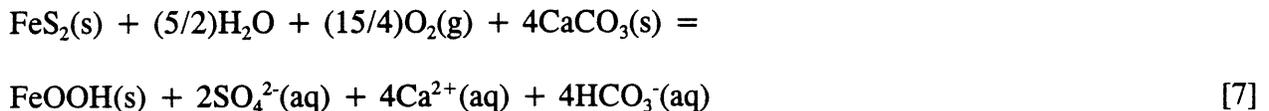


Dissolution of sulfate minerals such as melanterite and jarosite will also produce acid. It should be noted that the solubility of jarosite is slight, except at low pH. As was the case for the sulfide minerals, the dissolution of melanterite yields two moles of acid per mole of sulfate dissolved. In contrast, the dissolution of jarosite yields 1.5 moles of acid per mole of sulfate dissolved. The dissolution of sulfate minerals such as gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), anhydrite (CaSO_4), or barite (BaSO_4) will not produce acid.

The most effective minerals for neutralizing (consuming, buffering) acid are those containing calcium carbonate and magnesium carbonate, examples of which are calcite, magnesite, dolomite, and ankerite (CaCO_3 , MgCO_3 , $\text{CaMg}(\text{CO}_3)_2$, $\text{CaFe}(\text{CO}_3)_2$, respectively). Dissolution of calcium and magnesium carbonate components neutralizes acid (reactions 3-6). Reactions 3 and 5 are dominant above approximately pH 6.3, while reactions 4 and 6 are dominant below this pH.



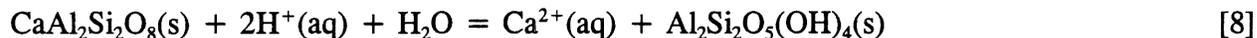
If both iron sulfide minerals and calcium carbonate or magnesium carbonate minerals are present in mine wastes, the net reaction of the mine waste can be expressed as the sum of acid producing and acid neutralizing reactions. For example reaction 7 is the sum of reactions 2 and 3. The reaction represents concurrent pyrite (FeS_2) oxidation and calcite (CaCO_3) dissolution releasing sulfate, calcium, and alkalinity to solution, and generating FeOOH(s) as a solid-phase reaction product.



When both iron sulfide and calcium/magnesium carbonate minerals are present, the drainage will remain neutral to alkaline as long as the rate of acid neutralization equals or exceeds the rate of acid generation. If the reactive iron sulfide minerals are depleted or rendered unreactive while calcium/magnesium carbonate minerals remain, the drainage will not acidify. If the carbonate minerals are rendered unreactive or depleted while reactive iron sulfide minerals remain, the drainage will acidify. The time required to deplete the neutralizing minerals has been referred

to as the "lag time" to acid production. Additional discussion on the lag time and its importance is presented in the introduction.

Dissolution of silicate minerals such as anorthite (reaction 8, Busenberg and Clemency 1976) and forsterite (reaction 9, Hem 1970) can also neutralize acid, but their dissolution rate and associated rate of acid neutralization is very slow in the neutral pH range. These minerals dissolve more rapidly as pH decreases and, therefore, provide more acid neutralization under acidic conditions. The rate of acid production must be relatively slow for this dissolution to maintain drainage pH in the neutral range.



4. METHODS

4.1. Mine Waste Samples

4.1.1. Sample Procurement

Western Governors' Association (WGA) member states and mining operations within these states were asked to provide mine waste samples with the following attributes. First, samples with field drainage quality data were preferred. Second, samples with a marginal potential for acid production were desirable. (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, reported sulfur and carbonate contents which were widely disparate (see parenthetical comment in section 4.1.1), and/or excessive oxidation of the sulfides originally present. The remaining 20 samples (12 tailings and 8 rock samples) were sent to Lerch Brothers, Inc. (Hibbing, MN) to be analyzed for sulfur, sulfate, and carbon dioxide. These values were used to estimate the acid production potential (APP) and neutralization potential (NP). 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 selected 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. Sample RK2 had been stockpiled for about 15 years, but the rock particles collected were fairly large and were crushed prior to distribution for analysis and predictive testing. Consequently, most of the rock surface was relatively fresh.

The ages of tailings TL1, TL4, and TL5 are unknown, but their appearance and chemistry suggest 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 appeared to be relatively unoxidized.

4.1.3. Sample Preparation and Solid-Phase Analysis

The waste rock samples, as received in five-gallon buckets, were all fairly coarse (approximately minus six inches), and were crushed to a nominal minus-one-inch size to obtain homogeneous samples. One of the tailings samples (TL4) was crushed to eliminate clumps and the consequent sample inhomogeneity. For the remaining tailings samples, subsamples were split from the samples as received using ASTM method E877-82 (Lerch Brothers, Inc.). To quantify the compositional variation introduced by the splitting procedure, the sulfur content (ASTM E395 using a Dietert furnace) and carbon dioxide content (ASTM E350-89C) of three sample splits were determined. The standard deviations for the sulfur and carbon dioxide determinations on the triplicate splits ranged from 0 to 6.8% of the mean value, except for the carbon dioxide content of samples RK2 and TL4 (50% and 17%, respectively; table 2).

The various splits were distributed for particle size distribution analysis (Lerch Brothers), chemical analysis (Lerch Brothers and Bondar-Clegg and Company Ltd., Ottawa, Ontario), mineralogical analysis (Midland Research Center, Nashwauk, MN; previously Hanna Research Center), Acid-Base Accounting (Sobek et al. 1978) by the Minnesota Department of Natural Resources, Division of Minerals (MN DNR, Hibbing, MN), and dissolution testing by the MN DNR (Babbitt, MN).

Lerch Brothers analyzed samples for sulfur, sulfate, and carbon dioxide. Sulfur was determined with a carbon rod furnace (Dietert) using ASTM 395 and sulfate was determined following a sodium carbonate leach. Carbon dioxide was analyzed using a gas evolution method (ASTM E350-89C). Bondar-Clegg analyzed the samples for 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 Inductively Coupled Plasma Emission Spectrophotometer (ICP) analytical package (Bi, Co, Ga, La, Li, Nb, Sc, Sn, Sr, Ta, Te, V, W, Y, Zr). Silicon and the major metal components were extracted using borate fusion and analyzed using Direct Current Plasma. The remaining metals were extracted using a solution of HF, HClO₄, HNO₃, and HCl and analyzed by ICP.

Mineralogical analyses were conducted by Louis Mattson of the Midland Research Center in Nashwauk, MN. X-ray diffraction (XRD, Phillips Electronic Instruments Inc.) was used in

conjunction with chemical analyses 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 which was separated using a Haultain Superpanner (Infrasizers Ltd.). The heavy mineral concentrate (specific gravity greater than about 3.5) was analyzed to more accurately identify the sulfides, siderite, and other heavy minerals present. This was necessary since the sulfide content of some samples was quite low.

The carbon dioxide content was used to determine the total carbonate mineral content. The carbonate minerals present were identified by XRD, and checked by scanning electron microscopy (SEM, Amray model 1200B) and energy dispersive spectroscopy (EDS, Noran Instruments model 2010). For some samples, optical microscopy (standard Zeiss petrographic microscope) was used for additional verification. The relative amounts of carbonate minerals present were determined by interpretation of the major peak heights based on the analyst's twenty years of experience. The formula for dolomite used by Midland Research Center was 30% CaO, 22% MgO, and 48% CO₂, 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 potential error in the XRD mineral determinations was estimated as 20%.

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 with the unaided eye, a hand lens, and/or a binocular microscope to qualitatively assess the surface area of sulfide and carbonate minerals available for reaction in the large particles.

Acid-base accounting (ABA, Sobek et al. 1978) was conducted on all samples. Sulfur content was determined by Lerch Brothers, Inc. and neutralization potential was determined by the MN DNR Hibbing Laboratory. These analyses were also conducted on one of the duplicate samples after 24 weeks of the Wet-Dry Cycle Test and after 24 (waste rock) or 26 weeks (tailings) of the Elevated Temperature Test.

Selected samples were analyzed to identify 1) non-carbonate minerals which dissolved to neutralize acid and 2) potential coating formation on sulfide or carbonate mineral surfaces. Samples of TL5, RK1, RK2, and TL6, both unleached and leached for 24 or 26 (TL6) weeks in the Elevated Temperature Test, were analyzed using XRD and SEM. Also analyzed were a TL6 sample leached for 173 weeks in the Elevated Temperature Test, and a sample which was similar to RK2 and had been leached for 289 weeks at room temperature.

The X-ray patterns of leached samples were compared to those generated by the unleached samples. Specific feldspar and pyroxene minerals were identified, as well as the percentages of these minerals and their physical characteristics (e.g., particle size). The +200 mesh fraction of the leached samples was separated by wet sieving and grains were selected for examination by SEM. However, the only +200 mesh particles in the leached RK1 sample were

agglomerates of mineral grains, therefore SEM analysis was conducted on a bulk mount of this sample.

In order to increase the probability of detecting changes in primary silicate minerals, a more highly weathered sample was selected for analysis. XRD analysis of the unleached rock indicated it was mineralogically similar to RK2 (olivine gabbro). The leached sample (1.63% S) was taken from a previous Wet-Dry Cycle experiment after 289 weeks of dissolution. At this time the drainage pH was between 4.0 and 4.1, and the non-carbonate acid neutralization was estimated to be equivalent to that resulting from dissolution of 1.1 grams of calcite (measured as 0.75 grams after 150 weeks of dissolution).

Waste rock samples RK3, RK4, and RK5 were selected for the Particle Size Experiment. RK3 and RK4 were the same solids as in the preceding two tests. RK5 was chosen since it was mineralogically similar to, and more readily available than, RK2; it did have a higher sulfur content than RK2 (1.63% vs 0.64%). After receipt for the initial experimental work, these rocks were crushed to a nominal minus-one-inch size to ensure the distribution of compositionally uniform samples (Lapakko 1993). The six size fractions arbitrarily selected for examination were: -270 mesh, +270/-100 mesh, +100/-35 mesh, +35/-10 mesh, +10 mesh/-0.25 inch, and +0.25/-0.75 inch. The corresponding sizes in millimeters were: $d \leq 0.047$ mm, $0.047 < d \leq 0.149$ mm, $0.149 < d \leq 0.5$ mm, $0.5 < d \leq 2.0$ mm, $2.0 < d \leq 6.25$ mm, $6.25 < d \leq 19.05$ mm.

Size fractions were separated by subjecting rock samples (150 - 200 g) to 15 minutes on a ro-tap apparatus loaded with U.S. standard mesh sieves. (Due to a missing 10 mesh sieve of compatible size, the -10/+12 mesh was separated from the -1/4-inch/+12 mesh fraction by hand sieving.) After the separation, the various size fractions were wet sieved by placing approximately 150 g of solid on the plus size sieve and rinsing it repeatedly with tap water, agitating the rock while rinsing. When the water ran clear, the rock was rinsed with distilled water. The size fractions of RK3 and RK4 rocks were then oven dried at about 38°C, and the RK5 rock was air dried. The drying times ranged from one to three days. Portions of each size fraction were retained for dissolution testing to assess the effect of particle size on waste rock dissolution.

A split of each particle size was submitted to Midland Research Center for chemical and mineralogical analysis. Sulfur, sulfate, and evolved carbon dioxide were determined for each size fraction. In an attempt to identify and quantify the relative surface areas of acid-producing and acid-consuming minerals, all particle size fractions were analyzed microscopically. As an alternative method the various size fractions were leached with 6N HCl, and the leachate was analyzed for sulfur, iron, calcium, magnesium, and silicon. Additional X-ray patterns were obtained for RK5 to confirm similarity to RK2 and to identify potential acid neutralizing phases.

4.2. Procedures

4.2.1. Wet-Dry Cycle Test

For the Wet-Dry Cycle Test (Lapakko 1988) rock samples were crushed to -100 mesh, tailing sample TL4 was crushed to eliminate clumps and the consequent sample inhomogeneity (see section 4.1.3), and the remaining tailing samples were run as received. Samples, run in duplicate for the first 24 weeks, were placed into the upper segment, or reactor, of a two-stage filter unit (figure 1). (After 24 weeks, one of each pair of duplicate reactors was terminated and the leached sample was subjected to ABA analysis, as described in section 4.1.3.) A glass fiber filter, onto which the sample was placed, rested on a perforated plastic plate within the reactor. Prior to the inception of the experiment all samples were rinsed with three distilled water volumes of 200 mL, to remove oxidation products which accumulated during sample storage. To each reactor, 200 mL of distilled water was added and allowed to drain overnight through the mine waste sample. Once the experiment started, single 200-mL rinses were repeated weekly for 132 weeks.

The volume of rinse water recovered was determined by weighing. The drainage was analyzed on site to determine pH, alkalinity (if $\text{pH} \geq 6.3$) or acidity, and specific conductance. Samples were then filtered for subsequent determination of sulfate, calcium, and magnesium concentrations. Samples taken for metal analyses were acidified with 0.2 mL AR Select nitric acid (Mallinckrodt) per 50 mL sample.

Between rinses the solids were retained in the reactors and stored in an uncovered box to further oxidize. A thermostatically controlled heating pad was placed beneath the box to control temperature. The box was stored in a small room equipped with an automatic humidifier and an automatic dehumidifier, to maintain a stable range of humidity. Temperature and relative humidity were monitored two to three times a week. The temperature ranged from 19.4 to 30.0°C, with an average of 25.3°C and a standard deviation of 1.92°C ($n = 451$). The relative humidity ranged from 30.0 to 68.0%, with an average of 52.3% and a standard deviation of 5.79% ($n = 434$, see also appendix B).

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 mineralogic factors. During the drying cycle the grains of samples RK1, RK3, and RK4, tended to cement and subsequently the solid bed would crack. To achieve more uniform flow through the bed it was necessary, prior to rinsing, to remove the consolidated solids from the reactor and break them up, or mix the solids with a stainless steel spatula in the reactor. Despite a slight cementation of the TL4 grains, these solids were not mixed during the first 63 weeks; the solids were mixed in subsequent weeks to increase flow through the bed. 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 TL4 tailings bed and add it to that in the receiving flask. The volume decanted from RK3 and RK4 was quite small, approximately

2% of the total sample volume, while the corresponding percentages decanted for RK1 and TL4 were about 15% and 21%, respectively.

4.2.2. Elevated Temperature Test

For the Elevated Temperature Test (modified from Renton 1983; Renton et al. 1985, 1988), rock samples were crushed to -100 mesh, tailings sample TL4 was crushed (see section 4.1.3), and the remaining tailings samples were run as received. Samples, run in duplicate for the first 24 or 26 weeks, were placed into the upper segment, or reactor, of a two-stage filter unit (figure 1). After 24 (waste rock) or 26 weeks (tailings), one of each pair of duplicate reactors was terminated, and the leached sample was subjected to ABA analysis, as described in section 4.1.3. 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 subsequently rinsed every two weeks for 130 to 131 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. (The water was heated to simulate the soxhlet extraction rinsing used by Renton (1983).) The procedure was repeated on the following day for additional recovery of the oxidation products. Specific conductance was determined for each of the two samples. The two samples were composited, weighed to determine total volume, and analyzed on site for pH, alkalinity (if pH \geq 6.3) or acidity, and specific conductance. Samples were then filtered for subsequent analysis of sulfate and metals. Metals were acidified with 0.2 mL AR Select nitric acid (Mallinckrodt) per 50 mL sample.

The solids were retained in the reactors and stored in a Thelco Precision Scientific oven. Temperature ranged from 82.0°C to 120.0°C, averaging 97.3°C, with a standard deviation of 4.07°C (n = 473, see also appendix C). During the drying cycle the grains of samples RK1, RK3, and RK4, tended to cement and crack. Consequently, it was necessary to either remove the consolidated solids from the reactor and break them up, or mix the solids with a stainless steel spatula in the reactor prior to rinsing. Despite a slight cementation in the grains of TL4, the solids were not mixed during the first 59 weeks. The degree of TL4 cementation increased and the solids were mixed in subsequent weeks to increase flow through the bed. Despite these preparations there were times when all of the rinse water did not pass through RK3, RK4, and TL4, and it was necessary to decant from the top of the bed. The decant water was then added to that which passed through the solids. The volume decanted from RK3 and RK4 was less than 3.5% of the total sample volume collected. Decanting contributed about 25% of the total sample volume from TL4 in this test.

4.2.3. Particle Size Experiment

For the Particle Size Experiment, the -270, +270/-100, and +100/-35 mesh fractions were leached with the apparatus and methods used for the Wet-Dry Cycle Test (figure 1). For larger size fractions (+35/-10 mesh, +10 mesh/-0.25 inch, and +0.25/-0.75 inch) a clear cylindrical acrylic reactor was used. The reactor measured 4.0 inches in diameter, 7.5 inches in height, and was equipped with a 1/8-inch outlet port and a cover with a 1/8-inch vent hole. The solids

rested on a glass fiber filter placed on the bottom of the reactor (figure 2). The mass of rock used in the larger reactors varied with particle size, as did the volume of distilled water added to the reactors for the weekly rinses (table 3). Due to the limited mass of RK3 available, the +0.25 inch/-0.75 inch fraction of this rock was omitted, and 500 g rather than 1000 g of the +10 mesh/-0.25 inch fraction was used in the experiment.

At the start of the experiment (week 0) the solids were rinsed between four and seven times to remove reaction products which had accumulated since the samples were rinsed during sieving. The rinse water was analyzed for specific conductance to provide an indicator of the decreasing masses of oxidation products removed from the solids (see appendix D for results).

Subsequently, the solids were rinsed weekly for 30 weeks with a volume sufficient to completely submerge the solids and then allowed to drain freely (table 3). One of the reactors (+1/4 inch/-3/4 inch RK4) drained rapidly after week 19, apparently due to a hole in the glass fiber filter, and the reactor outlet was plugged while the rinse water was added. After 10 minutes the water was allowed to drain into the receiving flask. The volume of drainage and the volume of rinse water retained by the solids were determined by weighing. The drainage was analyzed on site to determine pH, alkalinity (if $\text{pH} \geq 6.3$) or acidity, and specific conductance. Samples taken for sulfate and metals analysis were filtered through a 0.45-micron filter. Metals were acidified with 0.2 mL AR Select nitric acid (Mallinckrodt) per 50 mL sample.

Between rinses the solids were stored in the reactors in a room in which temperature and humidity were controlled. The smaller reactors were stored in the same box used to store the Wet-Dry Cycle Test reactors. For the larger reactors, a thermostatically controlled heating mat was placed onto each of two shelves and covered with a piece of perforated tag board. Each of the larger reactors was supported 3.8 cm (1.5 inches) above the tag board by a pair of wooden spacers. The humidity was maintained within a stable range with an automatic humidifier/dehumidifier. Temperature and relative humidity were monitored three to four times weekly. The temperatures for the box, lower shelf, and upper shelf were fairly uniform, with mean values of 24.4°C, 24.1°C, and 23.8°C, respectively. Relative humidity was more variable, with corresponding average values of 57%, 52%, and 51% (see also appendix D).

Between week 0 and week 1 the reactors were left uncovered and weighed on a daily basis to determine the variation in water retained over time. Due to the wide discrepancy of drying among reactors, it was determined that the covers be left on the reactors between rinses, except for reactors containing the -270 fractions of RK3 and RK4, which would not drain under wet conditions. The water remaining on top of these solids was pipeted from the reactor and added to the drainage before analysis. The percentage of the total volume decanted from the -270 mesh fractions of RK3 and RK4 was approximately 62% and 39%, respectively. It should be noted that, based on the weekly weights and the presence of moisture on the inside walls of the covered reactors, it was assumed that the relative humidity was near 100%. To determine the influence of the apparatus and procedure on drainage quality, 300 milliliters of distilled water was added weekly to a large reactor equipped with a glass fiber filter to produce a blank sample.

Two peripheral experiments were conducted to examine the effects of the reactor type used and to compare results from covered and uncovered reactors. The +100/-35-mesh size fraction of each rock was run in both a small (75 g) and large reactor (225 g) to determine if reactor type had any effect on drainage quality. Covered and uncovered reactors were compared using the +1/4 inch/-3/4 inch RK4 and the +270/-100 mesh, +35/-10 mesh, and +1/4 inch/-3/4 inch fractions of RK5. Results of these experiments are presented in appendix D.

4.3. Drainage Analysis

The drainage quality samples were analyzed on site to determine pH, alkalinity (if pH \geq 6.3) or acidity, and specific conductance. An Orion SA 720 pH meter, with a Ross combination pH electrode (8165), was used for pH determinations. Alkalinity and acidity were analyzed using standard titration techniques (APHA et al. 1992). A Myron L conductivity meter was used to determine specific conductance. Most of the sulfate and all metals analyses were conducted at the MN DNR Minerals laboratory in Hibbing. Except for Particle Size Experiment samples after week 16, sulfate was determined at the MN DNR laboratory using an HF Scientific DRT-100 nephelometer for the barium sulfate turbidimetric method (APHA et al. 1992). Sulfate determinations on samples collected from the Particle Size Experiment after week 16 were analyzed using ICP, at Midland Research Center. Calcium and magnesium were determined with a Perkin Elmer 603 atomic absorption spectrophotometer in flame mode. Data were checked by examining concentration variation over time, relationships of concentrations with conductance, and charge balances. Samples for which concentrations were anomalous were reanalyzed. If reanalysis was not possible (for example, due to inadequate sample volume) the anomalous values were deleted from the data tables and footnoted.

4.4. Calculations

The neutralization potential present as calcium carbonate and magnesium carbonate (NP[(Ca/Mg)CO₃]) expressed as kg/t CaCO₃ was calculated as indicated below. Error bars for

$$\text{NP}[(\text{Ca}/\text{Mg})\text{CO}_3] = 10 \times (\% \text{CaCO}_3) + 11.9 \times (\% \text{MgCO}_3) \quad [10]$$

the values determined were established by different methods, all of which accounted for error contributed by splitting and determination of total carbon dioxide content. For most of the samples (RK1, RK2, RK4, TL1, TL2, TL4, TL5, TL6) the upper error bar was determined by assigning the maximum potential carbonate content, as indicated by carbon dioxide determination, to neutralizing minerals. The lower error bar for these samples (minimum amount of carbonate occurring with calcium and magnesium) was calculated as the minimum total carbonate content minus the maximum possible carbonate occurring with iron. For all of these samples except TL6, the maximum iron carbonate content was calculated based on the presence of less than 0.5% siderite (i.e., not detected) in the heavy mineral fractions. For TL6 a maximum iron carbonate content of 0.5% in the entire sample was used. For samples containing substantial siderite, RK3 and TL3, a potential 50% error in calcium carbonate and magnesium carbonate analysis was used.

The masses of sulfate, calcium, and magnesium released were calculated as the product of the observed concentration in the drainage and the drainage volume. Missing concentrations were estimated by quadratically smoothed interpolation of the previous and subsequent concentrations. For each reactor sulfate, calcium, and magnesium release rates were calculated for numerous periods. Cumulative sulfate release over time was plotted for each reactor. Periods of linear sulfate release were selected based on visual examination of the plots, and the release rate for each period was determined by linear regression. For calcium and magnesium release rates, linear regression analyses were conducted over the same periods.

Empirical neutralization potentials (ENP) were calculated to determine the acid-neutralizing mineral dissolution prior to drainage pH decreasing below 6 and remaining in this range. The acid-neutralizing mineral dissolution was calculated as the sum of the cumulative calcium and cumulative magnesium released (expressed as kg/t CaCO₃) prior to the point at which drainage pH decreased below pH 6. The release was calculated both including and excluding the calcium and magnesium attributed to reaction products accumulated during sample storage. If the pH of drainage from a solid never decreased permanently below 6, the ENP was reported as "greater than" the sum of the total calcium and magnesium release for the period of record. The pH of drainages from RK1 and RK2 in the Elevated Temperature Test decreased below 6 for periods of 52 and 32 weeks, respectively, and then increased above pH 6. The ENP values for these solids were calculated as the total calcium and magnesium released prior to these extended periods.

5. RESULTS

5.1. Mine Waste Particle Size, Chemistry, Mineralogy

The particle size distributions of the various samples used in the Wet-Dry Cycle and Elevated Temperature Tests are presented in table 4. 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 5). The major metals present in the samples, in a general order of decreasing abundance, were silicon, aluminum, iron, potassium, magnesium, and calcium.

The predominant sulfur-bearing minerals in the samples were pyrite and pyrrhotite, and marcasite was detected in four samples (table 6). Lesser amounts of trace metal sulfides were detected in all samples. The most frequently encountered carbonate minerals were calcite, dolomite, and siderite (table 7). Ankerite, magnesite, and possibly rhodochrosite were each detected in one or two samples. Quartz, feldspar, and mica were the major rock-forming minerals (table 8).

The sulfide and carbonate minerals in all the tailings samples were well liberated due to the small particle size. Visual inspection of the waste rock samples, as received, 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 [to] 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.

For each of the three rock samples used in the particle size experiment, sulfur and carbonate contents varied with particle size (table 9). No pattern to the variation was obvious.

5.2. Wet-Dry Cycle Test

5.2.1. Introduction

Mine waste drainage quality prediction has at times been empirically based on the quality of drainage observed in kinetic tests, such as the Wet-Dry Cycle Test. That is, it is assumed that the quality of drainage generated in the kinetic test simulates the quality of drainage from mine wastes in the field. However, due in part to the relatively short test duration, the quality of kinetic test drainage from some samples may not be representative of that generated over the long period following mine abandonment. In particular, calcium and/or magnesium carbonate minerals may survive throughout a kinetic test, with their dissolution maintaining a non-acidic drainage. However, over a longer period these acid neutralizing minerals may be depleted or rendered essentially unreactive by coatings, while acid producing minerals remain and oxidize, with a consequent acidification of drainage.

Samples from the Wet-Dry Cycle Test were classified based on the observed drainage pH and concentrations of alkalinity, sulfate, calcium, and magnesium. The classifications were discussed in light of calculated residual solid-phase calcium and magnesium carbonate (NP[(Ca/Mg)CO₃]). The resultant groups were as follows.

Acid producers (TL5)

Non-acid producers with

NP[(Ca/Mg)CO₃] depleted (RK1, RK2)

NP[(Ca/Mg)CO₃] near depletion (RK3, RK4, TL2, TL4)

NP[(Ca/Mg)CO₃] remaining and controlling drainage quality (TL1, TL3, TL6)

The relative amount of calcium carbonate and magnesium carbonate minerals present in a sample was reflected by its drainage composition. Samples with an abundance of these minerals produced drainage with elevated pH and concentrations of calcium, magnesium, and alkalinity despite continued iron sulfide mineral oxidation (see reaction 7). As the calcium carbonate and magnesium carbonate mineral dissolution continues and these minerals approach depletion, drainage pH and concentrations of calcium, magnesium, and alkalinity tend to decrease. Caution must be used when interpreting drainage quality data since decreases in carbonate mineral dissolution may also be caused by decreasing iron sulfide oxidation and the attendant acid production. Furthermore, iron sulfide oxidation rates, as indicated by sulfate release, typically decreased over time in the Wet-Dry Cycle Test. The presence (or absence) of calcium and magnesium carbonate minerals qualitatively implied by drainage quality was compared to the residual NP[(Ca/Mg)CO₃] calculated from solid-phase analysis and the mass of calcium and magnesium released.

In addition to drainage quality and NP[(Ca/Mg)CO₃], acid production potential (APP), empirical neutralization potential (ENP), and release rates of sulfate, calcium, and magnesium are also presented to describe the dissolution of the samples. For convenience of data presentation the APP values presented were calculated based on total sulfur content (Sobek et al. 1978), and slightly exceed the more accurate APP values calculated based on sulfide sulfur. However, the extent of overestimation is small since almost all of the sulfur was present as sulfide (table 5). The ENP represents the observed potential of the sample to neutralize acid, as indicated by calcium and magnesium release. Wet-Dry Cycle Test results are summarized in table 10.

5.2.2. Acid Producer (TL5)

All of the carbonate NP was depleted from TL5 (158 kg/t CaCO₃ APP, 15 kg/t CaCO₃ NP[(Ca/Mg)CO₃]), the only sample which generated drainage pH values below 6.0 (figure 3). The TL5 drainage pH was above 6.0 for the week 0 rinses, decreased to a typical range of 2.7-2.8 between weeks 20 and 60, and subsequently remained between 2.8 and 3.0. Sulfate concentrations decreased until week 90 and then plateaued at about 100 mg/L. At this time the rate of iron sulfide oxidation, as inferred by sulfate release, was 0.21 millimoles/week (tables 10, 11). Concentrations of calcium and magnesium decreased and plateaued at low levels (figure 3), reflecting the depletion of the dolomite and magnesite reported to be present (table 12). The continued slow release of calcium and magnesium was apparently due to the dissolution of noncarbonate host rock minerals.

The acidic drainage is consistent with the presence (as indicated by the sulfur remaining) and oxidation of iron sulfides after the depletion of NP. By the end of the 132-week experiment 58% of the sulfur originally present remained. At this time the NP[(Ca/Mg)CO₃] had long been depleted. Comparison of calcium release with solid-phase chemistry (table 5) indicates that virtually all of the calcium (including that present in noncarbonate minerals) was leached from the sample by week 132.

The high rate of acid production (inferred by the sulfate release rate) and low rate of acid neutralization (inferred from the sum of calcium and magnesium release rates) were consistent with the low drainage pH. Over the last third of the period of record, the rate of sulfide oxidation, and attendant acid production, was 2 to 30 times that of the other samples (tables 10, 11). In contrast, the rate of calcium and magnesium release from TL5 (along with RK1 and RK2) was the lowest of the samples examined (tables 10, 11).

5.2.3. Non-Acid Producers, NP[(Ca/Mg)CO₃] Depleted (RK1, RK2)

The small amount of calcium and magnesium carbonates initially present in samples **RK1** and **RK2** also appeared to have been depleted (respectively 14, 20 kg/t CaCO₃ APP; 3, 1 kg/t CaCO₃ NP[(Ca/Mg)CO₃]). Next to TL5 these samples produced the lowest pH values in the Wet-Dry Cycle Test. The pH values observed were initially near 7.5, decreased below 7.0 after 25 to 45 weeks of dissolution, plateaued in the range of 6.5 to 7.0, and increased slightly over the last 40 to 50 weeks of the experiment. The release of sulfate, calcium, magnesium, and alkalinity decreased over time (figures 4, 5; table 11).

The temporal trends of pH, alkalinity, calcium, and magnesium in these two drainages are consistent with decreasing calcium/magnesium carbonate mineral dissolution. The decrease in calcium/magnesium carbonate mineral dissolution was apparently due to depletion of the carbonate minerals initially present. This contention is supported by mass release calculations, which indicate the NP[(Ca/Mg)CO₃] was depleted by week 132 (table 12).

The rates of sulfate release, and attendant acid release, from RK1 and RK2 (along with TL1) were the lowest observed, reflecting the low sulfur content of these samples (tables 10, 11). The dissolution of silicate minerals may have neutralized some, if not all, of the acid released at these slow rates. (For additional discussion of silicate mineral dissolution, see the last paragraph of section 3.) These samples contained 24% and 54% feldspar, respectively, and lesser amounts of chlorite and mica; respective pyroxene and olivine contents of 18% and 11% were reported for sample RK2 (table 8). The rates of acid neutralization by silicate mineral dissolution were enhanced by the fine nature of these samples, 63 to 85 percent of which were less than 0.053 mm in diameter (table 4). Furthermore, the particle size reduction required for the experiment artificially enhanced the rate of acid neutralization relative to that which would occur for coarser waste rock particles in the field. Whereas particle size reduction also may have increased the iron sulfide mineral area, the extent of this increase was apparently less than that for the silicate minerals. This is consistent with mineralogical analyses which indicate that the silicate mineral grains in this rock are larger than the sulfide mineral grains.

5.2.4. Non-Acid Producers, NP[(Ca/Mg)CO₃] Near Depletion (RK3, RK4, TL2, TL4)

Drainage quality data also indicated that calcium and magnesium carbonate NP was nearing depletion for samples RK3, RK4, TL2, and TL4 (respectively 51, 91, 47, 72 kg/t CaCO₃ APP; 5, 32, 16, 6 kg/t CaCO₃ NP[(Ca/Mg)CO₃]). Although these samples did not produce acidic drainage, the drainage pH, alkalinity, and (except for TL2) calcium and magnesium

concentrations tended to decrease near the end of the period of record (figures 6, 7, 8, 9). This was also the case for the rate of calcium plus magnesium release relative to sulfate release (table 11). These trends suggest that these samples may be nearing the end of their "lag period." The NP[(Ca/Mg)CO₃] remaining in samples RK3, TL2, and TL4 is consistent with this contention. The rates of sulfate release from these four samples at the end of the experiment was two to seven times that for RK1 and RK2 (tables 10, 11). Unlike RK1 and RK2, noncarbonate host rock mineral dissolution may not be capable of neutralizing the acid produced at these higher rates. Consequently, drainages from these samples may acidify when the calcium and magnesium carbonates are depleted.

At week 132 the calculated NP[(Ca/Mg)CO₃] of **RK3** was no more than about 1 kg/t CaCO₃. The rate of acid production, as indicated by sulfate release, from this sample was about twice that from RK1 and RK2. Assuming some calcite remains in this sample, the more rapid rate of acid production observed may lead to acidification of the drainage from this sample. That is, the dissolution of host rock minerals may not be fast enough to neutralize the acid produced.

The pH of drainage from **RK4** decreased over time, a trend which was most pronounced from 80 to 130 weeks (figure 7). Drainage alkalinity decreased from 25 to 5 mg/L as CaCO₃ over this one-year period, which is also consistent with decreasing availability of carbonate minerals. As further support for this contention, calcium and magnesium release rates decreased over time, a trend which would be expected to accompany the depletion of dolomite from the sample (figure 7, table 11). Furthermore, the molar rates of calcium and magnesium release were approximately equal throughout the experiment (table 11), which supports the contention that their release was due to dissolution of dolomite (CaMg(CO₃)), see reactions 5, 6). Whereas the release rate of sulfate also decreased, the extent of decrease was not as great as that for calcium and magnesium. The NP[(Ca/Mg)CO₃] of this sample remaining after 132 weeks of dissolution was calculated as 10 to 15 kg/t CaCO₃. The calcium and magnesium carbonates remaining may have been rendered unreactive due to coating by iron oxyhydroxide precipitates. The apparent remaining NP[(Ca/Mg)CO₃] may also be an artifact of cumulative errors in solid-phase and drainage analyses, as well as sample splitting.

Decreases in drainage pH, alkalinity, and the ratios of calcium plus magnesium to sulfate release were also observed for samples **TL4** and **TL2** after about 100 weeks of dissolution (figures 8, 9). The trends for these samples were more subtle than those observed for **RK4**. The remnant NP[(Ca/Mg)CO₃] values for **TL4** and **TL2** after 132 weeks of dissolution were calculated as 0 to 2 kg/t CaCO₃ and 0 kg/t CaCO₃, respectively (table 10). Drainage from these samples may acidify upon dissolution of the small amount of calcium and magnesium carbonates remaining.

5.2.5. Non-Acid Producers, NP[(Ca/Mg)CO₃] Remaining and Controlling Drainage Quality (TL1, TL3, TL6)

The drainage quality from the remaining three samples, **TL1**, **TL3**, and **TL6** (respectively 30, 68, 182 kg/t CaCO₃ APP; 19, 19, 46 kg/t CaCO₃ NP[(Ca/Mg)CO₃]), showed no indication of calcium and magnesium carbonate depletion (figures 10, 11, 12). The quality of drainage from

these samples was relatively constant over time. Drainage pH typically ranged from 7.5 to 8.0, with values from TL1 on the lower end of the range and those from TL3 on the upper end. Drainage pH from TL6, ranging from 7.1 to 7.95, was more variable than that from TL1 or TL3. Drainage alkalinities from TL1, TL3, and TL6 varied within ranges of 10-20, 50-60, and 35-50 mg/L as CaCO₃, respectively. The values for TL1 appeared to decrease slightly over time.

Release of calcium and magnesium from the solids was fairly constant. Substantial magnesium release was observed only for sample TL3, which contained 1.9% ankerite (tables 10, 11). The low magnesium release from TL1 is interesting since it was reported to contain 0.4% dolomite (table 10). Preferential dissolution of calcite is one reasonable explanation for the apparent slow dissolution of dolomite. Furthermore, additional examination of the XRD data indicated that the dolomite content may have been erroneously elevated due to interference from a secondary feldspar peak. The ratio of calcium plus magnesium to sulfate release for these three samples tended to increase over the course of the experiment. This implies the calcium/magnesium carbonate mineral dissolution rate increased relative to the sulfide mineral oxidation rate.

The calculated NP[(Ca/Mg)CO₃] remaining in the samples after 132 weeks of dissolution ranged from 0 kg/t CaCO₃ for TL3 to about 13 kg/t CaCO₃ for TL1 (tables 10, 12). The drainages from TL3 and TL6 would likely acidify sooner than that from TL1. Relative to TL1, the small amount of NP[(Ca/Mg)CO₃] remaining in samples TL3 and TL6 would be depleted rapidly due to the high rates of acid production associated with these samples (tables 10, 11). Upon depletion of the calcium and magnesium carbonates the drainages would acidify.

5.3. Elevated Temperature Test

5.3.1. Introduction

The objective of subjecting mine waste samples to higher than ambient temperatures is to accelerate the rate of sulfide oxidation and consequent acid generation. This will, in turn, accelerate the dissolution of acid-neutralizing minerals. The acceleration of mineral dissolution reduces the time required for drainage quality prediction. This reduced experimental duration, as well as the reduction in labor achieved by rinsing samples every other week rather than every week, are advantages of this test over the Wet-Dry Cycle Test. A disadvantage is that the drainage quality generated at the higher temperatures may not simulate that in the environment. For example acid-producing reactions may be disproportionately accelerated or decelerated relative to acid-neutralizing reactions at the elevated temperature. Rates of mineral coating reactions may also be disproportionately affected relative to other reaction rates. Other deviations from field conditions could also be introduced by the elevated temperature.

The elevated temperature accelerated sulfide mineral oxidation in six of the ten samples. For these samples the total APP release, as indicated by sulfate release, in the Elevated Temperature Test was about two to six times that in the Wet-Dry Cycle Test. However, APP release from

samples TL3, TL5, and TL6 was similar in the two tests, while that from RK2 in the Elevated Temperature Test was only 70% of that in the Wet-Dry Cycle Test (table 13).

Acceleration of sulfide mineral oxidation increased the rates of acid-neutralizing mineral dissolution, as indicated by the NP[(Ca/Mg)CO₃] release in the two experiments (table 13). The acceleration of acid-neutralizing mineral dissolution was further exemplified by the fact that seven samples (all except TL1, TL3, TL6) produced some acidic drainage in the Elevated Temperature Test. The acidification of drainage implies neutralization potential depletion in these seven samples. In contrast, only TL5 yielded acidic drainage in the Wet-Dry Cycle Test.

Based on the drainage quality in the Elevated Temperature Test, samples were classified as

- strong acid producers (TL5, RK4, TL4);
- moderate acid producers (RK3);
- mild acid producers (TL2);
- intermittent acid producers (RK1, RK2); and
- non-acid producers (TL1, TL3, TL6).

5.3.2. Strong Acid Producers: TL5, RK4, TL4

The three strong acid producers in the Elevated Temperature Test were, in decreasing order of acid generation, TL5, RK4, and TL4. The APP of these samples ranged from 72 to 158 kg/t CaCO₃ and NP[(Ca/Mg)CO₃] values ranged from 6 to 32 kg/t CaCO₃ (tables 7, 14). The pH of drainage from TL5, RK4, and TL4 decreased for periods of 14, 30, and 130 weeks, reaching minimum values of 2.6, 3.0, and 3.1, respectively. The acidic drainages reflected rates of acid generation (indicated by sulfate release) which exceeded rates of acid neutralization (indicated by calcium plus magnesium release; tables 14, 15).

The pH of drainage from TL5 was acidic throughout the test and remained below 3.3 after week 2, reaching a minimum of 2.56 at week 14 (figure 13). Sulfate release was elevated during the first 30 weeks, concurrent with the period of lowest pH values, and may have been the result of oxidation of the marcasite present in the sample (table 6). Subsequently, sulfate concentrations plateaued at about 80 mg/L. Calcium and magnesium concentrations in the drainage decreased during the initial 30 weeks and plateaued at low levels (figure 13).

The acidic pH observed at week 2 suggests that the 1.1% dolomite and 0.2% magnesite initially present had been depleted. The acid neutralization implied by calcium and magnesium release (empirical neutralization potential, ENP) at week 0 was equivalent to that provided by 8 kg/t CaCO₃, about half the 15 kg/t NP[(Ca/Mg)CO₃] determined based on solid phase analysis. Calcium and magnesium concentrations in the TL5 drainage decreased during the initial phase of dissolution, indicating a decrease in solid-phase sources of these metals (figure 13). These concentrations began to plateau at about week 22. At this time the ENP was calculated as 16 kg/t CaCO₃, a value closer to the NP[(Ca/Mg)CO₃].

The generation of acidic drainage despite the calculated presence of calcium/magnesium carbonates may have been solely an artifact of cumulative error introduced by solid-phase analyses, sample splitting, and aqueous-phase analyses. Two other scenarios, or a combination of these scenarios, are also possible. First, some of the calcium/magnesium carbonate minerals may have remained after week 0, dissolving during the subsequent 22 weeks at a rate which was too slow to offset the rapid rate of acid production. Second, calcium/magnesium carbonate mineral dissolution may have neutralized acid produced during sample storage prior to week 0, and the calcium and magnesium released formed sulfate minerals. These minerals then dissolved through week 22. More detailed assessment of the drainage quality data, in conjunction with chemical equilibrium considerations and additional solid-phase analyses, may identify the cause(s) of this apparent anomaly.

After 131 weeks of leaching, the total sulfur content of the sample was 2.8 percent, indicating a substantial potential for acid production remained. Since sulfate initially present was released in the initial stage of the experiment, virtually all of the sulfur was present as sulfide. The rate of sulfate release at this time was the highest of the 10 samples examined (tables 14, 15). The slow calcium and magnesium release was apparently due to dissolution of non-carbonate host rock minerals.

TL5 had the highest degree of sulfide oxidation of the samples examined and was, therefore, the most likely sample to manifest evidence of silicate mineral dissolution. The unleached sample contained 36% potassium feldspar and 16% sodium feldspar. For comparison, a sample leached for 26 weeks in the Elevated Temperature Test was examined by XRD and SEM. XRD patterns for the leached TL5 sample were not markedly different from those of the unleached sample. However, SEM examination revealed pitting on feldspar surfaces (figure 14). Numerous grains were examined and all manifested similar pitting. This indicates that feldspars dissolved, with attendant acid neutralization, during 26 weeks of the Elevated Temperature Test. This dissolution neutralized only a fraction of the acid produced, as indicated by the highly acidic drainage.

RK4 and **TL4** also produced acidic drainages over the majority of the test, with minimum values around pH 3. The time required to deplete the NP from RK4 and TL4 (and produce acidic drainage) was longer than that for TL5, due largely to a higher initial NP and a slower rate of acid production, respectively. At the end of the period of record, the rates of sulfate release from these two samples were lower than only that of TL5. The pH of drainage from RK4 decreased below 6.0 at week 16 (figure 15). Prior to this time the calcium and magnesium release was equivalent to the dissolution of 27 kg/t CaCO₃. This empirical neutralization potential (ENP) is about 30% lower than the NP[(Ca/Mg)CO₃] determined based on the RK4 mineralogy.

The pH of drainage from TL4 decreased steadily from near 8 at week 2 and, with one exception, remained below 6.0 after week 34. The ENP was calculated based on the calcium and magnesium release through week 34. The value of 4.2 kg/t CaCO₃ agreed reasonably well with the 6 kg/t CaCO₃ NP[(Ca/Mg)CO₃] determined based on the TL4 mineralogy (tables 14, 17).

Drainage pH continued to decrease and reached the low 3's at week 131. The pH decline after week 70 was concurrent with an increase in the sulfate release rate and a decrease in the rates of calcium and magnesium (figure 16, table 15). The increase in sulfate release was likely due to the commencement of bacterially catalyzed ferric iron oxidation of the iron sulfides as pH decreased (Nordstrom 1982; Kleinmann et al. 1981; Singer and Stumm 1970).

5.3.3. Moderate (RK3) and Mild (TL2) Acid Producers

Based on the minimum drainage pH values observed in the Elevated Temperature Test, RK3 and TL2 (respectively 51, 47 kg/t CaCO₃ APP; 5, 16 kg/t CaCO₃ NP[(Ca/Mg)CO₃]) were classified, respectively, as moderate and mild acid producers. Qualitatively, the variation of drainage pH from these samples was similar to that observed for the strong acid producers. However, the minimum pH values generated by RK3 and TL2 (3.5 and 4.7, respectively) were higher than those observed for the strong acid producers by one and two units, respectively.

Drainage pH from **RK3** decreased to and remained below 6.0 after week 18. At this time the acid neutralization implied by calcium plus magnesium release was equivalent to the dissolution of 4.9 kg/t CaCO₃. This ENP is in good agreement with the NP[(Ca/Mg)CO₃] of 5 kg/t CaCO₃. The drainage pH continued to decrease, with values around 4 over the last ten weeks of the test (figure 17). The pH of drainage from RK3 was slightly higher than values from the strong acid generators due to a lower rate of sulfide oxidation and attendant acid production (tables 14, 15). During the test the sulfur content of the sample decreased from 1.6% to 1.2% (tables 14, 16).

The pH of drainage from **TL2** decreased below 6.0 after week 51. At this time the sum of calcium and magnesium release was equivalent to an NP release of 20 kg/t CaCO₃, somewhat higher than the measured NP[(Ca/Mg)CO₃] of 16 kg/t (tables 14, 16). The drainage pH did not decrease much below 6.0, ultimately oscillating between 5.0 and 5.7 (figure 18). The rate of acid production, as inferred by sulfate release, was comparable to that for more acidic samples. However, the rate of acid neutralization was considerably higher than the range for the more acidic samples. Indeed the final rate of sulfate release (acid production) approximated the rate of calcium plus magnesium release (acid neutralization), which is consistent with the near neutral drainage pH (tables 14, 15). Dissolution of feldspars, which comprised 30% of the sample, may have contributed to the calcium release in the latter stages of the experiment, although it is also possible that some calcite remained. Over the course of the test the sulfur content was reduced from 1.5% to 0.9%.

5.3.4. Intermittent Acid Producers: RK1, RK2

The temporal variation of drainage pH from **RK1** and **RK2** (respectively 14, 20 kg/t CaCO₃ APP; 3, 1 kg/t CaCO₃ NP[(Ca/Mg)CO₃]) was distinctly different from that of the samples discussed previously. Whereas the pH of drainage from these samples initially decreased from the mid-sevens to values below six, drainage pH subsequently increased and plateaued near pH 6 (figures 19, 20). The ENP for samples RK1 and RK2 was calculated based on calcium and magnesium release during weeks 0-6 and weeks 0-66, respectively. Drainage pH decreased to

pH 6 or less for periods of 52 and 32 weeks, respectively, and then increased above pH 6. Respective ENP values of 2.5 and 2.9 kg/t CaCO₃ were determined for RK1 and RK2, and agreed fairly well with the NP[(Ca/Mg)CO₃] values of 3 and 1 kg/t CaCO₃ determined based on carbonate mineralogy (table 7). Sulfate concentrations decreased over time and plateaued at low levels, reflecting sulfate release rates which were the lowest of the samples examined.

Apparently dissolution of noncarbonate host rock minerals was fast enough to neutralize the acid produced by the slow rate of iron sulfide oxidation in these two samples. Feldspar was a major component of both RK1 (14% potassium feldspar (microcline), 10% sodium feldspar) and RK2 (4% potassium feldspar, 22% sodium feldspar, 28% calcium feldspar). In addition RK1 contained 14% chlorite, and RK2 contained 18% pyroxene and 11% olivine (table 8). Magnesium release accounted for a substantial fraction of the major cation release (tables 14, 15), suggesting that dissolution of one or more of these minerals contributed to acid neutralization. No etch pits or other dissolution features were detected by SEM analysis of a sample of RK1 leached for 24 weeks in the Elevated Temperature Test, reflecting the low extent of dissolution. Since the extent of dissolution of RK2 at this time was similar to that of RK1, it was not analyzed by SEM.

In order to increase the probability of detecting changes in primary silicate minerals, a sample leached for 289 weeks in a separate dissolution experiment at room temperature was subjected to SEM analysis. The unleached sample (1.63% S) was mineralogically similar to RK2 (olivine gabbro). The pH of drainage from the sample was between 4.0 and 4.1 and the non-carbonate acid neutralization was estimated to be the equivalent of dissolution of 1.1 grams of calcite (measured as 0.75 grams after 150 weeks of dissolution). This was approximately two and six times the neutralizing mineral (including calcium and magnesium carbonates) dissolution of RK1 and RK2 after 24 weeks in the Elevated Temperature Test.

SEM examination of the feldspars present in the rock leached for 289 weeks revealed mild pitting and iron oxide coating of feldspar grains (figure 21). These features are consistent with acidic drainage contacting the feldspar mineral surface, feldspar dissolution with attendant pH elevation, and consequent iron oxyhydroxide precipitation. Evidence was also observed for dissolution of pyroxene (augite), mica (biotite), and amphibole (probably hornblende) present in the sample (figures 22, 23, 24). It is assumed that dissolution of these minerals also neutralized acid and contributed to the release of calcium and magnesium from RK1 and RK2. However, SEM analysis did not detect etch pits on silicate minerals present in RK1 because they had not dissolved extensively. Dissolution was limited by the low sulfur content of the samples and the short time of dissolution. Since the molar release of calcium from RK2 was roughly twice that of magnesium, dissolution of calcium feldspar and clinopyroxene (the major silicate minerals) apparently exceeded that of the olivine, mica, and amphibole.

5.3.5. Non-Acid Producers: TL1, TL3, TL6

The quality of drainage from TL1, TL3, and TL6 (respectively 30, 68, 182 kg/t CaCO₃ APP; 19, 19, 46 kg/t CaCO₃ NP[(Ca/Mg)CO₃]) indicated that the acid generated as a result of iron

sulfide oxidation was neutralized by dissolution of calcium/magnesium carbonate minerals. Sulfate concentrations in the three drainages tended to decrease over time. With the exception of four values from TL1, the pH of drainage from these samples exceeded 6 (figures 25, 26, 27). Furthermore, at the end of the period of record typical alkalinity concentrations from TL1, TL3, and TL6 were 10, 40, and 20 mg/L as CaCO₃, respectively. These nonacidic qualities, in conjunction with the elevated release of calcium and magnesium (tables 14, 15), are consistent with the presence and dissolution of calcium/magnesium carbonate minerals.

The ultimate rates of sulfate release from TL1 and TL6 were similar in magnitude to those observed for acid producing samples (tables 14, 15). Despite these rapid rates of acid production the calcium and magnesium carbonates present were not depleted, although four pH values below 6.0 were observed in drainage from TL1. While the rate of iron sulfide oxidation for TL1 was accelerated by almost six times in the Elevated Temperature Test, the extent of sulfate release from samples TL3 and TL6 in the Elevated Temperature Test was approximately equal to that in the Wet-Dry Cycle Test (table 13). Since these two samples produced circum-neutral drainage in the Wet-Dry Cycle Test, nonacidic drainage would also be expected from these two samples in the Elevated Temperature Test.

The mass release of calcium and magnesium from these three samples indicates the carbonate mineral neutralization potential was near depletion after 131 weeks (table 16). Indeed, the mass of calcium and magnesium released from TL3 was 130% to 170% of that reported as occurring in the solid phase as carbonate minerals. The corresponding range for TL6 was 90% to 170% (table 16). Since 0.6% S to 4.0% S remained in the samples, additional iron sulfide oxidation, and the attendant acid production, after depletion of the calcium/magnesium carbonate minerals could lead to acidification of these drainages.

Sample TL6 was selected for additional dissolution and solid-phase analysis to 1) determine if drainage acidification was imminent; 2) clarify the contradictory implications on calcium/magnesium carbonate mineral presence based on a) drainage quality and b) solid phase calcium/magnesium carbonate content and mass calcium and magnesium release; and 3) identify non-carbonate minerals, if any, contributing to acid neutralization. The pH of drainage from TL6 decreased below 6.0 at week 163 and reached 3.45 at week 173. At this time the dissolution of this sample was discontinued.

The elevated alkalinity and calcium (and magnesium for TL3) concentrations, as well as pH, in the drainage clearly indicates the dissolution of calcium carbonate minerals until about week 163. The mass release calculations indicated calcium and magnesium release from TL6 (and TL3) may have exceeded the calcium and magnesium reported present as calcium/magnesium carbonate minerals in the solid phase. This suggests that non-carbonate minerals were dissolving to release calcium and/or magnesium, neutralize acid, and maintain the drainage pH in the neutral range.

Further examination revealed both 1) error in evolved carbon dioxide analysis and/or splitting and 2) some non-carbonate mineral dissolution. Reanalysis of the unleached TL6 sample

revealed an evolved carbon dioxide content of 2.8%, about 40% higher than the value originally determined (2.01%). This suggests that the NP[(Ca/Mg)CO₃] was actually 40% higher than originally calculated, and reduces the calculated calcium and magnesium release at week 131 to 65% to 120% of that occurring in the solid phase as carbonate minerals.

Examination of the TL6 sample after 173 weeks of dissolution indicated that noncarbonate dissolution probably neutralized some acid. SEM analysis of the leached solids revealed some of the clinopyroxene minerals, which comprised the majority of the sample, were altered to the point of being friable (figure 28). It must be noted that no alteration was detected on some grains. Most of the grains examined were of the hedenbergite-diopside series (CaFeSi₂O₆-CaMgSi₂O₆; 43% hedenbergite with 21% CaO and 2% MgO, 12% diopside with 25% CaO and 17% MgO). Energy dispersive spectroscopy (EDS) indicated that the grain in figure 28a had a relatively high iron content, suggesting that calcium was preferentially leached. EDS analysis of the needle-like crystals in figure 28b indicated a composition approximating that of the pyroxene in the sample, although these crystals appear to be secondary, possibly zeolites.

In summary, the SEM analyses indicate that dissolution of some of the clinopyroxene in this sample occurred by week 173. Some of this dissolution occurred under acidic conditions from week 163 to 173. During this period pH was below 6.0, and calcium concentrations increased by 50% and magnesium concentrations doubled over those observed from week 151 to 161. Due to a) the extensive weathering of some grains revealed by SEM examination and b) the calcium release in excess of that present in carbonate minerals prior to drainage acidification (calculated using the calcium/magnesium carbonate content based on reanalysis of evolved carbon dioxide), some of the clinopyroxene dissolution apparently occurred prior to acidification. This dissolution would neutralize acid produced by iron sulfide oxidation while drainage pH exceeded 6.0. Thus, some of the clinopyroxene present in sample TL6 may have contributed to the effective neutralization potential of the sample. Adjusting the solid-phase carbonate mineralogy based on the reanalysis for evolved carbon dioxide, the neutralization provided by clinopyroxene dissolution was estimated as equivalent to that by dissolution of about 0.5 g CaCO₃. Thus, neutralization by the clinopyroxene, which comprised 55% of the sample, was relatively small, representing at most 10% to 15% of the ENP. Additional study of this phenomenon is warranted.

5.4. Particle Size Experiment

Particle size reduction is often a necessity for predictive dissolution testing of waste rock. Unfortunately the quality of drainage, in particular drainage pH, from small waste rock particles may not accurately simulate the quality of drainage from operational scale waste rock. Iron sulfide oxidation and calcium/magnesium carbonate mineral dissolution are responsible, respectively, for the generation and neutralization of acid. The rates of these reactions are generally proportional to the surface area of the respective mineral available for reaction. Particle size reduction may result in preferential enhancement of acid-producing or acid-neutralizing mineral surface areas. This in turn will affect the relative rates of acid generation and acid neutralization and, consequently, drainage pH.

The effect of particle size on drainage quality was examined using RK3, RK4, and RK5, which was mineralogically similar to RK2 but with a slightly higher sulfur content (0.8% vs 0.6% S). Larger particles of each rock type were crushed and sieved to obtain the various size fractions. The sulfur and NP contents of the size fractions varied, introducing an additional variable. This variable was normalized in calculations by expressing APP and NP release as a percent of that originally present. The amount of moisture retained in reactors also tended to increase as particle size decreased, due in part to the increased influence of capillary forces in the smaller particles (table 18). The influence of this variable is addressed qualitatively. Boxplot figures, which are explained in figure 29, are used to present the pH data for the Particle Size Experiment.

The pH values for drainages from the various **particle size fractions of RK3** were typically between 7 and 8 during the 30-week experiment, with no strong trend with respect to particle size. With the exception of the largest particle size fraction (+10 mesh/-1/4 inch), from which drainage pH was the lowest, drainage pH decreased slightly as particle size decreased (figure 30). The rate of sulfate release, reflecting iron sulfide oxidation and the consequent acid production, was slightly higher at the small particle sizes. In contrast, the rate of calcium plus magnesium release, reflecting carbonate mineral dissolution and acid neutralization, increased substantially as particle size decreased (figure 30). This suggests that the available sulfide mineral surface area increased slightly and the available calcium/magnesium carbonate mineral surface area increased substantially as particle size decreased. The release rates of calcium, magnesium, and sulfate from the finest fraction may have been limited by inefficient transport of reaction products from the solids, as indicated by the low flow through the fine-grained solids. Over the course of the experiment, the total drainage volume from the minus 270 mesh fraction was only 27 percent of that from the +270/-100 mesh fraction (see section 4.2.3).

The reduction of RK3 particle size preferentially accelerated the dissolution of the acid-neutralizing carbonates relative to the oxidation of iron sulfides. Coarse and fine grained sulfide minerals were present in this rock, occurring both as disseminated grains and in veinlets. Since the sulfate release rate increased only slightly as particle size decreased, it was concluded that the available sulfide mineral surface area increased only slightly as particle size decreased. It must be noted that the sulfate release for the -270 fraction may have been limited by reaction product transport due to limited flow through the solids bed (see section 4.2.3.) rather than the sulfide oxidation rate. This relationship between sulfide surface area and particle size would be expected if the majority of the sulfides were present in veinlets along fracture planes.

In contrast, the calcium and magnesium release rate tended to increase as particle size decreased. This indicates that the calcium/magnesium carbonate mineral surface area increased as particle size decreased. Thus, the size reduction of RK3 particles tended to preferentially enhance calcium/magnesium carbonate dissolution relative to iron sulfide oxidation. In other words the reduction of RK3 size for predictive testing would tend to underestimate the tendency for large operation scale waste rock to produce acid. (Drainage pH did not increase strictly with calcium and magnesium release due to differences in the mass of solids used and the volume of drainage generated.)

The drainages from the two largest size fractions of **RK4** were acidic, while the pH of drainage from the smaller size fractions typically ranged from 7 to 8 (figure 31). The rates of sulfide oxidation for the larger particles were faster than those for the smaller particles and exceeded the corresponding rates of carbonate mineral dissolution. In contrast, the rate of sulfide mineral oxidation for the smaller particles was less than the rate of carbonate mineral dissolution.

Both the sulfide and carbonate minerals in **RK4** occurred in veinlets, very possibly along fracture planes. However, the sulfide veinlets were "relatively open and porous" and, therefore, were accessible to air and water even in the larger particles. That is, the available sulfide surface area was relatively constant among the size fractions examined. In contrast, the carbonates were present in "tight" veinlets. The available carbonate mineral surface area in the larger particles may have been limited by this mode of occurrence. As a result, the dissolution of carbonates in the larger particles may have been inhibited to the extent that they could not dissolve fast enough to neutralize the acid produced by the oxidation of iron sulfides. The acidic conditions may have given rise to bacterial mediation of the sulfide mineral oxidation, thereby accelerating the oxidation rate. In the smaller particle size fractions, a greater extent of the carbonate mineral surface area was available for reaction. Consequently, the carbonate mineral dissolution was adequately rapid to neutralize the acid produced by the iron sulfide mineral oxidation.

Physical factors associated with the finer size fractions may have enhanced the interaction of acid generated and alkaline components present. Reduction of particle size decreases the distance between sulfide and carbonate mineral grains, that is, there is more intimate contact between carbonates and sulfides. The increased moisture retention by finer particles may have further enhanced the interaction of acidic and alkaline components by providing a transport medium. For example, acid generated at sulfide mineral surfaces can diffuse through the water to reach calcium carbonate surfaces and be neutralized. These factors allow neutralization reactions to occur more or less continuously. In contrast, with larger particles neutralization reactions would occur only if sulfide grains and calcium/magnesium carbonate grains were adjacent or when rinse water was added. For example, the +35/-10 **RK4** fraction produced neutral drainage from week 1 to week 30, when the moisture content in the cell was 12.9 percent. However, at week 0 when the solids were essentially dry, a drainage pH of 3.92 was produced. During the 30-week experiment, the moisture content of the +35/-10 fraction was roughly 2.5 times values observed for the larger particle size fractions which produced acidic drainage.

Furthermore, with the more intimate contact of sulfide and carbonate mineral contact and elevated moisture content, acid is more likely to be neutralized before acidic microenvironments develop to a great extent. This in turn would inhibit bacterial acceleration of oxidation rates. Elevating the pH near sulfide minerals also enhances the precipitation of iron oxyhydroxides on the sulfide mineral surfaces, thereby inhibiting the rate of oxidation.

The pH of drainage from the **RK5** samples decreased as particle size decreased (figure 32). Release rates of sulfate, calcium, and magnesium increased as particle size decreased (figure 32). However, the rate of sulfate release increased to a greater extent, causing the decrease in pH with decreasing particle size. The sulfide minerals in this rock occurred included in or

interstitial to relatively coarse grained rock forming minerals. It is assumed that both the fraction of total surface area occupied by iron sulfide minerals (f_a) and that occupied by acid neutralizing minerals (f_n) was fairly constant over the particle sizes examined. If this is the case, the reduction of particle size does preferentially enhance the gross rates of acid production or acid neutralization.

The net rate of acid production by any solid can be expressed as

$$P = A K_a f_a - A K_n f_n = A (K_a f_a - K_n f_n) \quad [10]$$

- P = net rate of acid production (moles per unit time);
 A = total surface area (square meters).
 K_a, K_n = rates of acid production and acid neutralization, respectively (moles per unit time per square meter); and
 f_a, f_n = fractions of surface area occupied by iron sulfide and acid neutralizing minerals, respectively (dimensionless).

As can be seen from the right hand term in the equation, the net rate of acid production is proportional to the total surface area. The observed increase in the difference between the gross rates of acid production and neutralization ($A K_a f_a - A K_n f_n$) and decrease in drainage pH with decreasing particle size (figure 32) are consistent with this explanation. Also implied by this approach is that if the volume of water rinsing reaction products from rock surfaces remains constant, drainage pH will decrease with increasing numbers of particles (i.e., reactive surface area increases).

6. SUMMARY

The major objectives of this project were to describe the long term dissolution of mine waste, and to describe the effect of particle size on the quality of drainage from waste rock. Tests at room temperature (Wet-Dry Cycle Test) and at 100°C (Elevated Temperature Test) were conducted for 130-132 weeks to describe the quality of drainage from four waste rock and six tailing samples which had been physically, chemically, and mineralogically characterized. The APP, based on total sulfur content (almost all of the sulfur in the samples was present as sulfide), of the samples ranged from 14 to 182 kg/t CaCO_3 and the acid neutralization potential present as calcium carbonate and magnesium carbonate ($\text{NP}[(\text{Ca}/\text{Mg})\text{CO}_3]$) ranged from 1 to 46 kg/t CaCO_3 . In addition to pH, concentrations of alkalinity, sulfate, calcium, and magnesium in the drainages were determined. The rates and extents of iron sulfide and calcium/magnesium carbonate mineral dissolution were calculated based on the masses of sulfate, calcium, and magnesium released in the drainage from the samples. At both room temperature and 100°C, the rates of sulfide oxidation and calcium carbonate and magnesium carbonate dissolution generally decreased over time. General classifications of the samples based on drainage quality generated in the Wet-Dry Cycle and Elevated Temperature Tests are presented in table 19.

The fraction of initial sulfur content released during the Wet-Dry Cycle Test was 44 percent for TL5 and ranged from 6 to 25 percent for the remaining nine samples. The fraction of NP[(Ca/Mg)CO₃] released was 100 percent for TL5, and apparently for RK1 and RK2 as well. TL5 (158 kg/t CaCO₃ APP, 15 kg/t CaCO₃ NP[(Ca/Mg)CO₃]) was the only sample which produced acidic drainage in the Wet-Dry Cycle Test, with a typical drainage pH between 2.6 and 3.0. The low drainage pH indicated that iron sulfide minerals were oxidizing in the absence of calcium/magnesium carbonate minerals. Apparently the dissolution of silicate minerals present in RK1 and RK2 (14, 20 kg/t CaCO₃ APP; 3, 1 kg/t CaCO₃ NP[(Ca/Mg)CO₃], respectively) maintained drainage pH values between 6.5 and 7.0 despite a continued slow rate of acid production. The dissolution of the host rock silicates (per unit mass rock) was accelerated by the fine particle size used in the tests.

The fraction of NP[(Ca/Mg)CO₃] released from the remaining samples ranged from 30 percent to close to 100 percent. The declining pH (although usually above 7) and alkalinity of drainage from four of the samples, as well as the mass calcium and magnesium released, indicated that their calcium and magnesium carbonate minerals were near depletion at the end of the experiment (RK3, RK4, TL2, TL4: 51, 91, 47, 72 kg/t CaCO₃ APP; 5, 32, 16, 6 kg/t CaCO₃ NP[(Ca/Mg)CO₃]). The final three samples (TL1, TL3, TL6: 30, 68, 182 kg/t CaCO₃ APP; 19, 19, 46 kg/t CaCO₃ NP[(Ca/Mg)CO₃]) generated drainage with typical pH values in the range of 7.5 to 8.0 and alkalinities in the range of 10 to 40 mg/L as CaCO₃ near the end of the experiment. It was concluded that substantial calcium/magnesium carbonate and iron sulfide minerals remained in these samples at the end of the experiment (tables 12, 19). Over a longer experimental time frame, continued iron sulfide oxidation and the resultant acid production by these seven samples could deplete the NP[(Ca/Mg)CO₃] with an attendant acidification of drainage. That is, the alkaline drainage observed during the test would probably not simulate the long term drainage quality from the mine waste in the field.

The uncertainty regarding the ultimate drainage quality from these samples even after 132 weeks, underscores the difficulty in empirically simulating (in dissolution tests) the long term drainage quality from mining wastes with even modest neutralization potentials (typically less than 20 kg/t CaCO₃ for the solids examined). The results generated demonstrate the long kinetic test duration required to surpass the lag period for samples with even small amounts of neutralization potential.

For six of the ten samples examined, the rate of sulfide oxidation in the Elevated Temperature Test (100°C) was two to six times that at ambient temperatures in the Wet-Dry Cycle Test. The NP[(Ca/Mg)CO₃] was depleted from five of these six samples. The NP[(Ca/Mg)CO₃] was also depleted from TL5 (which also produced acidic drainage in the Wet-Dry Cycle Test) and RK2. For five (RK3, RK4, TL2, TL4, TL5) of the aforementioned seven samples, the neutralization potential depletion was inferred by the permanent decrease of drainage pH below 6. The pH of drainage from the remaining two samples (RK1 and RK2, from which the NP[(Ca/Mg)CO₃] was also depleted in the Wet-Dry Cycle Test) decreased below 6 for 32 to 42 weeks and then rose above pH 6. The amount of calcium and magnesium released in the drainages from these samples indicated that the calcium and magnesium carbonates had been depleted from the solids.

It is assumed that dissolution of noncarbonate host rock minerals neutralized the acid produced in the latter stages of the test.

The pH (and alkalinity) of drainage from TL1, TL3, and TL6 indicated that some NP[(Ca/Mg)CO₃] remained in these samples at the end of the test. The pH of drainage from TL1 was below 6 on four occasions, suggesting the calcium and magnesium carbonates may have been near depletion. The pH of drainages from TL3 and TL6 were typically in the middle to upper sevens, indicating pH control by calcium/magnesium carbonates. Since sulfides present in these three samples continued to oxidize, the neutral drainage generated during the test does not necessarily simulate the long term drainage quality which would occur in the field. That is, continued dissolution may deplete the calcium and magnesium carbonate minerals, with consequent drainage acidification.

Field scale waste rock size must typically be reduced in size for predictive dissolution testing. Since this reduction may bias predictive test results, the effects of particle size on drainage quality were examined using three different rock types: a quartz latite diatreme with coarse and fine iron sulfides occurring both as disseminated grains and in veinlets (RK3); a pyritized mudstone with sulfides occurring in "relatively open and porous veinlets" and carbonate minerals occurring in "tight" veinlets (RK4); and an olivine gabbro with sulfides occurring as disseminated grains (RK5).

The effect of particle size on drainage pH was apparently controlled by the changes in available sulfide mineral surface area relative to calcium/magnesium carbonate mineral surface area. As the particle size of RK3 was reduced, drainage pH remained relatively constant, but the dissolution rate of acid-neutralizing minerals increased while that of acid-producing minerals remained relatively constant. This suggests that the reduction of particle size would, over the short term, produce drainage less acidic in nature than that which would be generated by large particles. This general trend was demonstrated more explicitly by RK4. The largest size fractions of this rock generated drainage pH values in the low three's, while the pH of drainage from the smaller size fractions was almost always above seven. With RK5, a gabbro containing disseminated sulfides, both acid production and acid neutralization increased as particle size decreased. Since the rate of acid production exceeded the rate of acid neutralization, pH decreased with particle size. Field pH data for this rock were more closely simulated by the fine particles.

7. CONCLUSIONS

1. An extended duration is required for ambient temperature kinetic dissolution tests is required to deplete even a moderate (and available) neutralization potential in mine waste samples. Of the ten samples examined in the present study, the neutralization potential present as calcium and magnesium carbonate minerals (NP[(Ca/Mg)CO₃]) in four samples did not exceed 6 kg/t CaCO₃ and values for only two samples exceeded 20 kg/t CaCO₃. Despite the relatively small neutralization potentials, the calcium and magnesium carbonate

minerals were depleted from only three of the samples over the course of the 132-week dissolution experiment. The pH from drainage from one of these three samples (TL5: 5.05% S, 16 kg/t CaCO₃ NP[(Ca/Mg)CO₃]) was below 6.0 at week 1 and was below three for most of the test. Drainage pH from the other two samples remained above pH 6 due to acid neutralization by silicate mineral dissolution, which was enhanced due to the small particle size used in the experiment.

2. Even if mine waste samples generate neutral pH drainage over the course of relatively long dissolution tests, it cannot be concluded that these samples will generate similar drainage in the field after mine closure. The neutralization potential was not depleted from seven of the samples which generated neutral pH drainage for 132 weeks. Sulfide minerals in the samples continued to oxidize over the entire period of record, as indicated by sulfate concentrations in the drainages. Whereas these seven samples may continue to produce nonacidic drainage, additional dissolution could deplete their neutralization potential while iron sulfide minerals remain and oxidize, with a consequent acidification of drainage.
3. Dissolution testing at higher temperature generally accelerated rates of sulfide oxidation and carbonate mineral dissolution and, therefore, decreased the time required to deplete neutralization potentials. For six of the ten samples, rates of iron sulfide oxidation (and the resultant acid generation) at 100°C were two to six times those at ambient temperature.
4. The Elevated Temperature Test will reduce the time required for predictive testing on some samples. The acceleration of sulfide oxidation produced by elevating the reaction temperature reduced the time required for neutralization potential depletion. In the Elevated Temperature Test, the NP[(Ca/Mg)CO₃] was depleted from a total of seven samples, including the three for which neutralization potential depletion was observed at ambient temperature. The four additional samples produced drainage pH below six after periods ("lag times") of 14 to 55 weeks in the Elevated Temperature Test.
5. Although the rates of sulfide mineral oxidation generally decreased over the course of experimentation at both ambient and elevated temperature, sulfate release continued throughout the duration of both experiments. At the end of the ambient temperature experiment, sulfate release rates were typically 30 to 60 percent of those near the beginning of the experiment. The corresponding range for the Elevated Temperature Test was 10 to 30 percent.
6. The majority of acid neutralization potential in the samples examined occurred as calcium and magnesium carbonate minerals. The empirical neutralization potential (ENP) observed in the Elevated Temperature Test quantified the content of minerals that would dissolve and maintain a drainage pH of at least 6.0. The ENPs of the seven samples which produced drainage pH values below 6.0 were in reasonably good agreement with the calcium/magnesium carbonate content of the samples.

7. Some acid neutralization by silicate mineral dissolution was observed. For two samples (RK1, RK2) the silicate mineral dissolution was fast enough to neutralize the slow rate of acid production by the small amount of iron sulfides present (0.46% S, 0.64% S). The drainage from a third sample (TL6, 5.81% S) eventually acidified; however, mass release calculations and SEM examination of leached grains indicate that some of the clinopyroxene (hedenbergite) present dissolved to neutralize acid. Quantitatively, the neutralization supplied by the 40 g of clinopyroxene present was small, equivalent to that supplied by dissolution of approximately 0.5 g of calcite.
8. The drainage quality beyond the dissolution test duration can be approximated using the initial content of calcium and magnesium carbonates and acid producing minerals, and the rates of calcium, magnesium, and sulfate release.
9. Extreme care must be taken when splitting samples for analysis and experimental use. The carbon dioxide evolved from samples subjected to dissolution testing was reanalyzed. Although the difference from the mean for the pairs of analyses was generally small, with a median value of 11%, one value was reported as 32%. Such differences can introduce substantial error in NP determination. Post-test verification of solid-phase analyses is recommended to limit the introduction of such error.
10. The effects of rock particle size on drainage pH were variable. The fine fraction of one rock type produced the lowest drainage pH, while the largest size fraction produced the lowest drainage pH for a second rock type. With a third rock type there was little effect of particle size on drainage quality. The effect for a particular rock type was apparently due to the influence of particle size reduction on the relative abundance of iron sulfide and carbonate mineral surface areas.

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REFERENCES

American Public Health Association (APHA), American Water Works Association, Water Environment Federation. 1992. Standard methods for the examination of water and wastewater, 18th ed. American Public Health Association, Washington, D.C.

Busenberg, E., Clemency, C. 1976. The dissolution kinetics of feldspars at 25°C. *Geochim. Cosmochim. Acta*, 40. p. 41-49.

Hedin, R. S., Erickson, P. M. 1988. Relationships between the initial geochemistry and leachate chemistry of weathering overburden samples. *In Proc. 1988 Mine Drainage and Surface Mine Reclamation Conference*, vol. 1. BuMines IC 9183. p. 21-28.

Hem, J. D. 1970. Study and interpretation of the chemical characteristics of natural water. Geological Survey Water-Supply Paper 1473, Washington, D.C. 363 p.

Kleinmann, R. L. P., Crerar, D. A., Pacelli, R. R. 1981. Biogeochemistry of acid mine drainage and a method to control acid formation. *Mining Eng.*, vol. 33. p. 300-306.

Lapakko, K. A. 1993. Evaluation of tests for predicting mine waste drainage pH: Report to the Western Governors' Association. Minnesota Department of Natural Resources, Division of Minerals, St. Paul, MN. 76 p. plus appendices.

Lapakko, K. 1991. Mine Waste Drainage Quality Prediction: A Literature Review. First Draft. MN Dept. Natural Resour. St. Paul, MN. 50 p.

Lapakko, K. A. 1990a. Solid phase characterization in conjunction with dissolution experiments for prediction of drainage quality. *In Proc. Western Regional Symposium on Mining and Mineral Processing Wastes*, F. Doyle (ed.), Soc. for Mining, Metallurgy, and Exploration, Inc., Littleton, CO. p. 81-86.

Lapakko, K. A. 1990b. Regulatory mine waste characterization: A parallel to economic resource evaluation. *In Proc. Western Regional Symposium on Mining and Mineral Processing Wastes*, F. Doyle (ed.), Soc. for Mining, Metallurgy, and Exploration, Inc., Littleton, CO. p. 31-39.

Lapakko, K. A. 1988. Prediction of acid mine drainage from Duluth Complex mining wastes in northeastern Minnesota. *In Proc. 1988 Mine Drainage and Surface Mine Reclamation Conference*, vol. 1. BuMines IC9183. p. 180-190.

Lawrence, R. W., Ritcey, G. M., Poling, G. W., Marchant, P. B. 1989. Strategies for the prediction of acid mine drainage. *In Proc. of the Thirteenth Annual British Columbia Mine Reclamation Symposium*. June 7-9, 1989, Vernon, British Columbia. p. 52-67.

Miller, S. D., Murray, G. S. 1988. Application of acid-base analysis from base metal and precious metal mines. In Proc. 1988 Mine Drainage and Surface Mine Reclamation Conference, vol. 1. BuMines IC 9183. p. 29-32.

Nelson, M. 1978. Kinetics and mechanisms of the oxidation of ferrous sulfide. Ph.D. Thesis, Stanford University, Palo Alto, CA.

Nordstrom, D. K. 1982. Aqueous pyrite oxidation and the consequent formation of secondary iron minerals. In Acid Sulfate Weathering. Soil Sci. Am. Madison, WI.

Renton, J. J., Rhymer, T. E., Stiller, A. H. 1988. A laboratory procedure to evaluate the acid producing potential of coal associated rocks. Mining Science and Technology, 7. p. 227-235.

Renton, J. J., Stiller, A. H., Rhymer, T. E. 1985. Evaluation of the acid producing potential of toxic rock materials. In Stopping Acid Mine Drainage: A New Approach. West Virginia Geological and Economic Survey. p. 7-12.

Renton, J. J. 1983. Laboratory studies of acid generation from coal associated rocks. In Proceedings of Surface Mining and Water Quality, Clarksburg, W. Va. May 26, 1983.

Singer, P. C., Stumm, W. 1970. Acid mine drainage: The rate determining step. Science, 167. p. 1121-1123.

Sobek, A. A., Schuller, W. A., Freeman, J. R., Smith, R. M. 1978. Field and laboratory methods applicable to overburden and minesoils. EPA 600/2-78-054. 203 p.

Stumm, W., Morgan, J. J. 1981. Aquatic chemistry - an introduction emphasizing chemical equilibria in natural waters. John Wiley & Sons, Inc. p. 470.

Table 1. Samples selected for predictive testing.

Solid	Mine Type	Host Rock	Sulfur (%)			CO ₂ (%)	APP ²	Mod. APP ³	NP ⁴	Net NP ⁵	Field ⁶
			Total	Sulfate	Sulfide ¹						
RK1	Au	pyritized mudstone	0.46	0.04	0.42	0.11	14	13	3	-10	no data
RK2	Cu-Ni	troctolite-gabbro	0.64	0.01	0.63	0.03	20	20	0.7	-19	acid
RK3	Au	quartz latite	1.63	0.03	1.60	1.41	51	50	32	-18	acid
RK4	Au	adularized and pyritized mudstone	2.91	0.09	2.82	1.42	91	88	32	-56	acid
TL1	Mo	metasomatised aplite/andesite	0.96	0.06	0.90	0.87	30	28	20	-8	neutral
TL2	Mo	quartz monzonite w/quartz porphyry	1.49	0.04	1.45	0.80	47	45	18	-27	neutral
TL3	Au	sideroplessite quartz schist (?)	2.19	0.07	2.12	4.06	68	66	92	26	neutral
TL4	Cu	hydrothermal porphyry (?)	2.30	0.20	2.10	0.25	72	66	6	-60	neutral
TL5	Au	latite	5.05	0.20	4.85	0.65	160	152	15	-137	acid
TL6	Au	(pyrrhotite) skarn	5.81	0.63	5.18	2.01	180	162	46	-116	neutral

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"?" implies uncertainty

¹ Determined as difference between total sulfur and sulfate.

² APP = Acid Producing Potential in tons CaCO₃/1000 tons rock = 31.25 × Total Sulfur.

³ Mod. APP = Acid Producing Potential in tons CaCO₃/1000 tons rock = 31.25 × Sulfide.

⁴ NP = Neutralization Potential in tons CaCO₃/1000 tons rock = 22.73 × CO₂.

⁵ Net NP in tons CaCO₃/1000 tons rock = NP – Mod. APP.

⁶ Field = drainage quality observed in the field

Table 2. Average and standard deviation for sulfur and carbon dioxide content of triplicate sample splits.

Solid	Sulfur Content (%)					Carbon Dioxide (%)				
	A	B	C	Ave ¹	SD ²	A	B	C	Ave	SD
RK1	0.45	0.47	0.45	0.46	0.012	0.12	0.11	0.11	0.11	0.006
RK2	0.63	0.64	0.64	0.64	0.006	0.02	0.03	0.05	0.03	0.015
RK3	1.61	1.75	1.53	1.63	0.111	1.30	1.44	1.48	1.41	0.095
RK4	2.87	2.97	2.88	2.91	0.055	1.38	1.47	1.42	1.42	0.045
TL1	0.91	0.98	0.98	0.96	0.040	0.90	0.84	0.86	0.87	0.031
TL2	1.48	1.48	1.50	1.49	0.012	0.75	0.84	0.82	0.80	0.047
TL3	2.19	2.21	2.16	2.19	0.025	4.18	4.00	4.00	4.06	0.104
TL4	2.14	2.23	2.28	2.22	0.071	0.18	0.24	0.25	0.22	0.038
TL5	5.43	4.84	4.98	5.08	0.308	0.68	0.64	0.64	0.65	0.023
TL6	6.00	6.05	5.37	5.81	0.379	1.99	2.10	1.95	2.01	0.078

¹ Ave = average (mean)

² SD = standard deviation

Table 3. Sample mass and rinse volume for the Particle Size Experiment.

Solid	Particle Size (mesh) ¹	Mass (g)	Rinse Volume (mL)
RK3	-270	75	200
	+270/-100	75	200
	+100/-35	75	200
	+35/-10	1000	400
	+10/-¼"	500	200
RK4	-270	75	200
	+270/-100	75	200
	+100/-35	75	200
	+35/-10	1000	400
	+10/-¼"	1000	400
	+¼"/-¾"	1000	400
RK5	-270	75	200
	+270/-100	75	200
	+100/-35	75	200
	+35/-10	1000	300
	+10/-¼"	1000	300
	+¼"/-¾"	1000	300

¹ Unless otherwise indicated.

Table 4. Particle size distribution for mine waste samples used in the Wet-Dry Cycle and the Elevated Temperature Tests.

Sample	+100 M (+0.149 mm)	+270 M (+0.053 mm)	+500 M (+0.025 mm)	-500 M (-0.025 mm)
RK1	0.00	14.80	15.18	70.02
RK2	0.02	37.10	26.20	36.68
RK3	0.05	29.35	19.42	51.18
RK4	0.00	11.60	13.65	74.75
TL1	75.49	11.69	4.14	8.68
TL2	27.57	26.65	14.61	31.17
TL3	0.59	31.22	29.90	38.24
TL4	27.10	23.16	12.08	37.66
TL5	31.08	21.10	12.10	35.72
TL6	22.57	31.41	18.31	27.71

Table 5. Chemical analysis for sulfur, carbon dioxide, and major components in mine waste samples.

Solid	concentrations in percent															
	S _{TOT}	SO ₄ as S	S ²⁻	CO ₂	Al ₂ O ₃	CaO	Fe ₂ O ₃	K ₂ O	MgO	MnO	Na ₂ O	P ₂ O ₅	SiO ₂	TiO ₂	LOI	Total
RK1	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
RK2	0.64	0.01	0.63	0.03	17.20	7.79	14.52	0.61	7.90	0.15	2.59	0.23	45.73	1.54	0.15	98.42
RK3	1.63	0.03	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
RK4	2.91	0.09	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
TL1	0.96	0.06	0.90	0.87	11.30	2.05	2.87	5.98	1.47	0.07	1.35	0.25	69.80	0.52	2.40	98.06
TL2	1.49	0.04	1.45	0.80	9.91	1.66	4.17	4.53	1.11	0.08	0.34	0.21	74.98	0.26	2.70	99.96
TL3	2.19	0.07	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
TL4	2.30	0.20	2.10	0.25	14.40	0.35	4.12	4.84	0.67	0.04	0.29	0.11	68.80	0.35	4.24	98.21
TL5	5.05	0.20	4.85	0.65	13.60	0.33	7.35	6.70	0.78	0.01	1.84	<0.01	62.40	0.29	5.09	98.40
TL6	5.81	0.63	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

Table 6. Mine waste mineralogy: Sulfur-bearing minerals (values in weight percent).

Sulfur-Bearing Minerals		RK1	RK2	RK3	RK4	TL1	TL2	TL3	TL4	TL5	TL6
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	-	<0.01	-	-	-	-	-	-	-	-
Arsenopyrite	As,S	?	-	0.01	0.02?	-	0.01?	0.05	<0.01?	-	0.08?
Maucherite	Ni,As,Ag	-	0.01	-	-	-	-	-	-	-	-
Tennantite	Cu,As,S	0.02?	-	-	?	-	-	-	-	0.02	-
Proustite	Ag,As,S	-	-	-	-	-	-	-	0.07	-	<0.01?
Chalcopyrite	Cu,S	?	0.27	0.04	<0.01	0.04	0.02	0.02	?	0.02	0.23
Cubanite	Cu,S	-	0.67	-	-	-	-	-	?	-	-
Bornite	Cu,S	-	0.04	-	-	-	-	-	0.13	<0.01	-
Chalcocite	Cu,S	?	-	-	0.01	?	0.03	-	-	-	-
Covellite	Cu,S	?	-	-	<0.01	?	-	-	-	<0.01	0.18
Stibnite	Sb,S	?	-	-	0.01	-	-	-	-	-	-
Tetrahedrite	Cu,Sb,S	<0.01?	-	<0.01	?	-	-	?	<0.01	-	-
Galena	Pb,S	<0.01?	-	0.25	<0.01	<0.01	<0.01	<0.01	0.04	0.01	0.02
Sphalerite	Zn,Cd,S	0.02	-	0.79	0.02	0.01	0.04	0.01	-	0.02	0.03
Acanthite	Ag,S	-	-	<0.01	-	-	-	-	-	-	-
Gypsum	SO ₄	-	-	-	0.5	0.4	-	0.3	-	-	-
Anhydrite	SO ₄	-	-	-	-	-	-	0.1	-	-	-
Barite	Ba,SO ₄	?	-	0.3	?	-	0.4	-	?	0.1	-
Jarosite	SO ₄	0.1?	-	-	-	?	-	-	?	-	-
Melanterite	SO ₄	0.2	0.1?	-	0.2?	-	-	-	-	0.2?	5.4?

"?" indicates the mineral was probably present but not precisely identified by XRD.

"-" indicates the mineral was not detected by XRD in the sample.

Table 7. Mine waste mineralogy: Carbonate minerals and neutralization potential present as calcium and magnesium carbonate (NP[(Ca/Mg)CO₃]).

	RK1	RK2	RK3	RK4	TL1	TL2 ¹	TL3	TL4	TL5	TL6
Carbonate Minerals (weight percent)										
Calcite	?	0.1	0.5	-	1.5	0.7	0.2	0.6	-	4.6
Dolomite	?	-	-	3.0	0.4 ³	0.8 ³	-	-	1.10	-
Ankerite	-	-	-	-	-	-	1.9	-	-	-
Siderite ²	0.3	-	3.2	-	-	0.2	8.3	-	-	-
Rhodochrosite	-	-	?	-	<0.1	-	-	-	-	-
Magnesite	-	-	-	-	-	-	-	-	0.23	-
Carbonate (percent)										
Total CaCO ₃ ⁴	0	0.1	0.5	1.61	1.71	1.13	1.23	0.60	0.59	4.60
Total MgCO ₃ ⁴	0	0	0	1.39	0.18	0.37	0.60	0	0.74	0
NP[(Ca/Mg)CO ₃], kg/t CaCO ₃										
NP[(Ca/Mg)CO ₃]	3 ⁵	1	5	32	19	16	19	6	15	46
Error Interval	0-2.9	0-2.3	1.9-9.7	28-37	17-23	13-21	8.1-33	3.7-6.6	9.8-17	35-52

"?" indicates the mineral was probably present but not precisely identified by XRD.

"-" indicates the mineral was not present in the sample.

¹ Trace amounts of copper carbonates were noted in TL2.

² Some magnesium may be associated with siderite.

³ Secondary feldspar XRD peak may make false contribution to dolomite peak.

⁴ Values represent all calcium or magnesium associated with carbonate.

⁵ Calculated as CO₂ content (in percent) × 22.73.

Table 8. Mine waste mineralogy: Rock forming minerals (values in weight percent)¹.

Mineral	RK1	RK2	RK3	RK4	TL1	TL2	TL3	TL4	TL5	TL6
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	-

"?" indicates the mineral was probably present but not precisely identified by XRD.

"-" indicates the mineral was not present in the sample.

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.

Table 9. Solid phase analysis for the Particle Size Experiment: Sulfur and carbon dioxide contents as a function of particle size.

Solid	Particle Size (mesh) ¹	Assays (%)		
		S (total)	S as SO ₄	CO ₂
RK3	-270	0.95	0.16	0.96
	-100/+270	1.98	0.04	1.32
	-35/+100	2.34	0.03	1.60
	-10/+35	1.90	0.05	1.73
	-¼"/+10	1.50	0.04	1.46
RK4	-270	2.83	0.28	0.88
	-100/+270	3.01	0.08	1.64
	-35/+100	2.61	0.07	1.68
	-10/+35	2.79	0.11	1.40
	-¼"/+10	3.52	0.13	1.27
	-¾"/+¼"	3.46	0.14	1.89
RK5	-270	1.51	0.08	0.32
	-100/+270	0.87	0.08	0.10
	-35/+100	1.29	0.09	0.06
	-10/+35	0.88	0.07	0.05
	-¼"/+10	0.83	0.06	0.09
	-¾"/+¼"	0.93	0.03	<0.01

¹ Unless otherwise indicated.

Table 10. Wet-Dry Cycle Test summary.

Solid	Initial Sulfur (%)	Initial Sulfide (%)	Carbonate Mineral Content ¹ (%)				APP (kg/t CaCO ₃)		NP [(Ca/Mg)CO ₃] (kg/t CaCO ₃)			Release Rates (t ₁₃₂) (μmol/g·wk)			
			C	D	A	S	t ₀ ²	t ₁₃₂	t ₀	t ₁₃₂ ³	ENP ⁴	SO ₄	Ca+Mg	Ca	Mg
RK1	0.46	0.42	tr	tr	--	0.3	14	12	3 ⁵	0	>(3-4)	0.093	0.15	0.053	0.11
RK2	0.64	0.63	0.1	--	--	--	20	16	1	0	>(3-4)	0.11	0.15	0.080	0.067
RK3	1.63	1.60	0.5	--	--	3.2 ⁶	51	47	5	0-1	>(4-5)	0.20	0.21	0.080	0.15
RK4	2.91	2.82	--	3.0	--	--	91	76	32	10-15	>(17-22)	0.40	0.41	0.21	0.20
TL1	0.96	0.90	1.5	0.4 ⁶	--	--	30	27	19	12-13	>(6-7)	0.093	0.43	0.40	0.027
TL2	1.49	1.45	0.7	0.8 ⁶	--	0.2	47	42	16	0	>(17-19)	0.65	1.4	1.3	0.093
TL3	2.19	2.12	0.2	--	1.9	8.3	68	57	19	0	>(21-25)	0.47	1.5	0.82	0.67
TL4	2.30	2.10	0.6	--	--	--	72	67	6	0-2	>(4-7)	0.20	0.28	0.15	0.13
TL5	5.05	4.85	--	1.1 ⁶	--	--	160	91	15	0-7	0-6	2.8	0.15	0.067	0.080
TL6	5.81	5.18	4.6	--	--	--	180	140	46	0-9	>(37-65)	1.4	2.2	2.1	0.093

t_x = at time equals x, in weeks

¹ C = calcite; D = dolomite; A = ankerite; S = siderite; tr = trace; -- = not detected.

² Based on total sulfur.

³ NP[(Ca/Mg)CO₃] at 132 weeks calculated by subtracting calcium and magnesium release from NP[(Ca/Mg)CO₃] at t₀. Minimum value includes release from weeks 0-132, while maximum value excludes the release attributed to removal of oxidation products generated prior to week 0 (weeks 0-5).

⁴ ENP = Empirical Neutralization Potential. Total NP release prior to the point at which the drainage pH dropped below and remained below 6.0. For solids where the drainage pH did not remain below 6.0, NP was reported as greater than the NP release at the end of the test. The lower end of the range includes release from weeks 0-5, while the upper end of the range excludes release from weeks 0-5.

⁵ Non-standard neutralization potential calculation, see table 7 for additional detail.

⁶ See table 7 for additional detail.

Table 11. Rates of release of sulfate, calcium plus magnesium, calcium, and magnesium for the Wet-Dry Cycle Test (Rocks RK1 - RK4).

Solid	Period (weeks)	No. of Measured Values	Sulfate		Calcium+Magnesium		Calcium		Magnesium		Ca+Mg ----- SO ₄
			m*	r ^{2**}	m	r ²	m	r ²	m	r ²	
RK1	0-3	6	0.086	0.528	0.090	0.941	0.032	0.933	0.057	0.945	1.047
	4-59	56	0.013	0.975	0.027	0.994	0.010	0.988	0.017	0.995	2.077
	60-132	73	0.007	0.993	0.011	0.992	0.004	0.989	0.008	0.993	1.571
RK2	0-24	27	0.044	0.962	0.037	0.960	0.024	0.958	0.013	0.958	0.841
	25-83	59	0.017	0.993	0.020	0.994	0.010	0.996	0.010	0.989	1.177
	84-132	49	0.008	0.992	0.011	0.998	0.006	0.999	0.005	0.988	1.375
RK3	0-6	9	0.110	0.877	0.115	0.937	0.072	0.944	0.043	0.923	1.046
	7-25	19	0.024	0.987	0.036	0.998	0.025	0.998	0.011	0.998	1.500
	26-105	80	0.011	0.992	0.021	0.988	0.011	0.976	0.010	0.995	1.909
	106-132	27	0.015	0.995	0.016	0.998	0.006	0.995	0.011	0.999	1.067
RK4	0-4	7	0.444	0.868	0.498	0.916	0.253	0.899	0.245	0.933	1.122
	5-40	36	0.022	0.947	0.080	0.996	0.045	0.998	0.035	0.994	3.636
	41-122	82	0.085	0.991	0.117	0.978	0.065	0.975	0.052	0.983	1.377
	123-132	10	0.030	0.993	0.031	0.995	0.016	0.996	0.015	0.994	1.033

* m = slope = release in mmol/week

** r² = squared correlation coefficient

Table 11 (con't). Rates of release of sulfate, calcium plus magnesium, calcium, and magnesium for the Wet-Dry Cycle Test (Tailings TL1 - TL6).

Solid	Period (weeks)	No. of Measured Values	Sulfate		Calcium+Magnesium		Calcium		Magnesium		Ca+Mg ----- SO ₄
			m [*]	r ^{2**}	m	r ²	m	r ²	m	r ²	
TL1	0-1	4	0.088	0.183	0.168	0.305	0.135	0.282	0.033	0.425	1.909
	2-32	31	0.018	0.992	0.044	0.998	0.041	0.999	0.003	0.946	2.444
	33-132	100	0.007	0.992	0.032	0.997	0.030	0.999	0.002	0.937	4.571
TL2	0-1	4	0.184	0.499	0.381	0.574	0.334	0.557	0.047	0.708	2.071
	2-109	108	0.012	0.979	0.098	0.996	0.091	0.998	0.007	0.951	8.167
	110-132	23	0.049	0.994	0.104	1.000	0.097	1.000	0.007	0.984	2.122
TL3	0-1	4	0.320	0.182	0.551	0.363	0.345	0.381	0.207	0.334	1.722
	2-10	9	0.159	0.989	0.242	1.000	0.149	1.000	0.094	1.000	1.522
	11-20	10	0.084	0.973	0.159	0.990	0.099	0.988	0.059	0.993	1.893
	21-132	112	0.035	0.998	0.112	1.000	0.062	1.000	0.050	0.998	3.200
TL4	0-4	7	0.117	0.597	0.189	0.773	0.180	0.774	0.009	0.741	1.615
	5-19	15	0.027	0.997	0.046	0.997	0.039	0.993	0.007	0.982	1.704
	20-85	66	0.010	0.986	0.025	0.999	0.014	0.994	0.011	0.994	2.500
	86-103	18	0.007	0.994	0.018	0.993	0.008	0.994	0.009	0.991	2.571
	104-132	29	0.015	0.997	0.021	0.999	0.011	0.999	0.010	0.997	1.400
TL5	0-21	24	0.661	0.997	0.297	0.931	0.102	0.666	0.195	0.995	0.449
	22-85	64	0.361	0.997	0.029	0.950	0.006	0.945	0.023	0.950	0.080
	86-132	47	0.209	0.999	0.011	0.989	0.005	0.941	0.006	0.999	0.053
TL6	0-4	7	2.187	0.783	2.880	0.829	2.807	0.833	0.074	0.568	1.317
	5-19	15	0.313	0.987	0.428	0.988	0.412	0.988	0.016	0.990	1.367
	20-59	40	0.153	0.999	0.226	1.000	0.216	1.000	0.010	0.997	1.477
	60-132	73	0.103	0.997	0.167	0.999	0.160	0.999	0.007	0.999	1.621

* m = slope = release in mmol/week

** r² = squared correlation coefficient

Table 12. Percent depletion of acid production potential (APP) and neutralization potential (NP[(Ca/Mg)CO₃]) for the Wet-Dry Cycle Test for weeks 0 - 132.

Solid	Initial Total Sulfur	Initial APP	APP Released	APP Percent Depletion ¹		APP Remaining kg/t CaCO ₃
	%	kg/t CaCO ₃	mg as CaCO ₃	weeks 0-5	weeks 0-132	
RK1	0.46	14.4	216	8.6	20	12
RK2	0.64	20.0	269	4.2	18	16
RK3	1.63	51.0	303	3.4	7.9	47
RK4	2.91	90.9	1150	5.0	17	76
TL1	0.96	30.0	193	3.2	8.6	27
TL2	1.49	46.6	315	2.3	9.0	42
TL3	2.19	68.4	848	5.4	17	57
TL4	2.30	71.9	341	3.1	6.3	67
TL5	5.05	158	5030	5.5	43.0	91
TL6	5.81	182	3390	11	25.0	140

Solid	Initial NP	Calcium Released	Magnesium Released	NP Released	NP Percent Depletion ¹		NP Remaining ² kg/t CaCO ₃
	kg/t CaCO ₃	mg	mg	mg as CaCO ₃	weeks 0-5	weeks 0-132	
RK1	3	45.3	48.9	314	34.9	140	-0.15 to -1.2
RK2	1	63.4	28.9	277	66.1	370	-2.0 to -2.7
RK3	5	89.4	41.9	396	30.0	105	1.3 to -0.27
RK4	32	356	176	1610	14.0	67.3	15 to 11
TL1	19	199	12.2	546	7.74	38.3	14 to 12
TL2	16	526	25.7	1420	13.2	118	-0.77 to -2.9
TL3	19	434	197	1890	24.1	133	-1.7 to -6.2
TL4	6	158	32.5	528	45.7	117	1.7 to -1.0
TL5	15	264	163	1330	65.1	118	7.1 to -2.7
TL6	46	1870	58.2	4900	61.8	142	9.1 to -19

¹ Weeks 0-5 represent release attributed to rinsing off of oxidation products accumulated during sample storage prior the beginning of the experiment. Weeks 0-132 represent release attributed to mineral dissolution plus release from weeks 0-5.
² Range of depletion represents weeks 6-132 to weeks 0-132; negative sign indicates calcium and magnesium release exceeded that reported with solid phase carbonate analysis.

Table 13. Comparison of APP and NP[(Ca/Mg)CO₃] release in the Elevated Temperature (weeks 1 - 130/131) and the Wet-Dry Cycle (weeks 1 - 132) Tests.

	APP Release (kg/t CaCO ₃)			NP[(Ca/Mg)CO ₃] Release (kg/t CaCO ₃)		
	Wet-Dry Cycle	Elevated Temperature	Ratio ¹	Wet-Dry Cycle	Elevated Temperature	Ratio ¹
RK1	1.9	8.0	4.2	3.7	8.3	2.2
RK2	3.3	2.2	0.67	3.5	3.7	1.1
RK3	3.0	12	4.0	4.5	8.3	1.8
RK4	13	47	3.6	20	31	1.6
TL1	1.7	9.7	5.7	6.2	17	2.7
TL2	3.5	16	4.6	18	25	1.4
TL3	8.3	9.3	1.1	22	28	1.3
TL4	2.7	6.6	2.4	5.2	5.8	1.1
TL5	63	65	1.0	11	11	1.0
TL6	33	33	1.0	49	55	1.1

¹ Ratio of Elevated Temperature Test release to Wet-Dry Cycle Test release.

Table 14. Elevated Temperature Test summary.

Solid	Initial Sulfur (%)	Initial Sulfide (%)	Carbonate Mineral Content ¹ (%)				APP (kg/t CaCO ₃)		NP [(Ca/Mg)CO ₃] (kg/t CaCO ₃)			Release Rates (t ₁₃₀) (μmol/g·wk)			
			C	D	A	S	t ₀ ²	t ₁₃₀	t ₀	t ₁₃₀ ³	ENP ⁴	SO ₄	Ca+Mg	Ca	Mg
RK1	0.46	0.42	tr	tr	--	0.3	14	5.4	3 ⁵	0	0-2.5	0.11	0.11	0.040	0.067
RK2	0.64	0.63	0.1	--	--	--	20	17	1	0	2-3	0.093	0.13	0.093	0.040
RK3	1.63	1.60	0.5	--	--	3.2 ⁶	51	37	5	0	2-5	0.44	0.19	0.053	0.13
RK4	2.91	2.82	--	3.0	--	--	91	41	32	0-8	13-22	1.5	0.19	0.080	0.11
TL1	0.96	0.90	1.5	0.4 ⁶	--	--	30	19	19	1-3	>(16-18)	0.52	0.99	0.96	0.013
TL2	1.49	1.45	0.7	0.8 ⁶	--	0.2	47	29	16	0	17-20	0.60	0.64	0.52	0.11
TL3	2.19	2.12	0.2	--	1.9	8.3	68	55	19	0	>(25-32)	0.16	1.5	0.81	0.71
TL4	2.30	2.10	0.6	--	--	--	72	63	6	0-1	3-6	0.87	0.24	0.12	0.11
TL5	5.05	4.85	--	1.1 ⁶	--	--	160	87	15	0-8	0-8	2.3	0.11	0.027	0.080
TL6	5.81	5.18	4.6	--	--	--	180	130	46	0-4	>(42-79)	0.87	1.7	1.6	0.12

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t_x = at time equals x, in weeks

¹ C = calcite; D = dolomite; A = ankerite; S = siderite; tr = trace; -- = not detected.

² Based on total sulfur.

³ NP[(Ca/Mg)CO₃] at 130 weeks calculated by subtracting calcium and magnesium release from NP[(Ca/Mg)CO₃] at t₀. The minimum value includes release from weeks 0-130, while the maximum value excludes the release attributed to the removal of oxidation products generated prior to week 0 (weeks 0-6).

⁴ ENP = Empirical Neutralization Potential. Total NP release prior to the point at which the drainage pH dropped below and remained below 6.0. For solids where the drainage pH did not remain below 6.0, NP was reported as greater than the NP release at the end of the test. The lower end of the range includes release from weeks 0-6, while the upper end of the range excludes release from weeks 0-6.

⁵ Non-standard neutralization potential calculation, see table 7 for additional detail.

⁶ See table 7 for additional detail.

Table 15. Rates of release of sulfate, calcium plus magnesium, calcium, and magnesium for the Elevated Temperature Test (Rocks RK1 - RK4).

Solid	Period (weeks)	No. of Measured Values	Sulfate		Calcium + Magnesium		Calcium		Magnesium		Ca + Mg ----- SO ₄
			m*	r ^{2**}	m	r ²	m	r ²	m	r ²	
RK1	0-14	10	0.227	0.990	0.236	0.992	0.098	0.993	0.139	0.991	1.040
	16-22	4	0.082	0.989	0.076	0.993	0.031	0.992	0.045	0.994	0.927
	24-28	3	0.101	0.930	0.108	0.913	0.044	0.914	0.064	0.911	1.069
	30-52	12	0.029	0.996	0.037	0.989	0.016	0.985	0.021	0.991	1.276
	54-66	7	0.016	0.997	0.021	0.979	0.010	0.963	0.011	0.988	1.313
	68-130	32	0.008	0.985	0.008	0.985	0.003	0.985	0.005	0.984	1.000
RK2	0-4	5	0.084	0.813	0.125	0.894	0.087	0.908	0.038	0.861	1.488
	6-24	10	0.017	0.992	0.028	0.999	0.019	0.998	0.009	0.997	1.647
	26-62	19	0.013	0.992	0.026	0.990	0.015	0.993	0.011	0.978	2.000
	64-76	7	0.010	1.000	0.014	0.963	0.009	0.953	0.005	0.977	1.400
	78-82	2	0.013	1.000	0.022	1.000	0.011	1.000	0.011	1.000	1.692
	84-130	25	0.007	0.999	0.010	0.998	0.007	0.999	0.003	0.996	1.429
RK3	0-8	7	0.287	0.952	0.221	0.963	0.142	0.969	0.079	0.951	0.770
	10-28	10	0.107	0.972	0.085	0.976	0.041	0.940	0.044	0.988	0.794
	30-54	13	0.071	0.994	0.052	0.994	0.015	0.990	0.037	0.995	0.732
	56-130	38	0.033	0.994	0.014	0.971	0.004	0.985	0.010	0.960	0.424
RK4	0-18	12	0.906	0.994	1.045	0.989	0.561	0.990	0.485	0.986	1.153
	20-28	5	0.508	0.989	0.282	0.981	0.179	0.979	0.103	0.984	0.555
	30-88	30	0.173	0.998	0.040	0.934	0.022	0.899	0.018	0.968	0.231
	90-130	21	0.109	0.993	0.014	0.999	0.006	0.999	0.008	0.999	0.128

* m = slope = release in mmol/week

** r² = squared correlation coefficient

Table 15 (con't). Rates of release of sulfate, calcium plus magnesium, calcium, and magnesium for the Elevated Temperature Test (Tailings TL1 - TL6).

Solid	Period (weeks)	No. of Measured Values	Sulfate		Calcium+Magnesium		Calcium		Magnesium		Ca+Mg ----- SO ₄
			m*	r ^{2**}	m	r ²	m	r ²	m	r ²	
TL1	0-2	4	0.086	0.230	0.172	0.358	0.151	0.373	0.021	0.276	2.000
	4-8	3	0.016	0.997	0.058	1.000	0.055	1.000	0.003	0.964	3.625
	10-18	5	0.069	0.976	0.130	0.991	0.122	0.990	0.008	0.997	1.884
	20-45	14	0.085	0.992	0.145	0.999	0.139	0.999	0.005	0.990	1.706
	47-65	10	0.060	0.990	0.098	0.993	0.095	0.992	0.004	0.986	1.633
	67-131	33	0.039	0.993	0.074	0.994	0.072	0.994	0.001	0.998	1.897
TL2	0-2	4	0.180	0.535	0.390	0.643	0.358	0.644	0.033	0.630	2.167
	4-12	5	0.053	0.995	0.189	0.994	0.169	0.993	0.020	0.999	3.566
	14-30	9	0.290	0.983	0.475	0.996	0.439	0.996	0.036	0.997	1.638
	32-45	8	0.124	0.987	0.184	0.998	0.166	0.998	0.019	0.991	1.484
	47-63	9	0.079	0.998	0.099	0.997	0.085	0.997	0.013	0.999	1.253
	65-131	34	0.045	0.996	0.048	0.994	0.039	0.992	0.008	1.000	1.067
TL3	0-4	5	0.466	0.717	0.618	0.777	0.396	0.795	0.223	0.746	1.326
	6-24	10	0.160	0.994	0.309	0.998	0.202	0.990	0.107	0.992	1.931
	26-51	14	0.041	0.995	0.153	0.995	0.086	0.994	0.066	0.995	3.732
	53-63	6	0.026	0.995	0.127	0.997	0.071	0.998	0.056	0.997	4.885
	65-131	34	0.012	0.976	0.114	0.972	0.061	0.969	0.053	0.975	9.500
TL4	0-2	4	0.216	0.301	0.310	0.428	0.295	0.430	0.015	0.376	1.435
	4-6	2	0.030	1.000	0.057	1.000	0.054	1.000	0.003	1.000	1.900
	8-20	7	0.018	0.987	0.051	0.996	0.040	0.989	0.011	0.988	2.833
	22-77	29	0.014	0.987	0.037	0.978	0.020	0.971	0.017	0.985	2.643
	79-131	27	0.065	0.997	0.018	0.905	0.009	0.915	0.008	0.893	0.277
TL5	0-8	7	0.725	0.926	0.498	0.766	0.265	0.576	0.233	0.948	0.687
	10-22	7	1.730	0.994	0.200	0.978	0.048	0.902	0.152	0.990	0.116
	24-28	3	0.590	0.999	0.080	0.999	0.020	0.955	0.061	0.999	0.136
	30-47	10	0.212	0.956	0.033	0.997	0.007	0.904	0.026	0.995	0.156
	49-131	42	0.169	0.996	0.008	0.968	0.002	0.917	0.006	0.978	0.047
TL6	0-2	5	2.879	0.694	3.759	0.690	3.645	0.696	0.115	0.469	1.306
	4-18	7	0.449	0.999	0.741	0.996	0.705	0.996	0.035	0.993	1.650
	20-30	6	0.239	0.974	0.366	0.989	0.347	0.989	0.019	0.987	1.531
	32-63	17	0.126	0.984	0.263	0.999	0.250	0.999	0.014	0.998	2.087
	65-131	34	0.065	0.993	0.131	0.992	0.122	0.991	0.009	0.999	2.015

m = slope = release in mmol/week; ** r² = squared correlation coefficient

Table 16. Percent depletion of acid production potential (APP) and neutralization potential (NP[(Ca/Mg)CO₃]) for the Elevated Temperature Test for weeks 0 - 130/131.

Solid	Initial Total Sulfur	Initial APP	APP Released	APP Percent Depletion ¹		APP Remaining kg/t CaCO ₃
	%	kg/t CaCO ₃	mg as CaCO ₃	weeks 0-6	weeks 0-130	
RK1	0.46	14.4	676	18	63	5.4
RK2	0.64	20.0	198	4.1	13	17
RK3	1.63	51.0	1010	6.1	27	38
RK4	2.91	90.9	3780	9.9	55	41
TL1	0.96	30.0	802	4.0	36	19
TL2	1.49	46.6	1280	3.3	37	30
TL3	2.19	68.4	979	8.8	19	55
TL4	2.30	71.9	654	3.6	12	63
TL5	5.05	158	5290	6.8	45	88
TL6	5.81	182	3760	15	28	130

Solid	Initial NP	Calcium Released	Magnesium Released	NP Released	NP Percent Depletion ¹		NP Remaining kg/t CaCO ₃
	kg/t CaCO ₃	mg	mg	mg as CaCO ₃	weeks 0-6	weeks 0-130	
RK1	3	114	97.7	685	82	305	-3.7 to -6.1
RK2	1	78.7	23.4	292	79	390	-2.1 to -2.9
RK3	5	131	90.6	699	52	187	-0.76 to -4.3
RK4	32	555	275	2520	29	105	7.5 to -1.6
TL1	19	531	14.7	1380	10	97	2.5 to 0.55
TL2	16	704	49.5	1960	19	160	-7.0 to -10
TL3	19	576	240.4	2430	37	170	-6.2 to -13
TL4	6	177	39.2	602	51	130	1.0 to -2.0
TL5	15	284	159	1360	72	120	7.7 to -3.2
TL6	46	2250	80.4	5940	81	170	4.1 to -33

¹ Weeks 0-6 represent release attributed to rinsing off of oxidation products accumulated during sample storage prior to the beginning of the experiment. Weeks 0-130 represent release attributed to mineral dissolution plus release from weeks 0-6.

² Range of depletion represents weeks 8-132 to weeks 0-132; negative sign indicates that calcium and magnesium release exceeded that reported with solid phase carbonate analysis.

Table 17. Comparison of Elevated Temperature Test empirical neutralization potential (ENP) and neutralization potential present as calcium and magnesium carbonate (NP [(Ca/Mg)CO₃]).

Solid	NP [(Ca/Mg)CO ₃] (kg/t CaCO ₃)	ENP (kg/t CaCO ₃)	Week
RK1	3	0-2.5	6 ¹
RK2	1	2.0-2.9	66 ¹
RK3	5	2-4.9	18
RK4	32	13-22	14
TL1	19	>(16-18)	131 ²
TL2	16	17-20	51
TL3	19	>(25-32)	131 ²
TL4	6	3-5.9	55
TL5	15	0-7.7	0
TL6	46	>(42-79)	131 ²

¹ Drainage pH dropped below pH 6.0, but did not remain below 6.0 for duration of test.

² Drainage pH remained above 6.0 for duration of test.

Table 18. Percent moisture content of the covered reactors as a function of particle size at day seven of the drying cycle for the Particle Size Experiment.

Solid	Particle Size (mesh ¹)	Mass (g)	Mean Volume (mL)	Moisture ² (%)
RK3	+270/-100	75	30.4	28.8
	+100/-35	75	26.5	26.1
	+35/-10	1000	186	15.7
	+10/-¼"	500	44.2	8.1
RK4	+270/-100	75	37.1	33.1
	+100/-35	75	36.0	32.4
	+35/-10	1000	148	12.9
	+10/-¼"	1000	52.4	5.0
	+¼"/-¾"	1000	46.6	4.5
RK5	-270	75	24.3	24.5
	+270/-100	75	25.0	25.0
	+100/-35	75	25.6	25.5
	+35/-10	1000	122	10.9
	+10/-¼"	1000	31.5	3.1
	+¼"/-¾"	1000	17.6	1.7

¹ Unless otherwise indicated.

² Percent moisture is reported as the mean volume of water retained in the reactors through week 30.

Table 19. Classification of samples based on drainage quality and neutralization potential (NP[(Ca/Mg)CO₃]) remaining in the Wet-Dry Cycle and in the Elevated Temperature Tests.

Drainage pH	Wet-Dry Cycle Test	Elevated Temperature Test
NP[(Ca/Mg)CO ₃] Depleted		
pH ≤ 3.5	TL5	RK4 (3.7) ¹ , TL4 (2.4), TL5 (1.0)
3.5 < pH ≤ 4.5	none	RK3 (4.1)
4.5 < pH ≤ 6.0	none	TL2 (4.6)
occasionally below 6.0	none	RK1 (4.2), RK2 (0.68)
6.5 ≤ pH < 7.0	RK1, RK2	none
NP[(Ca/Mg)CO ₃] Nearing Depletion		
6.5 ≤ pH pH decreasing	RK3, RK4, TL2, TL4	TL1 (5.6) ²
NP[(Ca/Mg)CO ₃] Remaining and Controlling Drainage Quality		
7.2 ≤ pH < 8.0	TL1, TL3, TL6	TL3 (1.1) ² , TL6 (1.0) ²

¹ The parenthetical values represent the ratio of sulfate release (weeks 1-130/132) in the Elevated Temperature Test to that in the Wet-Dry Cycle Test.

² NP[(Ca/Mg)CO₃] calculated as nearing depletion.

Figure 1. Experimental apparatus (reactor) for the Wet-Dry Cycle and the Elevated Temperature Tests, and for the 75 g samples of the Particle Size Experiment.

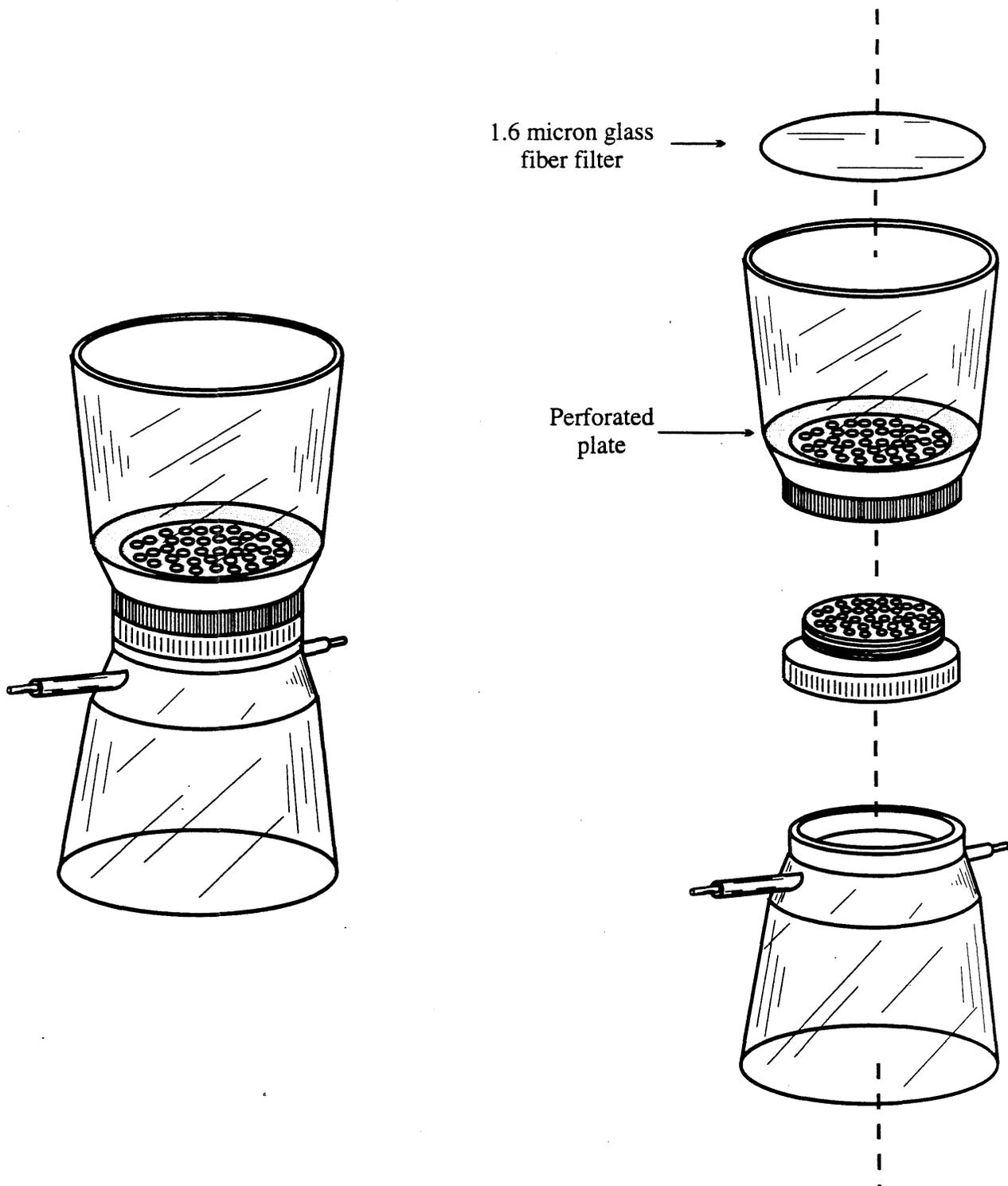


Figure 2. Drainage sample collection from large experimental reactor for the Particle Size Experiment.

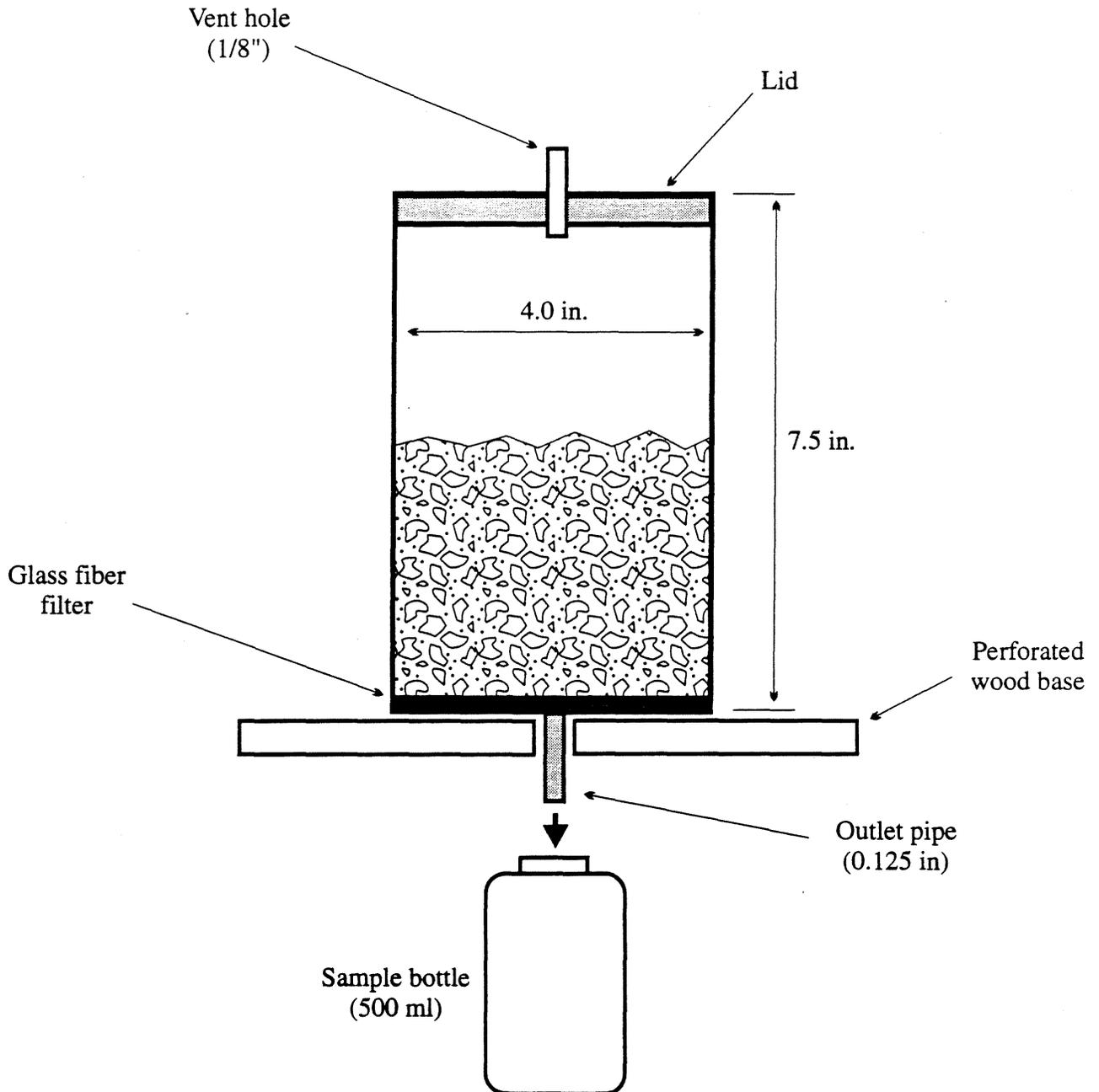


Figure 3. pH and concentrations of net alkalinity, sulfate, calcium, and magnesium in drainage from TL5 in the Wet-Dry Cycle Test (weeks 1 - 132).

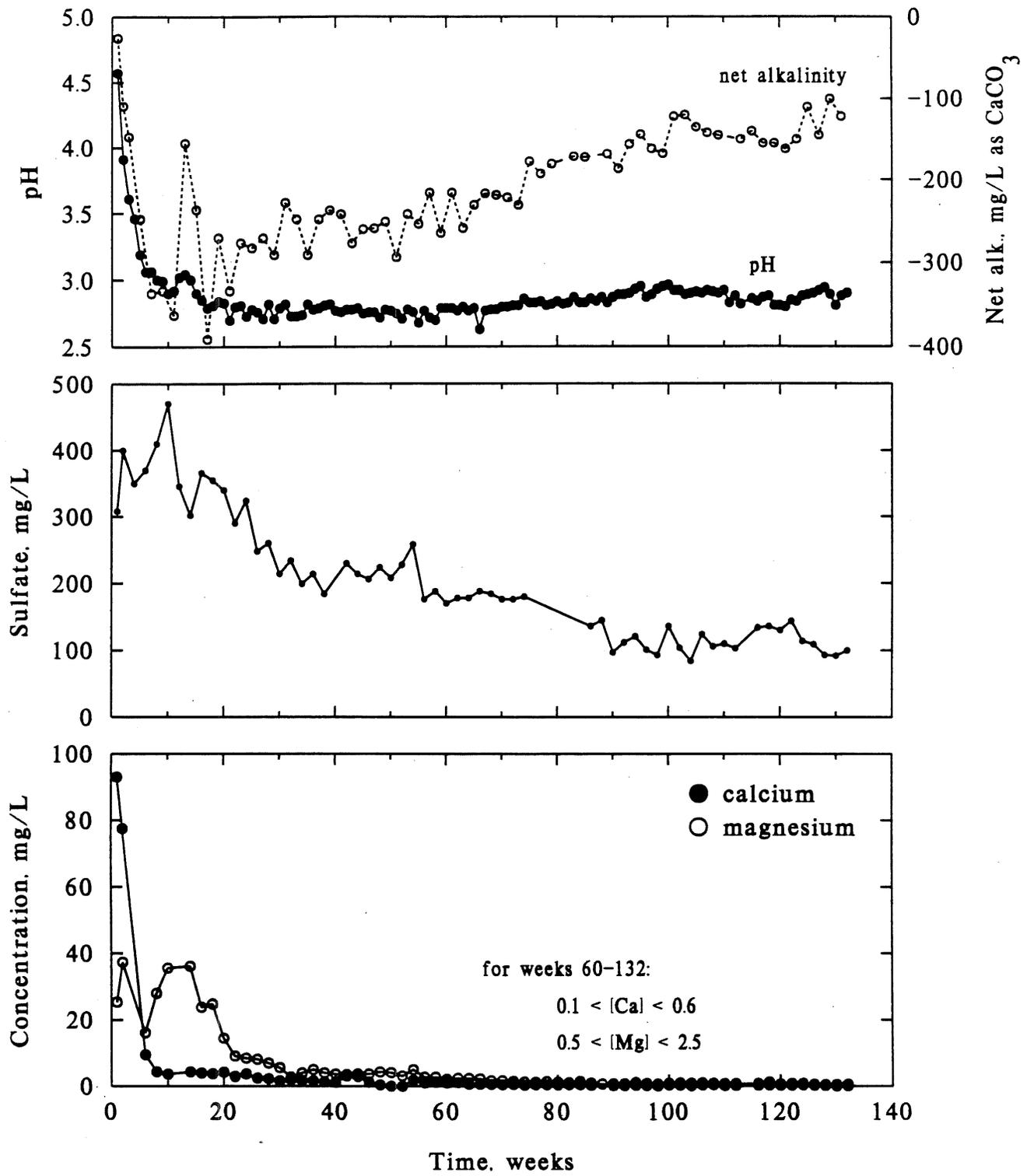


Figure 4. pH and concentrations of net alkalinity, sulfate, calcium, and magnesium in drainage from RK1 in the Wet-Dry Cycle Test (weeks 1 - 132).

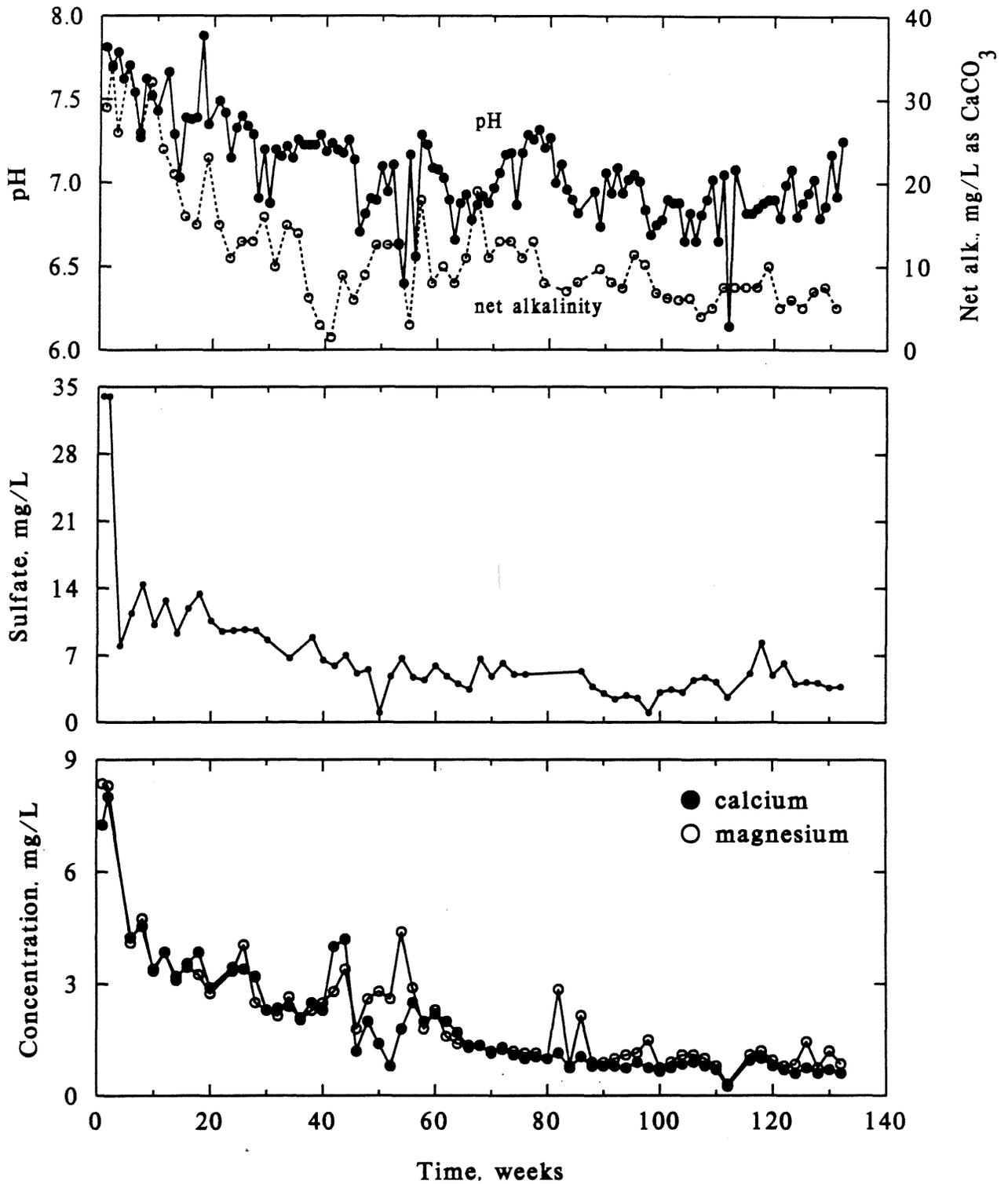


Figure 5. pH and concentrations of net alkalinity, sulfate, calcium, and magnesium in drainage from RK2 in the Wet-Dry Cycle Test (weeks 1 - 132).

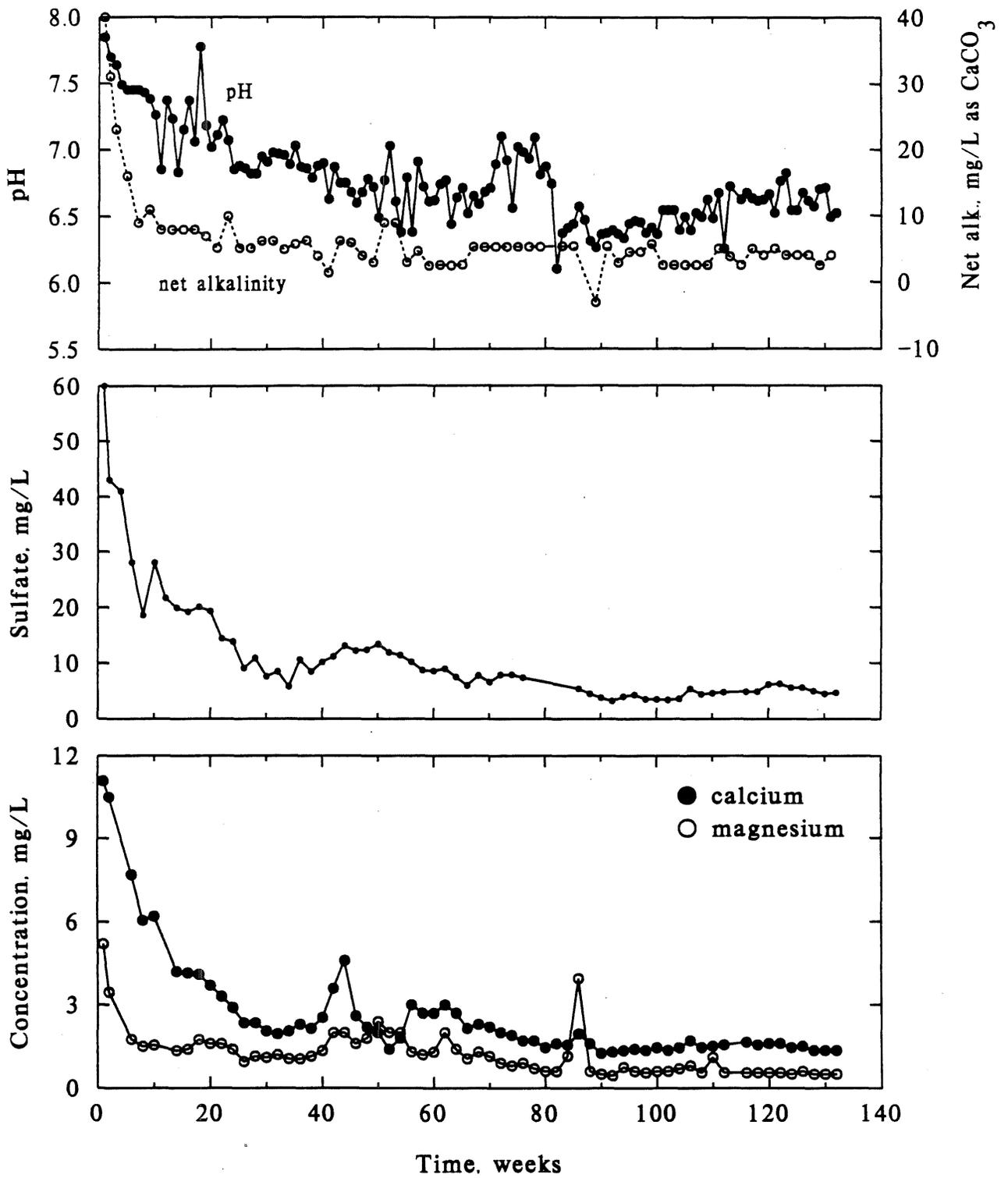


Figure 6. pH and concentrations of net alkalinity, sulfate, calcium, and magnesium in drainage from RK3 in the Wet-Dry Cycle Test (weeks 1 - 132).

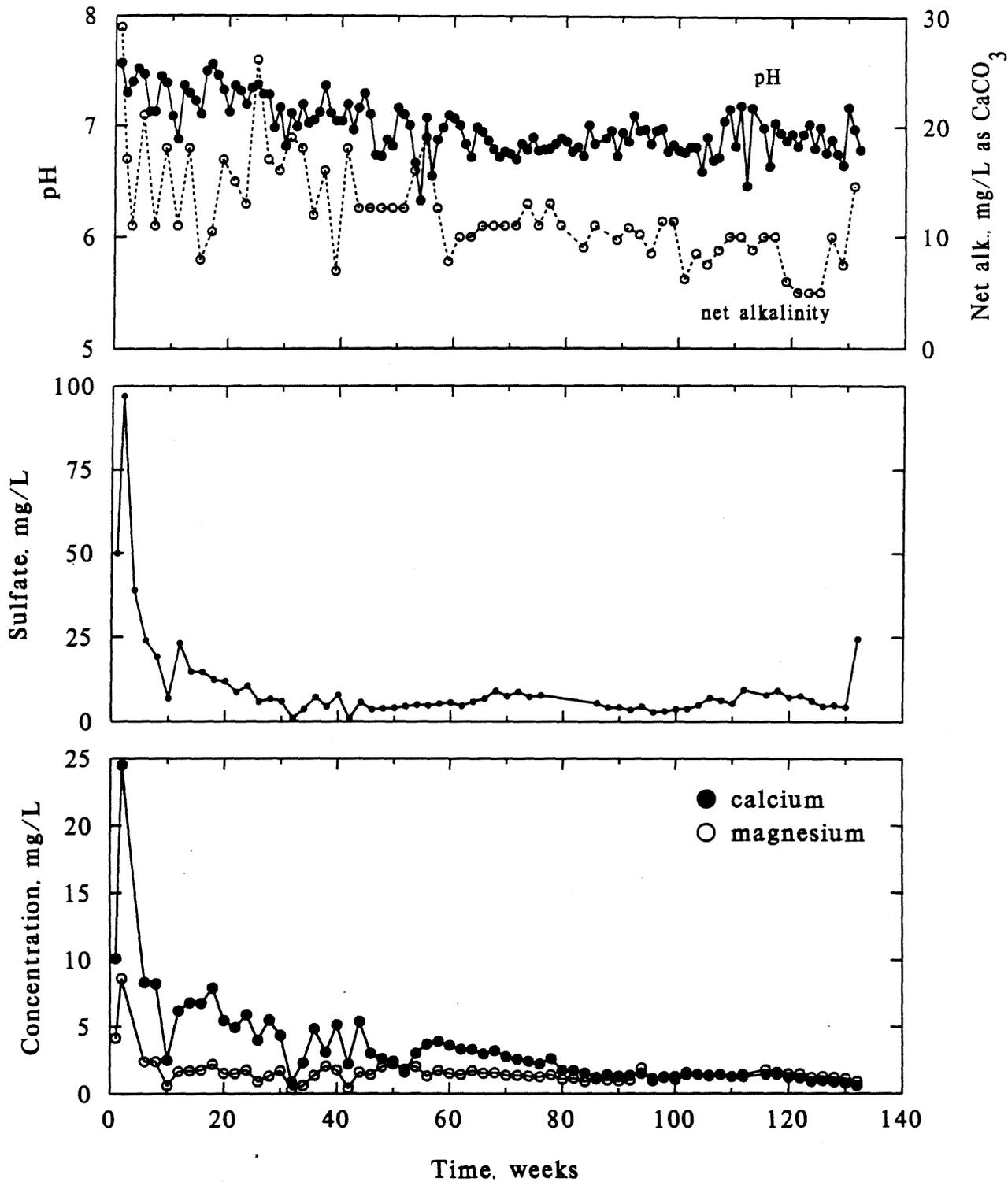


Figure 7. pH and concentrations of sulfate, net alkalinity, calcium, and magnesium in drainage from RK4 in the Wet-Dry Cycle Test (weeks 1 - 132).

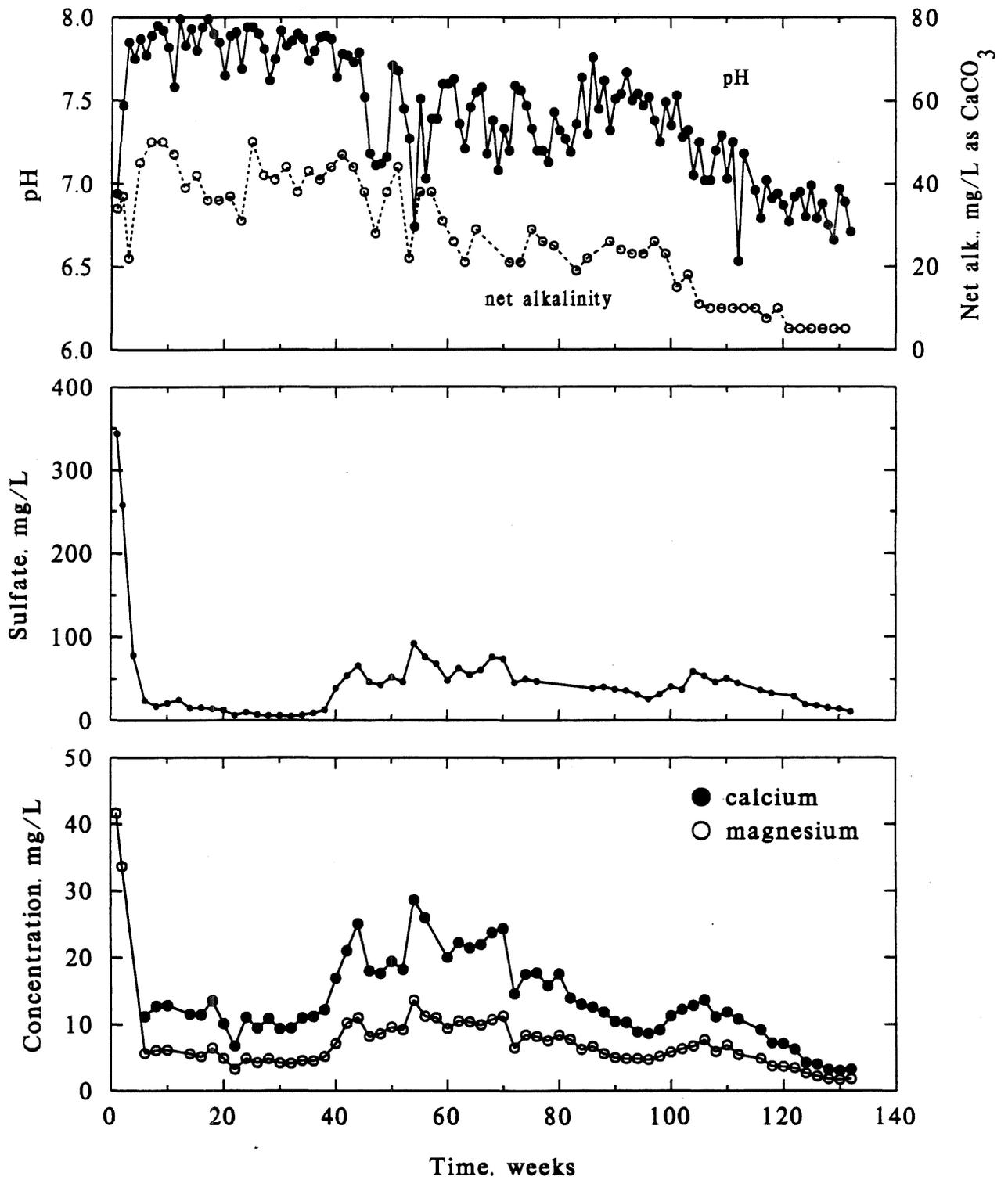


Figure 8. pH and concentrations of net alkalinity, sulfate, calcium, and magnesium in drainage from TL4 in the West Dry Cycle Test (weeks 1 - 132).

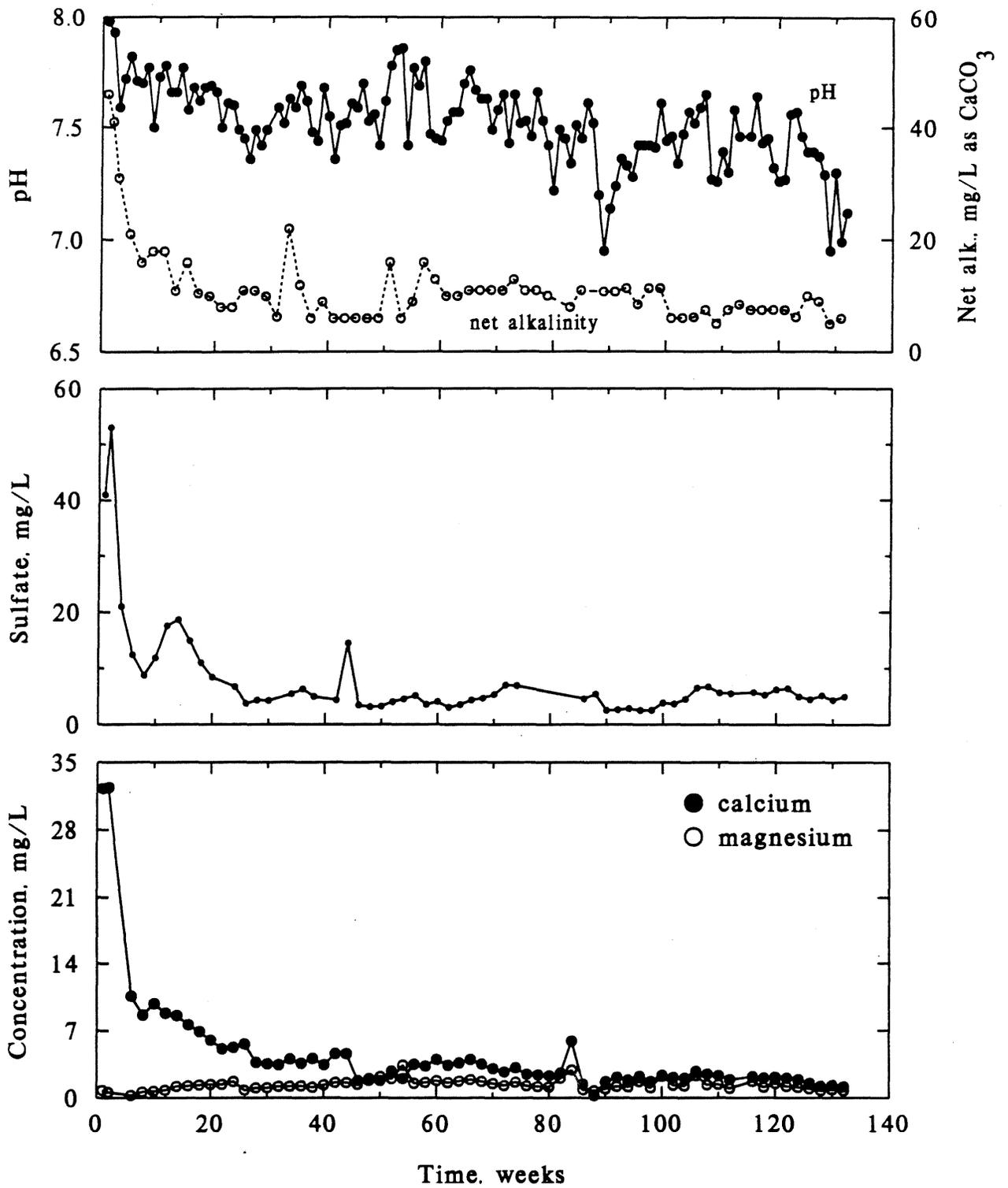


Figure 9. pH and concentrations of net alkalinity, sulfate, calcium, and magnesium in drainage from TL2 in the Wet-Dry Cycle Test (weeks 1 - 132).

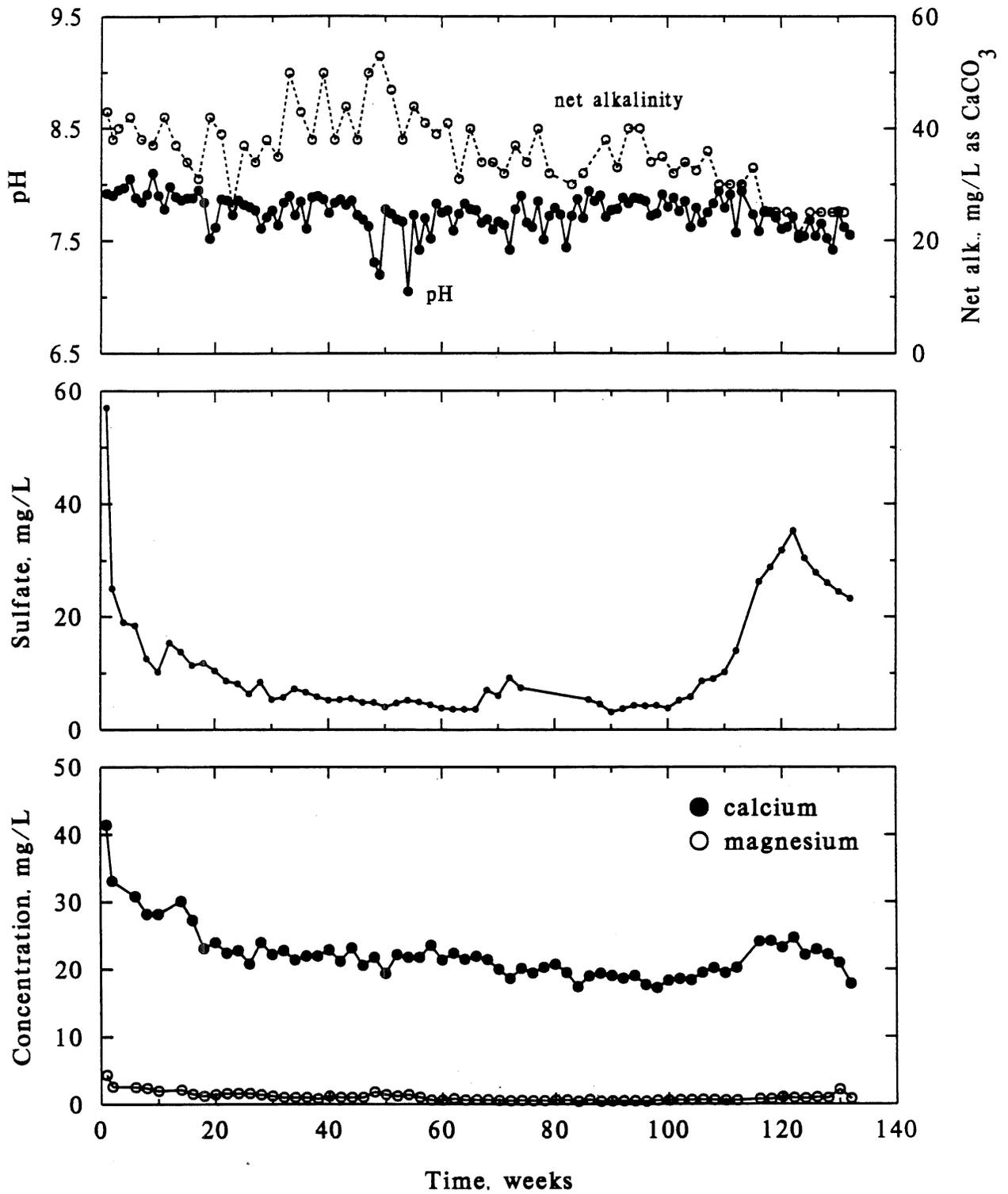


Figure 10. pH and concentrations of net alkalinity, sulfate, calcium, and magnesium in drainage from TL1 in the Wet-Dry Cycle Test (weeks 1 - 132).

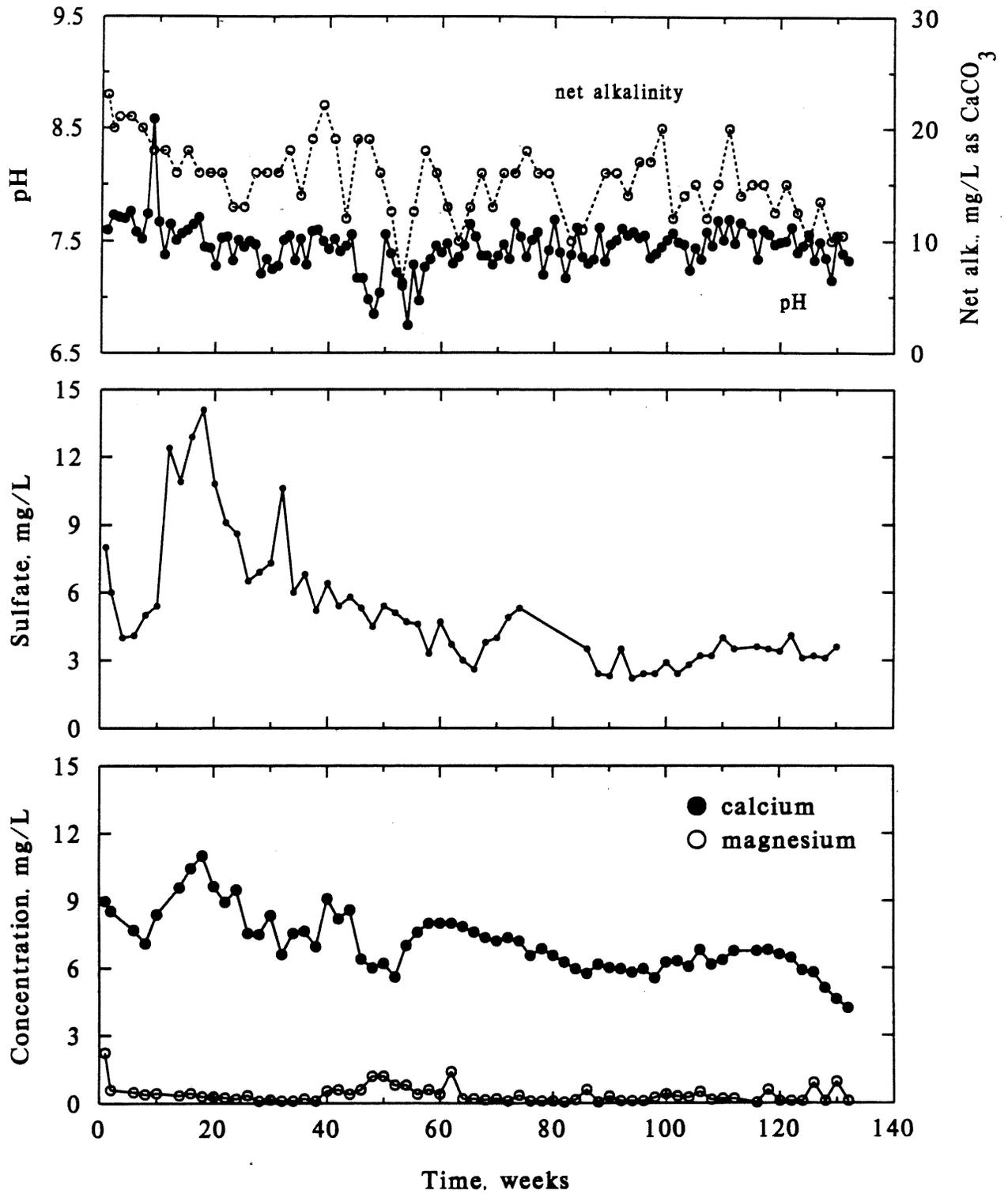


Figure 11. pH and concentrations of net alkalinity, sulfate, calcium, and magnesium in drainage from TL3 in the Wet-Dry Cycle Test (weeks 1 - 132).

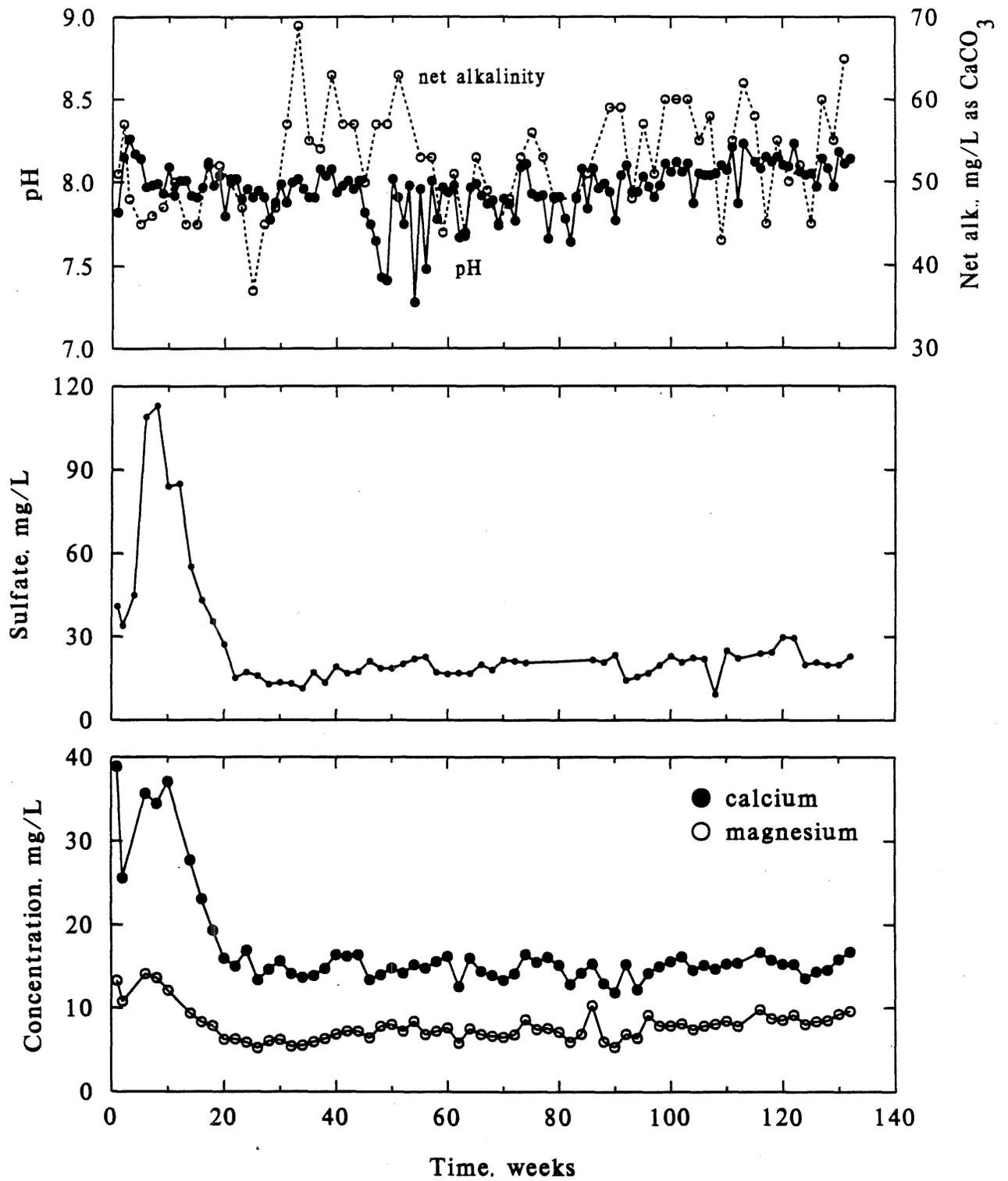


Figure 12. pH and concentrations of net alkalinity, sulfate, calcium, and magnesium in drainage from TL6 in the Wet-Dry Cycle Test (weeks 1 - 132).

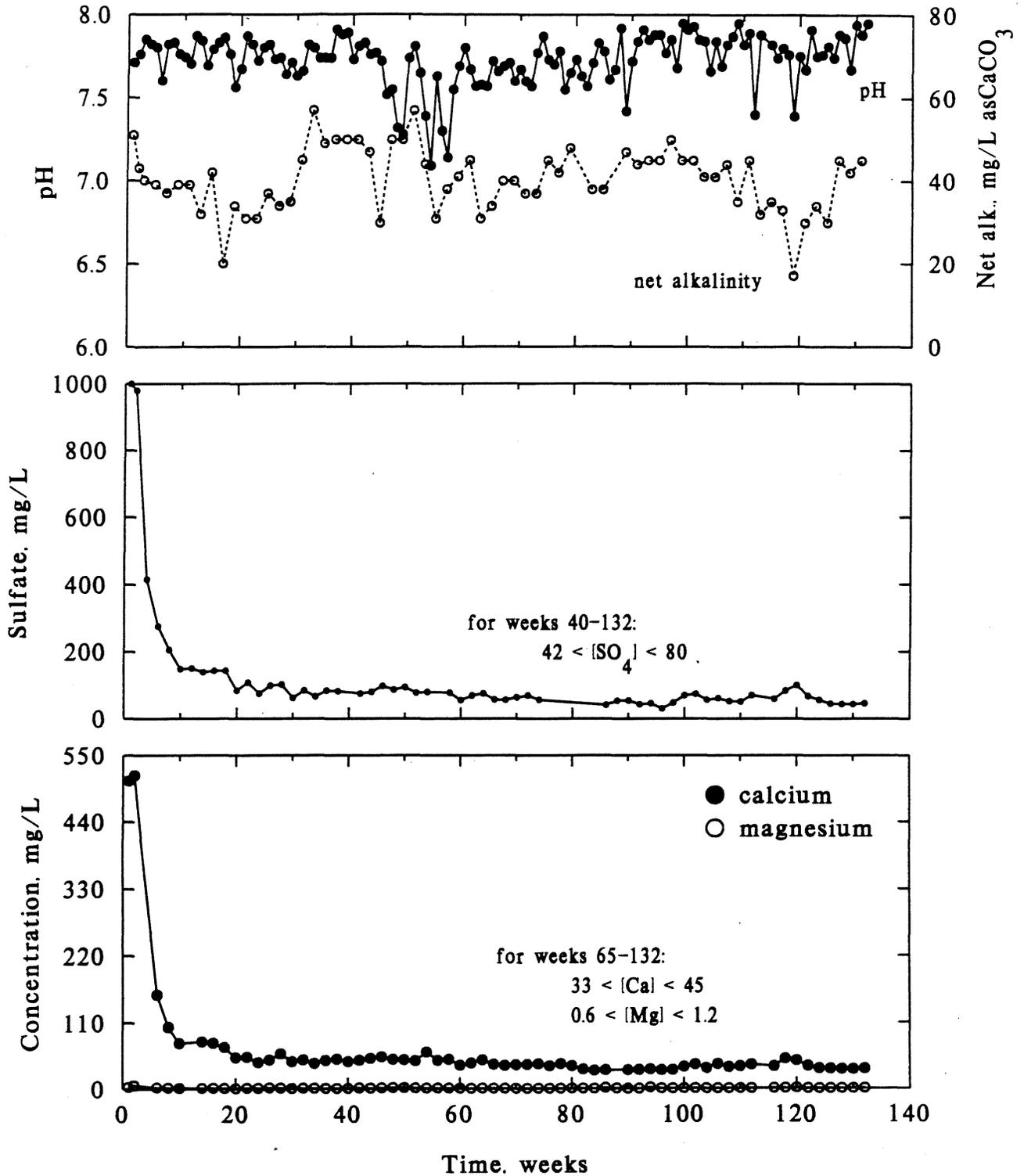


Figure 13. pH and concentrations of net alkalinity, sulfate, calcium, and magnesium in drainage from TL5 in the Elevated Temperature Test (weeks 1 - 131).

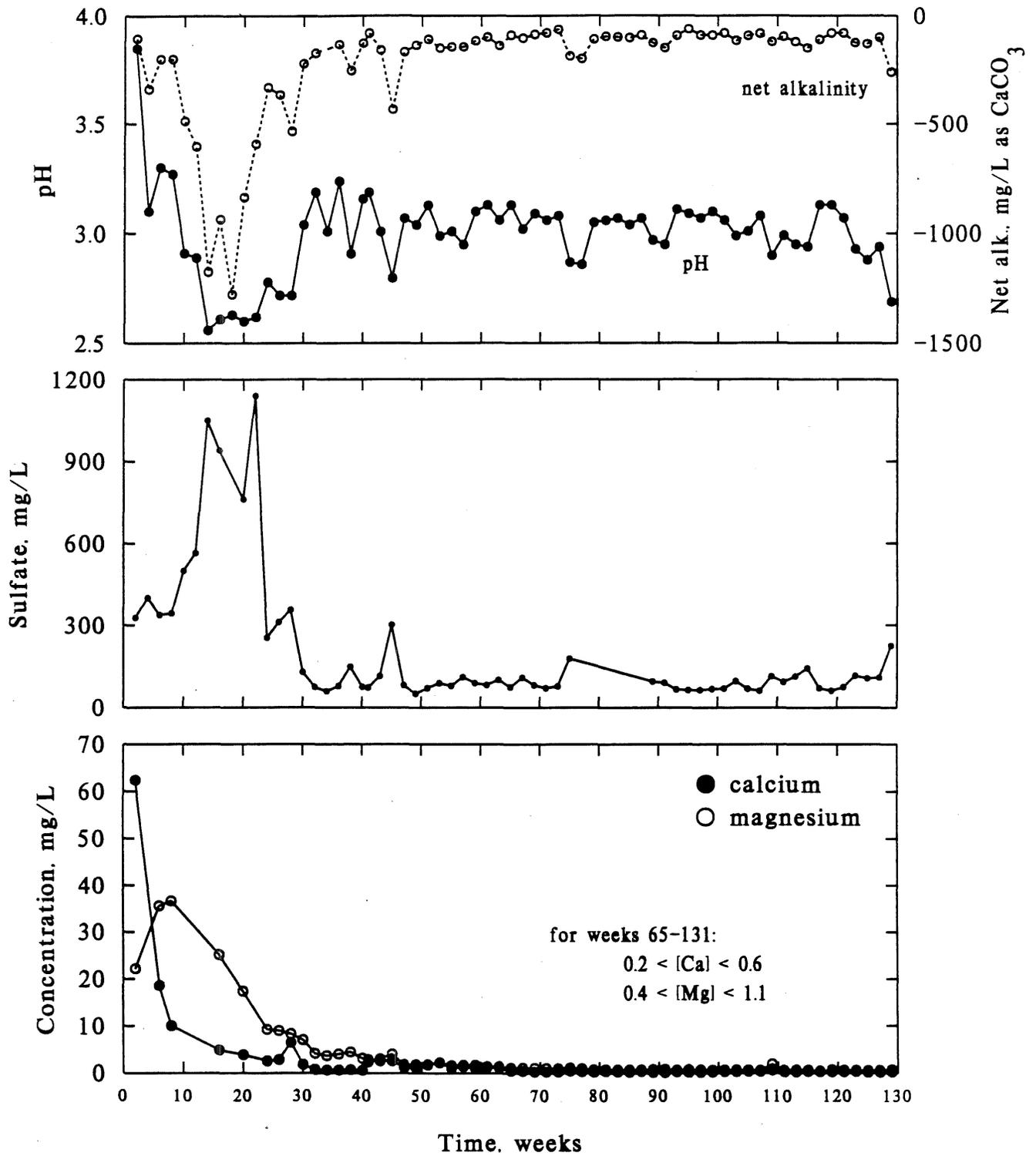


Figure 15. pH and concentrations of net alkalinity, sulfate, calcium, and magnesium in drainage from RK4 in the Elevated Temperature Test (weeks 1 - 130).

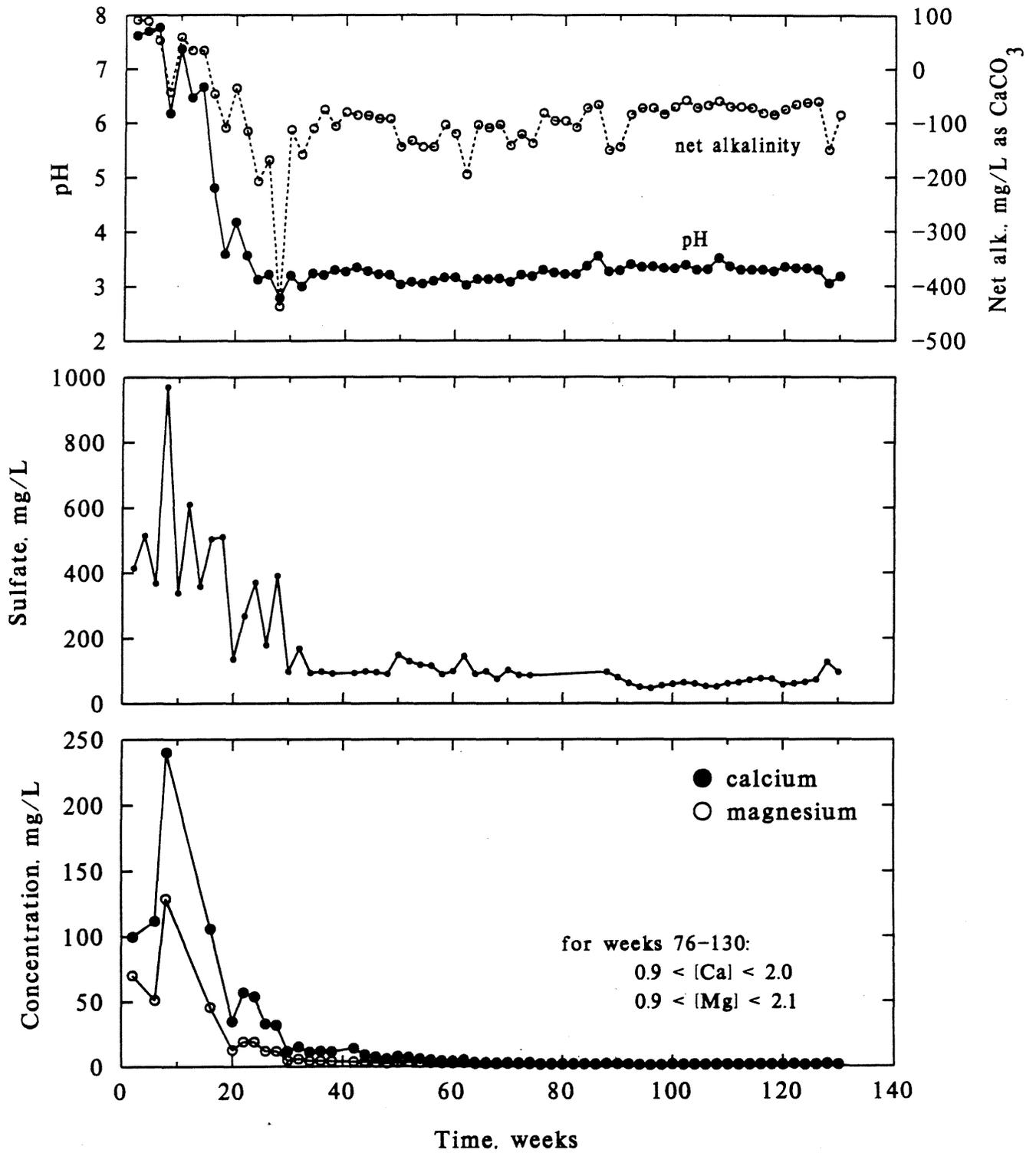


Figure 16. pH and concentrations of net alkalinity, sulfate, calcium, and magnesium in drainage from TL4 in the Elevated Temperature Test (weeks 1 - 131).

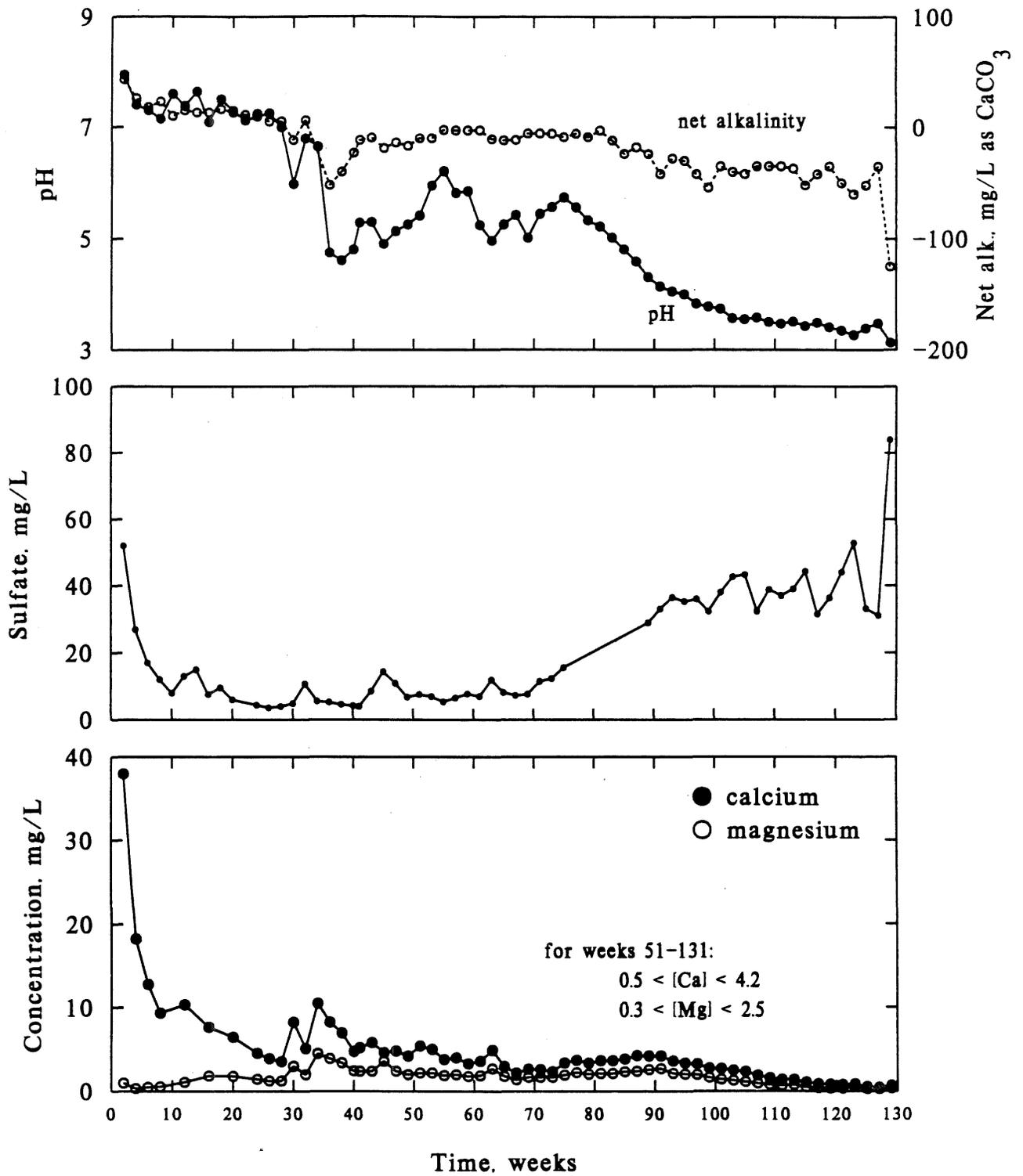


Figure 17. pH and concentrations of net alkalinity, sulfate, calcium, and magnesium in drainage from RK3 in the Elevated Temperature Test (weeks 1 - 130).

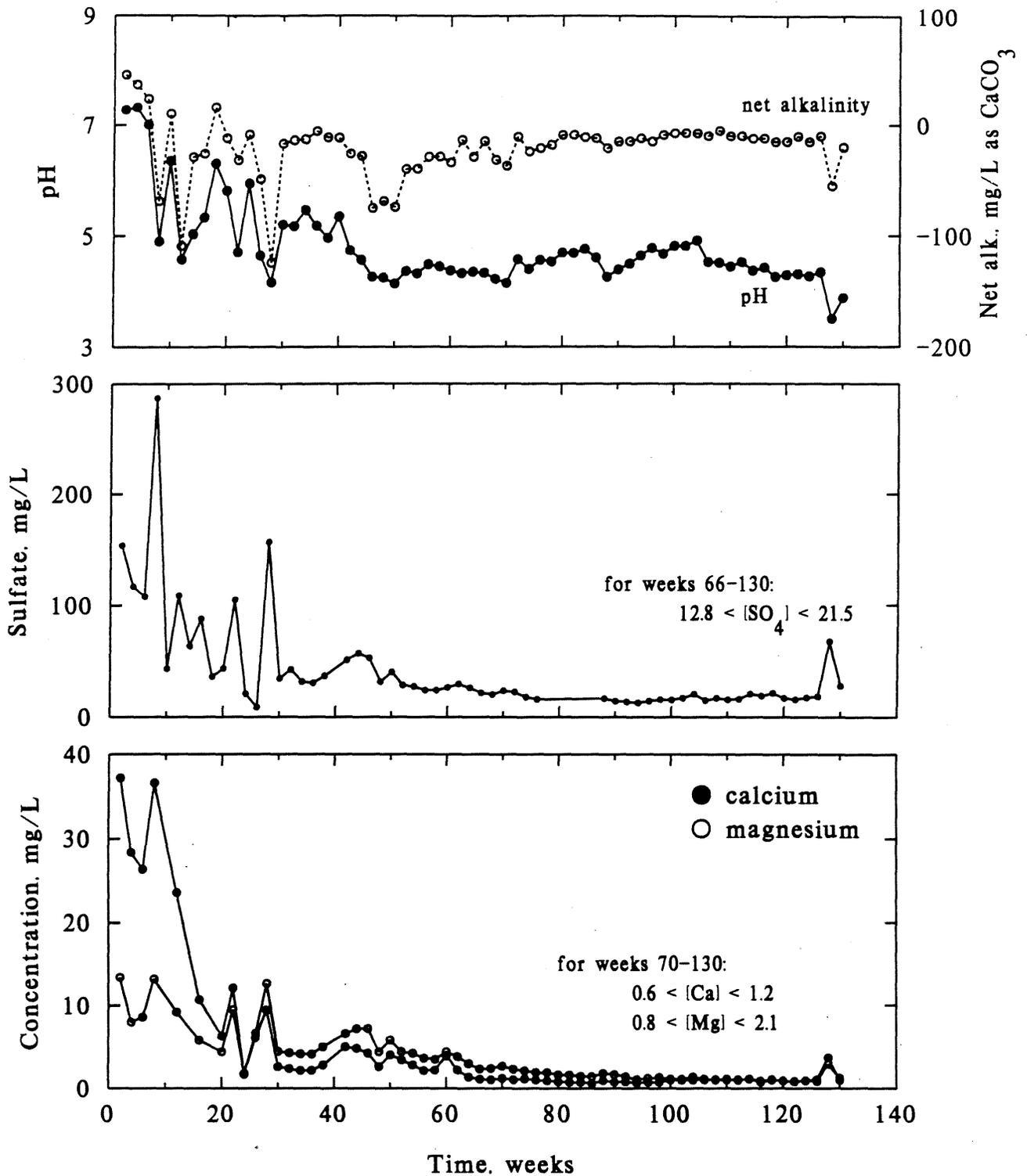


Figure 18. pH and concentrations of net alkalinity, sulfate, calcium, and magnesium in drainage from TL2 from the Elevated Temperature Test (weeks 1 - 131).

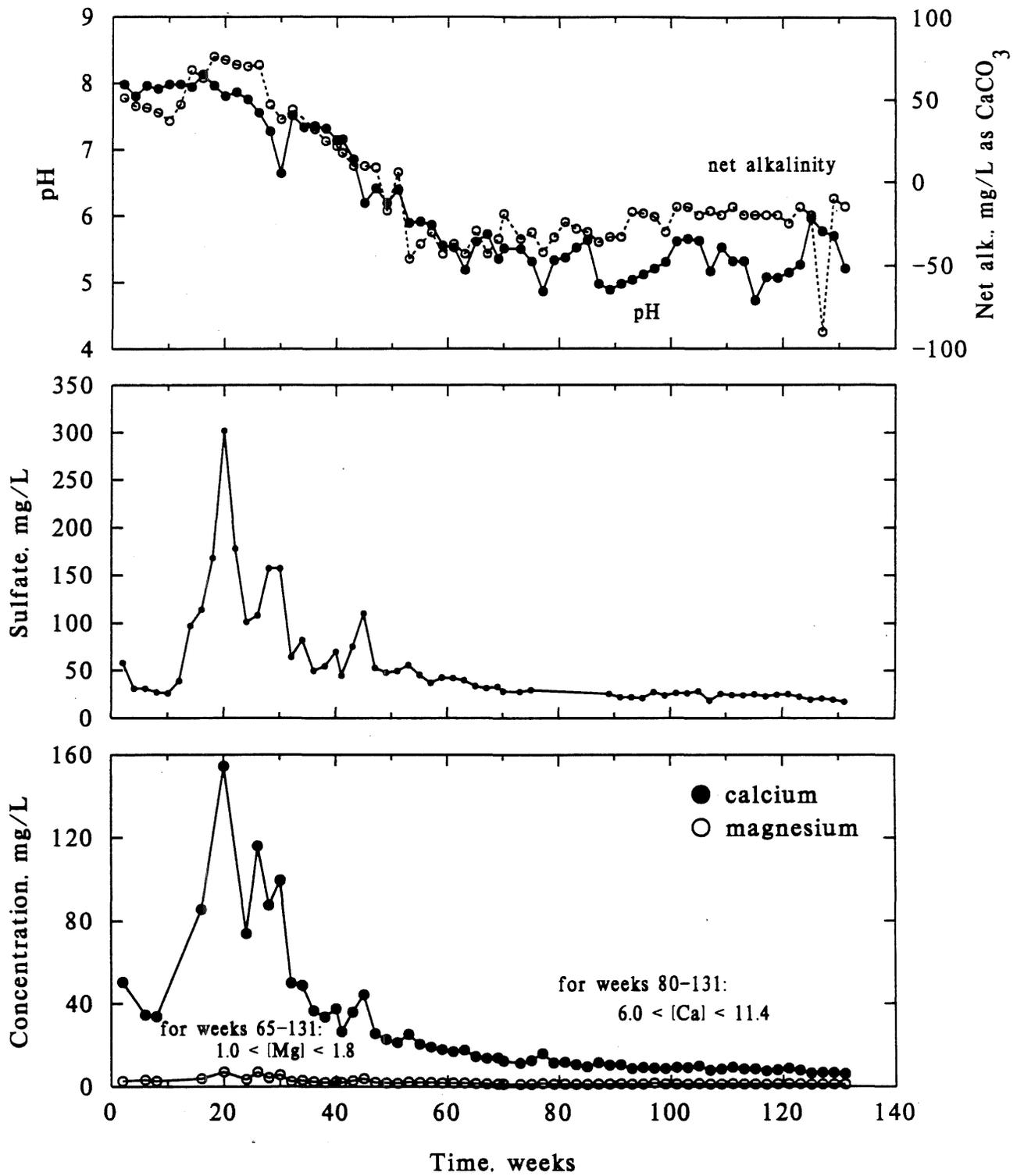


Figure 19. pH and concentrations of net alkalinity, sulfate, calcium, and magnesium in drainage from RK1 in the Elevated Temperature Test (weeks 1 - 130).

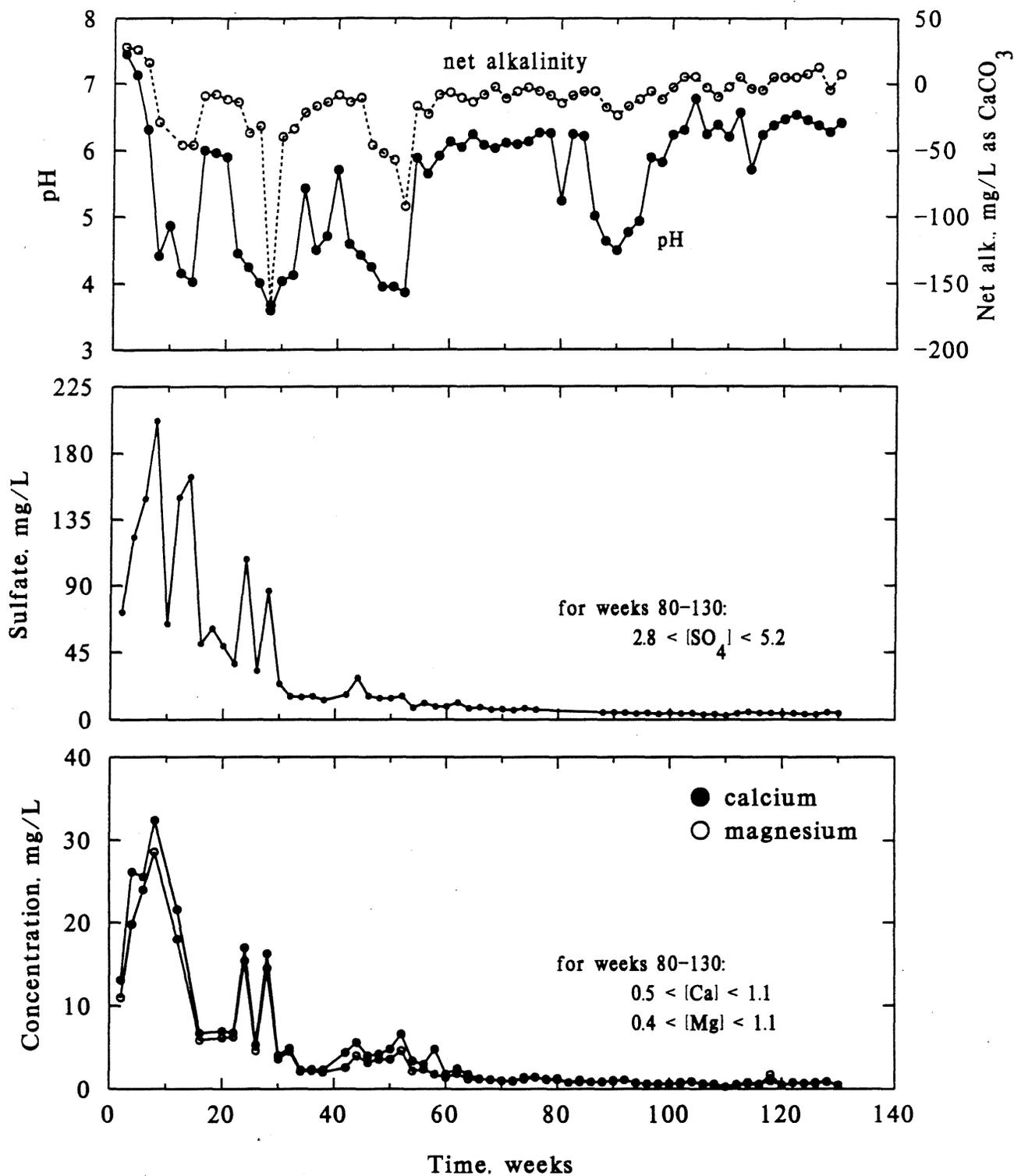


Figure 20. pH and concentrations of net alkalinity, sulfate, calcium, and magnesium in drainage from RK2 in the Elevated Temperature Test (weeks 1 - 130).

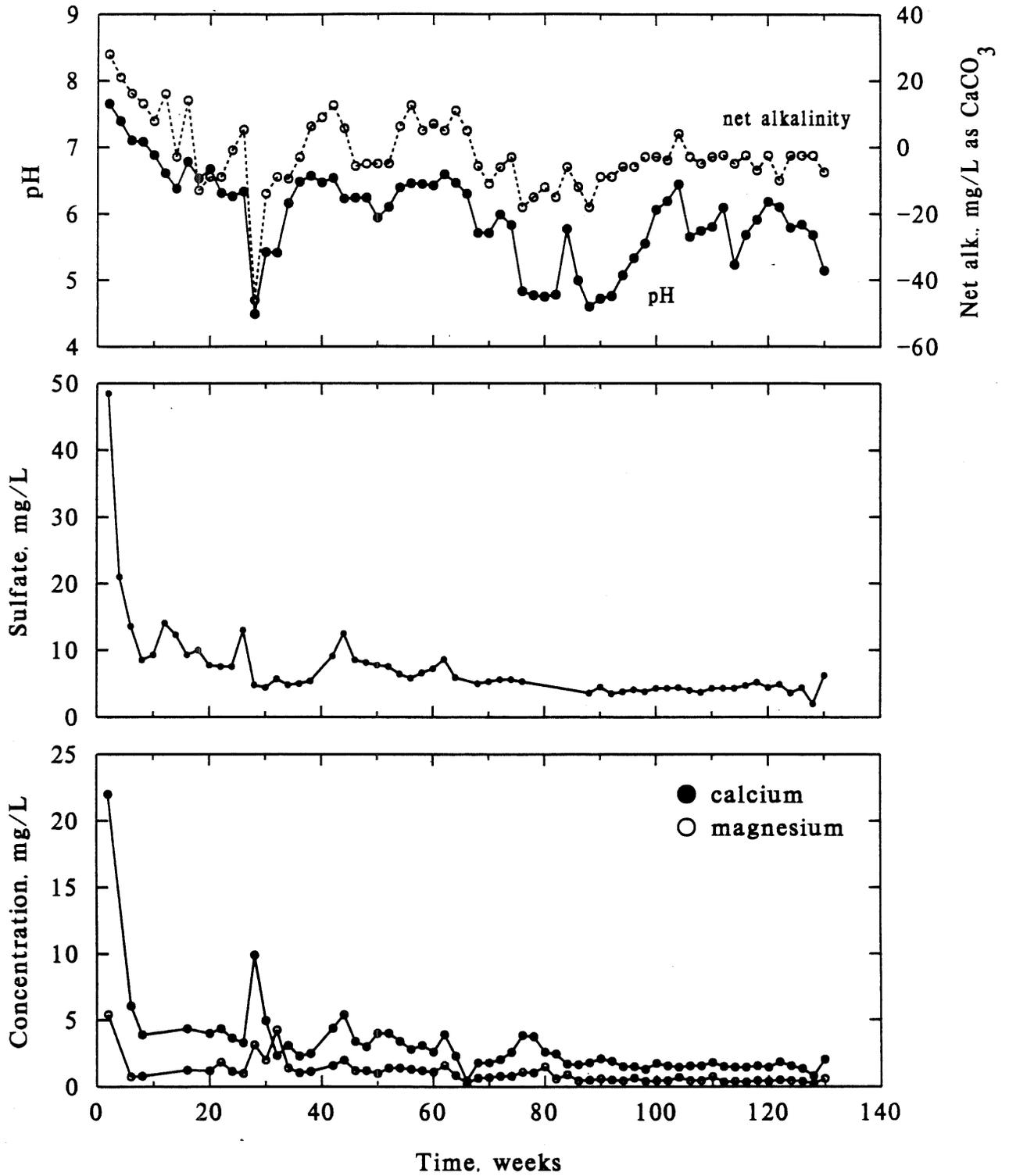


Figure 25. pH and concentrations of net alkalinity, sulfate, calcium, and magnesium in drainage from TL1 in the Elevated Temperature Test (weeks 1 - 131).

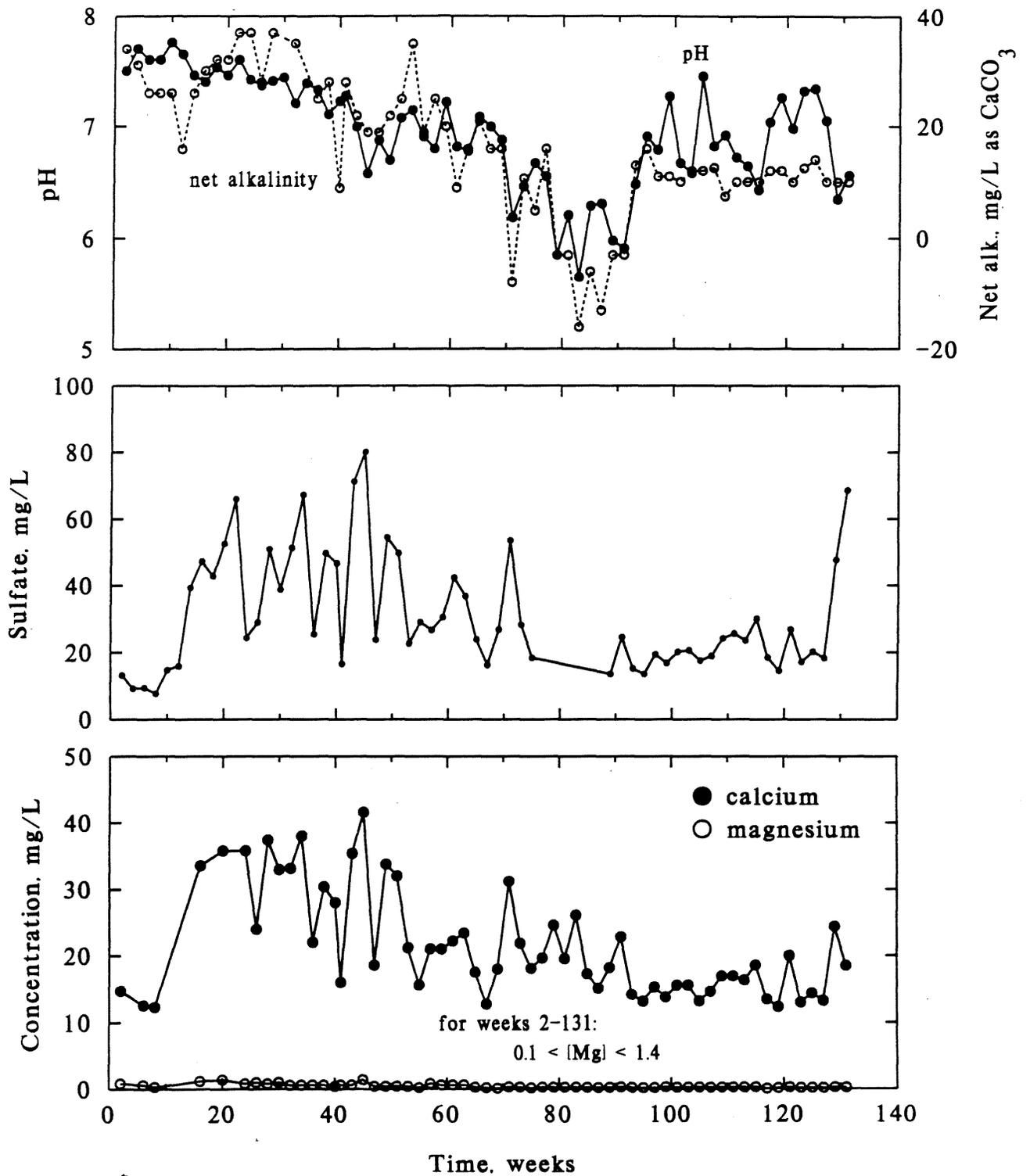


Figure 26. pH and concentrations of net alkalinity, sulfate, calcium, and magnesium in drainage from TL3 in the Elevated Temperature Test (weeks 1 - 131).

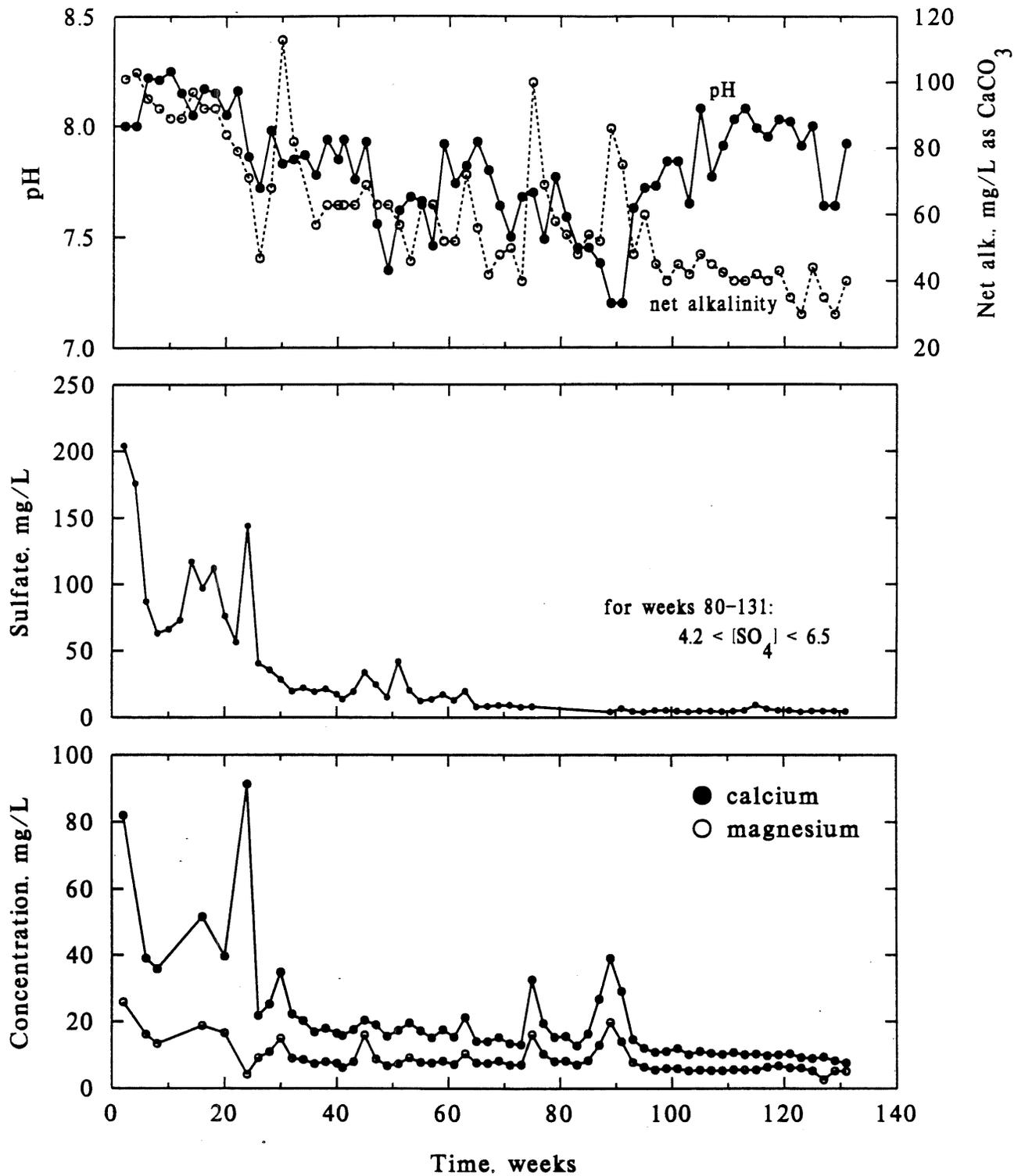


Figure 27. pH and concentrations of net alkalinity, sulfate, calcium, and magnesium in drainage from TL6 in the Elevated Temperature Test (weeks 1 - 131).

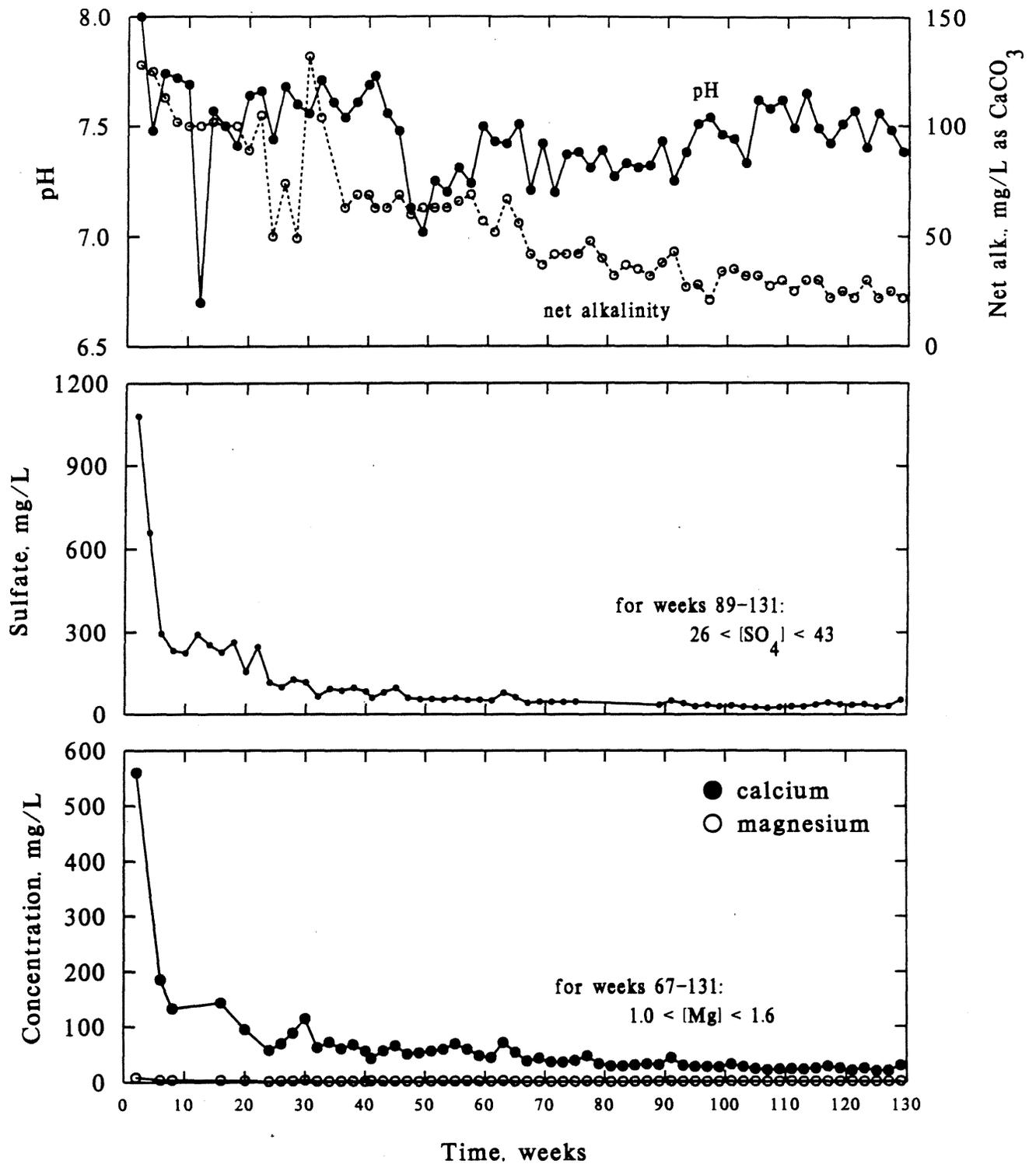


Figure 29. Explanation of box plot figure.

The box plot is comprised of the *central box*, the *whiskers*, and the *outliers*.

- Within the *central box*, the median of the data set is depicted by the center horizontal line, and the lower and upper hinges are depicted by the other two horizontal lines of the central box. The median splits the ordered data set in half, and the hinges split those two resulting halves in half again (i.e. the three horizontal lines in the central box represent the 25th, 50th, and 75th percentiles of the entire data set). The distance between the two hinges is called the *H-spread* (*H*).
- The *whiskers* (the two vertical lines) represent the range of values that fall within 1.5 H-spreads of the two hinges.
- The *outliers* represent values that fall outside of the *inner and outer fences*. Asterisks represent those values that lie outside of the inner fences but within the outer fences. The inner and outer fences are defined as:

$$\begin{aligned} \text{inner fence} &= \text{lower hinge} - 1.5H \\ &= \text{upper hinge} + 1.5H \end{aligned}$$

$$\begin{aligned} \text{outer fence} &= \text{lower hinge} - 3H \\ &= \text{upper hinge} + 3H \end{aligned}$$

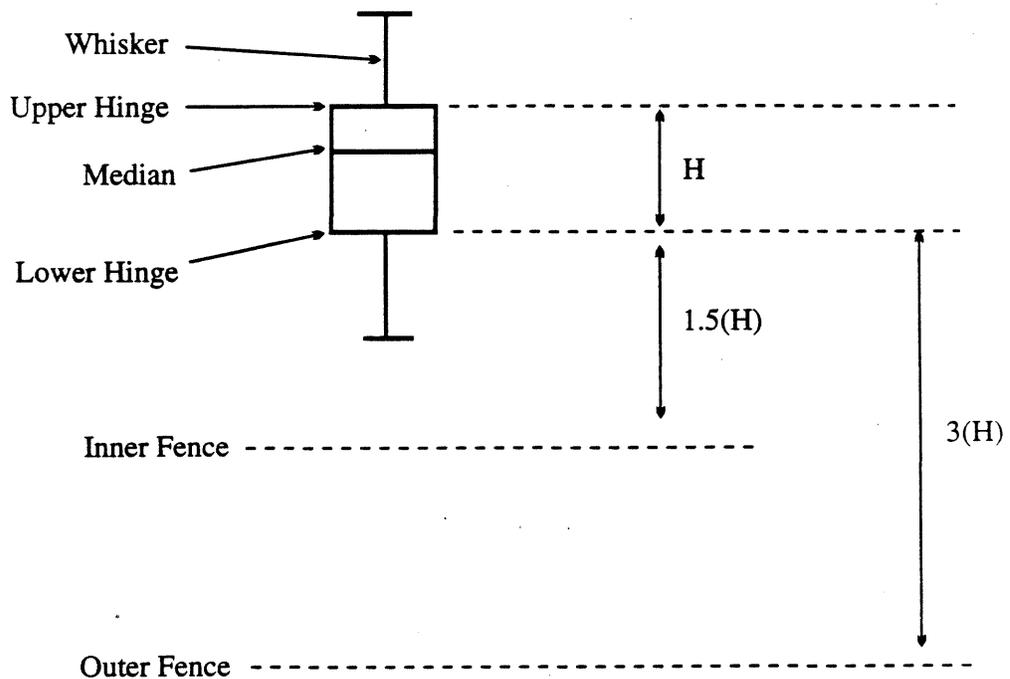


Figure 30. Drainage pH and release rates for sulfate and calcium plus magnesium as a function of particle size from the Particle Size Experiment: RK3 (weeks 15-30).

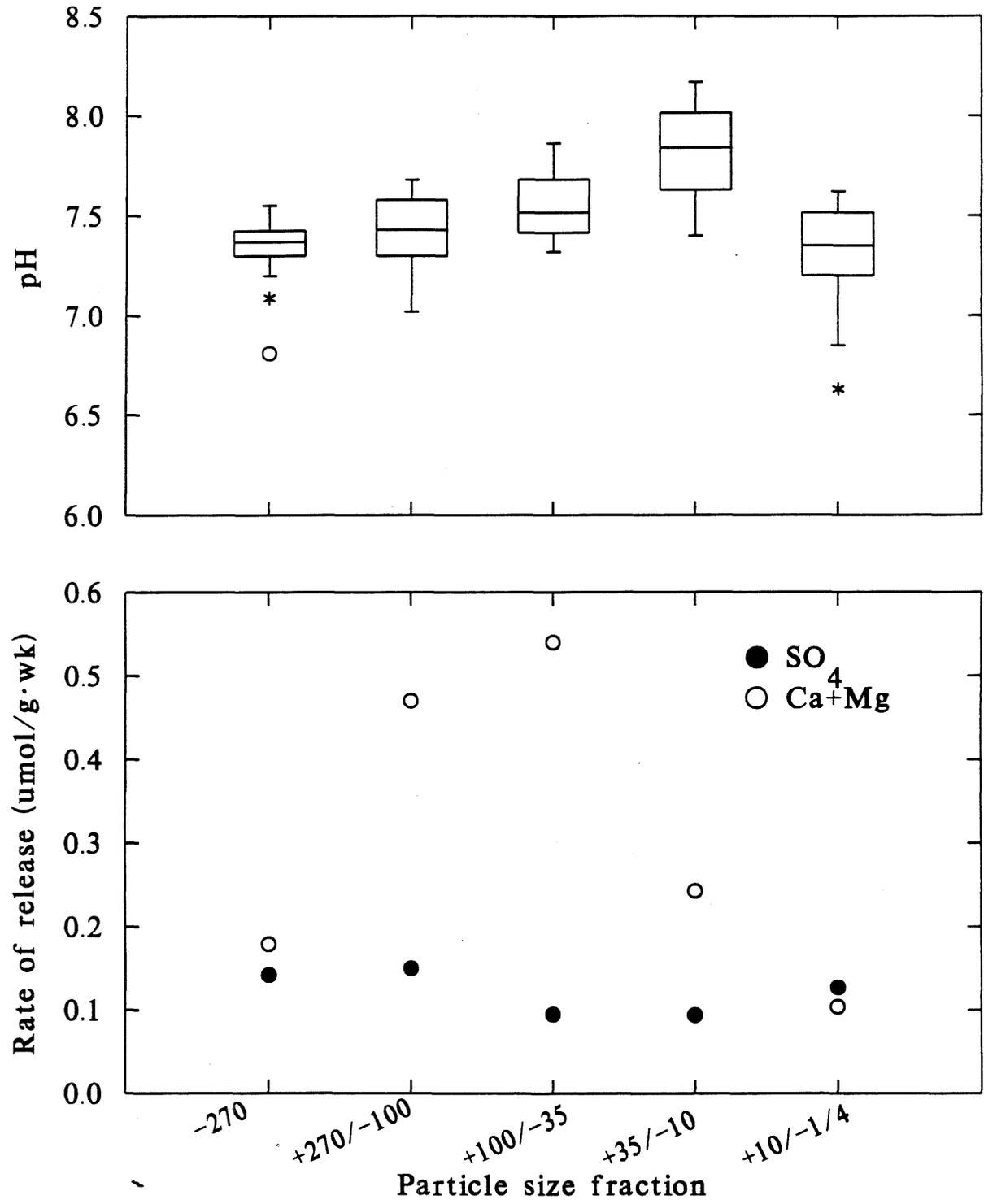


Figure 31. Drainage pH and release rates of sulfate and calcium plus magnesium as a function of particle size from the Particle Size Experiment: RK4 (weeks 15-30).

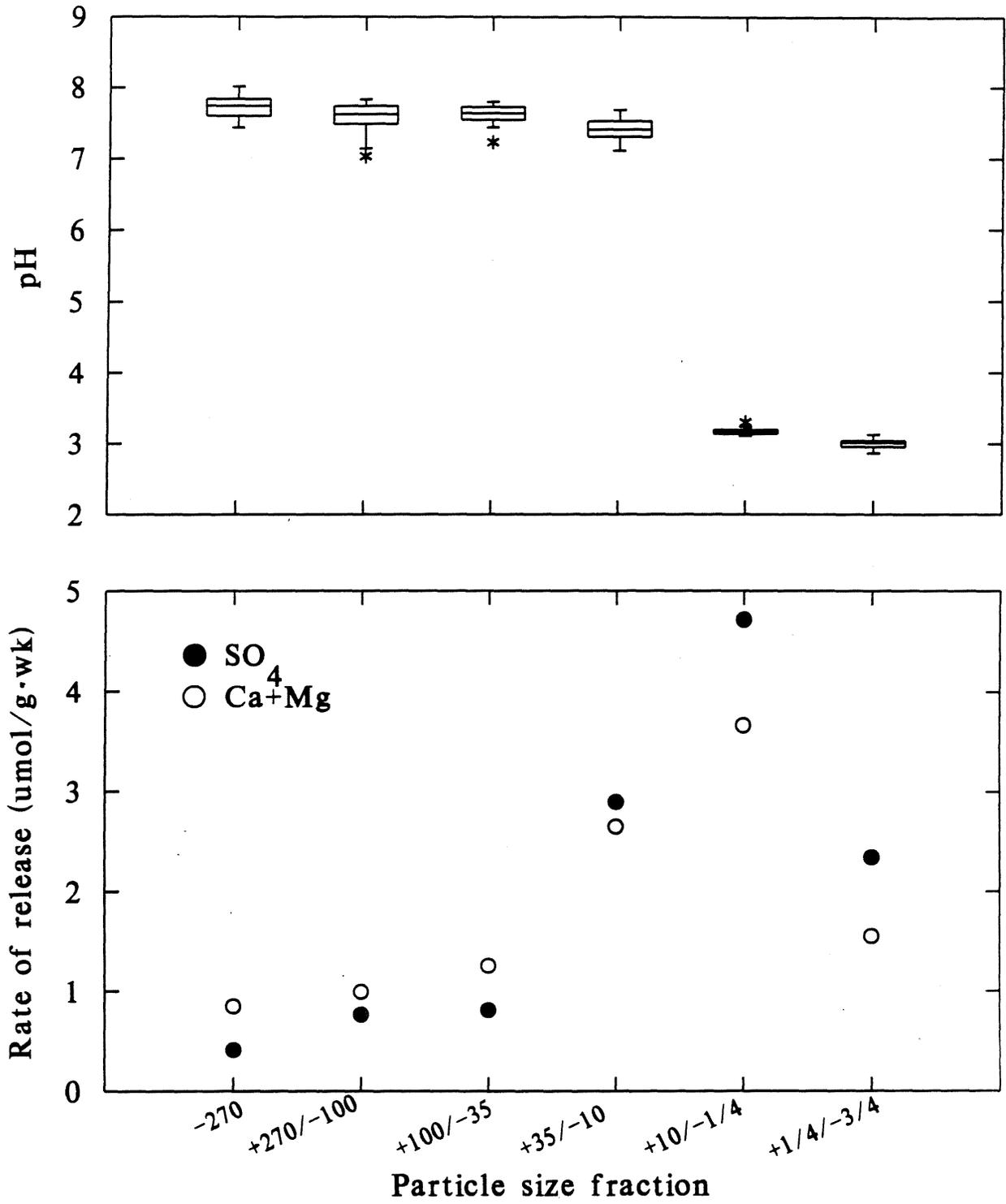


Figure 32. Drainage pH and release rates of sulfate and calcium plus magnesium as a function of particle size from the Particle Size Experiment: RK5 (weeks 15-30).

