Controlling Mine Drainage Problems-
New Approaches for Waste Rock Stockpiles

A Final Report to the Minerals Coordinating Committee

June 30, 2003

Minnesota
DEPARTMENT OF
NATURAL RESOURCES

Minnesota Department of Natural Resources
Division of Lands and Minerals
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0. EXECUTIVE SUMMARY

Four field test piles containing Archean greenstone rock (38 cubic meters ~ 63 tons) were constructed to provide data to aid in predicting drainage quality from greenstone waste rock. The four piles were constructed from 21 July to 19 September 2000 and had sulfur contents of 0.02%, 0.20%, 0.39% and 0.67%. The piles were instrumented to provide data on the temperature and gas composition within the pile, collect drainage from the piles, and determine the amount of drainage from the piles. Six tanks containing three different mixtures of rock and limestone were also used to examine the effectiveness of limestone addition in limiting release of acid from rock with a sulfur content of 0.49%. Funding for the construction was provided by the Minnesota Department of Natural Resources Division of Lands and Minerals (MN DNR).

Rock samples were characterized for particle size and chemistry. Roughly 75% of the rock in test piles 1 and 2 was coarser than 3/4-inch, as compared to about 55% of the rock in test piles 3 and 4. The -100 mesh fraction for the four piles ranged from 0.8% to 1.9%. Drainage quality data were collected for only one to three months in 2000. All drainages were in the circumneutral pH range, with elevated concentrations of sulfate. Due to problems with flow measurement, no rates of chemical release were determined. Funding for the initial solid-phase characterization and drainage quality analyses was provided by the Minerals Coordinating Committee (MCC), Minnesota Environmental Cooperative Research Program, and MN DNR Division of Lands and Minerals (Lapakko et al. 2001).

The Minerals Coordinating Committee provided funding to continue field experiments from 1 July 2001 to 30 June 2003, the period addressed in the present report. The objectives of this phase were to 1) conduct additional analyses on the rock used in field tests, 2) continue field scale predictive tests on Archean greenstone waste rock samples to evaluate the effects of solid-phase composition and time of reaction on drainage quality, and 3) continue investigating the feasibility of adding fine grained limestone to acid generating Archean greenstone waste rock to control acid release with drainage from the rock.

Environmentally sound management of waste rock generated by mining must consider the quantity and quality of drainage generated by waste rock piles. The quantity of drainage generated by waste rock piles is a function of physical properties of the rock and climatic conditions. Drainage quality from waste rock is a function of solid-phase composition, reaction conditions, and time. The solid-phase, gaseous-phase, and temperature data collected in the present study will provide essential data on the reactants present and the reaction conditions in the field. This information will aid in the comparative analysis of laboratory and field results and extrapolation of results to operational conditions.

Water yield coefficients changed substantially from 2001 to 2002, and the 2002 values are more consistent with previously reported data. Additional data collection will further increase confidence in these values. Drainage quality data suggests that sulfide oxidation rates in the 0.39% and 0.67% sulfur piles are increasing. If this trend continues, these drainages may acidify in the upcoming years. Additional data on drainage quantity and quality are necessary to evaluate the long-term

behavior of waste rock in the environment. These data, in conjunction with laboratory data, will provide considerable insight into the long-term behavior of operational-scale waste rock. This insight will allow for the efficient and environmentally effective management of these waste rock from mining operations in the Archean greenstones.

Chemical analyses were conducted to determine the variation of chemistry as a function of particle size. Sulfur contents in the 0.02% and 0.39% sulfur piles tended to increase as particle size decreased, and in the 0.67% S pile tended to decrease as particle size decreased. In the 0.20% S pile, sulfur content was elevated in the +1/4-inch fractions and relatively constant in the finer fractions. The carbon dioxide content of all piles increased as particle size decreased, indicating any acid-neutralizing carbonate minerals were concentrated in the fine fractions. Analyses were also conducted to determine the mineral content of the four piles, chemistry of individual minerals, and the degrees of sulfide and carbonate mineral liberation. The degrees of liberation are key factors influencing, respectively, rates of acid production and acid neutralization. The mineralogical analyses were not completed in time for the present report and will be presented in the future.

Measurement of the gas-phase composition within the piles in 2000 suggested that oxygen was not substantially depleted within the piles in 2000. Measurements in 2001 and 2002 indicated that oxygen content of the gas phase in the piles was essentially the same as that in the atmosphere. The temperature within the piles was determined concurrently with gas-phase composition and ranged from -2 to -23°C. It should be noted that no measurements were made between 13 December and 27 March.

Drainage volumes in 2001 ranged from 73 to 85 percent of the input precipitation, which was the only input to the piles. In contrast, drainage volumes in 2002 ranged from 51 to 67 percent of the input precipitation, and this range is more consistent with previously reported values.

Drainage pH values from all piles typically ranged from 7.5 to 8.0 over the course of the study, and concentrations of trace metals (Cu, Ni, Co, Zn) were typically less than 0.02 mg L^{-1}. Sulfate concentrations were elevated in drainages from all four piles, indicating that the pyrite present was oxidizing and, consequently, acid was being produced. The neutral drainage pH values indicate that the acid produced was neutralized by other reactions within the piles. Dissolution of calcium bearing minerals neutralized the majority of acid from all but the 0.02% S pile, in which sodium bearing minerals dominated acid neutralization. From 2001 to 2002, rates of sulfate release from the two low sulfur piles decreased by roughly 25 percent, and rates of sulfate release from the two high sulfur piles increased by 60 to 70 percent. This suggests that rates of sulfide oxidation, and attendant acid production, in the two higher sulfide piles are increasing. Furthermore, this may indicate that drainage from these piles may acidify in the future. The first two samples in 2003 indicate the pH of drainage from the two high sulfur piles remains in the range observed in 2001 and 2002.

Fine grained limestone (manufactured sand) was added to Archean greenstone rock (0.49% S, 0.39% CO_2, NP_{Sobek} = 6.3 g $CaCO_3$ eq (kg rock)$^{-1}$) obtained from Soudan State Park. The mixtures each weighed approximately 3500 pounds and were contained in polyethylene tanks (d = 48 in, h = 42 in).

The acid neutralization potential to acid production potential ratios (NP_{Sobek}:$AP(S_T)$) of the controls and two treatments, each of which were run in duplicate, were 0.41, 1.4:1, and 2.5:1, respectively.

In 2001 the volume of drainage from the tanks ranged from 85 to 98 percent of the input precipitation, which was the only input to the tanks. In 2002 the observed range decreased to 48 to 53 percent. As mentioned in the previous discussion, this is more consistent with previously reported values.

After two full years of operation, drainage from the controls and treatments remains in the circumneutral range. Drainage pH from the controls is on the lower end of the observed range, and several values below 7.5 have been observed. Drainage pH values from the rock to which limestone was added have typically ranged from 7.7 to 8.4. Concentrations of alkalinity in the drainages tended to increase with limestone loading. The pH and alkalinity trends indicate limestone dissolution is affecting drainage quality. Acidification of the control tanks in the future will be necessary to provide an assessment of the practical effectiveness of this treatment.

1. INTRODUCTION

Greenstone belts are hosts to numerous gold and base metal deposits. There is presently no mineral development in the Archean greenstone belts of northern Minnesota. However, these greenstone belts extend north and northeast into Ontario, where a number of gold and base metal mines are located. Due to the promising mineral potential of Minnesota's greenstone belts, there are presently 37 state metallic mineral exploration leases covering more than 13,000 acres in these areas. There are also private metallic mineral exploration leases, although the number and extent of these leases are not public information.

The Minnesota Department of Natural Resources (MN DNR) is charged with both encouraging mineral resource development and protecting other natural resources, including water quality. If mineral development occurs in Minnesota's greenstone belts, characterization and dissolution testing of mine wastes will be necessary to determine the quality of drainage that would be generated. Rock that would not impair water quality, or have other deleterious environmental effects, could be put to productive use, in construction for example. Rock with potential to adversely affect water quality would require mitigative measures to prevent such impacts.

Determination of the quality of drainage from a mine waste is a complex process and can require subjecting a variety of samples from a specific rock type to long-term dissolution testing. To gain insight into the quality of drainage from Archean greenstone waste rock a laboratory dissolution study was initiated in January 2000. Fourteen samples were characterized (particle size, chemistry, mineralogy) and subjected to laboratory dissolution testing for 100 weeks (Lapakko et al. 2002). Sulfur contents of the samples ranged from 0.04% to 1.22% and carbonate was detected in only two samples. Samples for which sulfur content did not exceed 0.16% sulfur produced drainage pH values above 6.0, a common water quality standard, and samples containing 0.20% sulfur or more produced drainage pH values below 6.0. Rates of pyrite oxidation were calculated using sulfur content as a function of particle size and degree of sulfide mineral liberation to determine pyrite surface area. These rates were in good agreement with published rates.

Samples used in the laboratory studies were collected during excavation of a cavern, unrelated to mining, in the greenstone formation near Soudan, MN (www.hep.umn.edu/minos). Rock from this excavation was also collected to construct four field test piles of variable sulfur contents. These piles will provide field data for correlation of laboratory data. Additional samples were collected to fill six tanks. These tanks were used to examine the effectiveness of blending limestone with acid-producing rock to control generation of acidic drainage. These two studies were initiated in the second half of 2000 and data generated through 2001 are described in this report.

It is important to note that the major mineral components of greenstone rocks vary even within the state of Minnesota. Furthermore, the samples used in this study were not taken from an area with economic levels of base or precious metals. Consequently, trace elements present in the samples tested do not simulate those commonly associated with economic ore deposits. Such mineralogical and chemical variations must be considered when applying data from this study to other areas in greenstone belts.

2. OBJECTIVES

The objectives of the field studies using Archean greenstone rock are as follows.

1. Determine the variation of field drainage pH and pyrite oxidation rates with solid-phase sulfur content of greenstone rock samples and dissolution time.
2. Compare the relationship between solid-phase composition of drainage quality in the field with that observed in the laboratory.
3. Determine, as a function of limestone loading, the effectiveness of limestone addition to waste rock in controlling acid generation.

3. BACKGROUND

3.1. Hydrology of Waste Rock Piles

The hydrologic focus of the present study is limited to amount of drainage from a waste rock pile relative to the amount of precipitation falling on the pile. This can be presented as a yield coefficient, which is the ratio of drainage volume from a waste rock pile to the volume of precipitation onto the pile. Two uncovered waste rock test piles in northeastern Minnesota had average yield coefficients over six years of 0.44 and 0.58 (Eger and Lapakko 1985). More recently Smith and Beckie (2003) reported a yield coefficient of 0.55 for a test pile in northern Saskatchewan.

3.2. Mine Waste Dissolution

3.2.1. Acid Production

The major water quality concern regarding mine waste drainage quality is generation of acidic drainage, although release of metals in neutral drainage can also adversely impact water quality. Acid is released as a result of the oxidation of iron sulfide minerals (equation 1), which are common in both hydrothermal quartz carbonate gold deposits and base metal deposits in greenstones.

$$FeS_2\,(s) + (15/4)\,O_2 + (5/2)\,H_2O = FeOOH(s) + 2SO_4^{2-}\,(aq) + 4H^+\,(aq) \qquad [1]$$

Williamson and Rimstidt (1994) used literature data (Smith and Shumate 1970, McKibben 1984, Nicholson et al. 1988, Moses and Herman 1991) to derive the rate law for the abiotic rate of pyrite oxidation by oxygen at 25°C, defined by the equation

$$dFeS_2/dt = 10^{-8.19\,(\pm0.10)}\, m_{DO}^{\,0.5\,(\pm0.04)} m_{H+}^{\,(-0.11\pm0.01)} \qquad [2]$$

where, m_{DO} and m_{H+} are molalities of dissolved oxygen and H^+ in units of mol kg^{-1}, and where the rate of pyrite destruction is expressed in mol $m^{-2}\,s^{-1}$. Ranges of m_{DO} and pH for which the expression is applicable are approximately $10^{-5.5}$ to $10^{-1.5}$ and 2 to 10, respectively. For oxygen saturation at 25°C at pH 3 and pH 7, this yields respective rates of 2.2×10^{-10} and 6.2×10^{-10} mol m^{-2} s^{-1}.

In the environment the rate of sulfide mineral oxidation increases as pH decreases into a range conducive to bacterial mediation of ferrous iron oxidation. Nordstrom (1982) reported that as pH decreases to 4.5, ferric iron becomes more soluble and begins to act as an oxidizing agent. As pH further decreases, bacterial oxidation of ferrous iron becomes the rate limiting step in the oxidation of pyrite by ferric iron (Singer and Stumm 1970), which is the only significant oxidizing agent in this pH range (Nordstrom 1982; Singer and Stumm 1970; Kleinmann et al. 1981). The bacterially mediated rate of pyrite oxidation by ferric iron is roughly two to three orders of magnitude faster than the abiotic oxidation by oxygen at pH 2 (Nordstrom and Alpers 1999). In laboratory experiments conducted on hydrothermal quartz carbonate tailings (Lapakko and Wessels 1995) the sulfate release rate from pyrite in the pH range of 3.0 to 3.2 was approximately 13 times that at pH 8 (MN DNR 2000).

3.2.2. Acid Neutralization

Some or all of the acid generated as a result of iron sulfide oxidation may be neutralized by dissolution of other minerals present in a mine waste. Calcium and magnesium carbonates are the most effective of these neutralizing minerals and may be associated with greenstone ore deposits. Calcite ($CaCO_3$) is the most reactive carbonate, with a reported dissolution rate of approximately 2.4×10^{-3} mol m^{-2} s^{-1} at pH 6 ($p_{CO2} = 0.1$ atm, 25°C; Busenberg and Plummer 1986). Relative to calcite dissolution at pH 6, siderite dissolution under anoxic conditions is about three orders of magnitude slower (Greenberg and Tomson 1992). Dissolution of silicate minerals will also neutralize acid, but this dissolution is much slower than that of calcium and magnesium carbonates.

Chlorite, sericite and albite are three silicate minerals that can occur in greenstones. Chlorite is commonly associated with greenstones, forming as a result of low-temperature metamorphism (Klein and Hurlbutt 1985), and is one of the minerals that lend the color for which greenstones are named (Bayly 1968). Sverdrup (1990) presented the following equations as a possible stoichiometry for the initial protonation of the chlorite surface and the reaction of the partially protonated surface.

$$Mg_3Fe_3AlSi_3O_{10}(OH)_7 + 11.2\ H^+ \rightarrow 3\ Mg^{2+} + 2.6\ Fe^{2+} + H_{11.2}Fe_{0.4}AlSi_3O_{10}(OH)_7 \qquad [3]$$

$$H_{11.2}Fe_{0.4}AlSi_3O_{10}(OH)_7 + 2.8H^+ \rightarrow Al^{3+} + 0.4Fe^{2+} + 7H_2O{\bullet}H_7Si_3O_{10}^- \qquad [4]$$

A chlorite dissolution rate of 7.6×10^{-13} mol m^{-2} s^{-1} (25°C, pH 5) was calculated using the chlorite composition and rate of base metal cation release reported by Sverdrup (1990). May et al. (1995) reported a chlorite dissolution rate of 3.0×10^{-13} mol m^{-2} s^{-1} based on silica release for the same reaction conditions. Malmström et al. (1996) used magnesium release to determine a rate of 5.8×10^{-13} mol m^{-2} s^{-1} after about 25 days of dissolution at 25°C and pH 8.2. The rate after three days of dissolution was about 2.8 times this value. The order of the rate with respect to $[H^+]$ over the approximate pH range of 3 to 5 was reported as approximately 0.5 by May et al. (1995) and 0.7 by Sverdrup (1990).

Sericite is a fine-grained muscovite ($KAl_2(AlSi_3O_{10})(OH)_2$), which has a specific gravity of 2.76 to 2.88, a hardness of 2 to 2.5 (Klein and Hurlbutt 1985) and a reported surface roughness factor of 71 (Nickel 1973). Rates of dissolution have been reported based on observed release of its component elements. Reported rates (pH 5 - 5.6, 22-25°C) range from 1.2×10^{-14} to 1.7×10^{-12} mol m^{-2} sec^{-1}, with four of the six values ranging from 1×10^{-13} to 2.4×10^{-13} mol m^{-2} sec^{-1} (Nickel 1973; Lin and Clemency 1981; Stumm et al. 1987; Kalinowski and Schweda 1996). The dependence of the rate on pH was reported as 0.1 by Nickel (1973, pH 0.2-5.5), 0.08 by Stumm et al. (1987, pH 3-5), and 0.2 by Kalinowski and Schweda (1996, pH 1-4).

Albite is a sodium silicate ($NaAlSi_3O_8$) with a specific gravity of 2.62 and a hardness of 6 (Klein and Hurlbutt 1985). Blum and Stillings (1995) reported the surface roughness factor of freshly ground and washed feldspars averaged 9 ± 6, based on data from Blum (1994). Blum and Stillings (1995) compiled published data on albite dissolution (Chou 1985; Chou and Wollast 1985 and Sverdrup 1990) and expressed it in the form

$$\log \text{rate} = \log k_{H+} - \text{npH} \qquad [5]$$

The values of k_{H+} ranged from -9.66 to -9.5 and n from 0.49 to 0.5. For application in the present study, values of -9.67 and 0.5 were chosen for k_{H+} and n. These represent the averages of values reported by Chou (1985) and Chou and Wollast (1985).

Mine waste drainage will acidify if the rate of acid production exceeds the rate of acid neutralization. In the present study acidification is considered to occur when pH decreases below 6.0, a common water quality standard in the United States. Equation 2 implies a pyrite oxidation rate of 4.8×10^{-10} mol m^{-2} s^{-1} at pH 6 and an associated rate of acid production of 1.9×10^{-9} mol m^{-2} s^{-1}. The rate of acid neutralization by calcite is roughly six orders of magnitude faster, while that by siderite under anoxic conditions is about three orders of magnitude faster. In contrast, the rates of chlorite, sericite and albite dissolution at pH 6.0 are on the order of 1×10^{-13} mol m^{-2} s^{-1}. This yields a rate of acid neutralization roughly four orders of magnitude lower than the rate of acid production by pyrite oxidation at pH 6. Thus, in a system containing only pyrite and these silicate minerals, the silicate mineral surface area must be roughly four orders of magnitude higher than that of pyrite in order to maintain pH in excess of 6.0.

3.3. Blending Alkaline Solids with Acid-Producing Rock

Acid release from reactive mine waste may be decreased by the mixing of alkaline solids with the rock. The alkaline solids neutralize acid produced by the oxidation of sulfide minerals. This neutralization has three secondary effects. First, the elevated pH yields an environment which is unsuitable for *Acidithiobacillus ferrooxidans*, a strain of bacteria which catalyzes sulfide mineral oxidation. The elimination of these bacteria limits the rate of sulfide oxidation, and therefore, the rate of acid production. Second, the elevated pH enhances the oxidation of ferrous iron and the subsequent precipitation of ferric oxyhydroxides. If the pH is elevated in the immediate neighborhood of iron sulfide mineral surfaces, precipitates will form on the mineral surface. This would impede chemical transport to and from the iron sulfide mineral surface, and consequently, inhibit iron sulfide oxidation and the attendant acid production. Third, as pH increases the equilibrium concentrations of trace metals decrease. The decrease in concentrations is due to increased trace metal precipitation (as hydroxides, oxides, and/or carbonates) and adsorption.

Laboratory data have been generated on drainage quality from sulfidic mine wastes containing naturally-occurring calcium and magnesium carbonates. Finely-crushed Duluth Complex rock containing naturally occurring calcite was subjected to laboratory dissolution. An NP:AP ratio of 0.8 was determined using the calcite and sulfur contents (3% and 1.17%, respectively), and the sample produced neutral drainage over a period of 33 weeks of wet/dry cycle leaching (Lapakko 1988). However, over a longer period the calcium carbonate may have been depleted or rendered ineffective by precipitate coating. If this occurred, and iron sulfide minerals remained and oxidized, the drainage would have become acidic. Such depletion and acidification was reported after a period of 122 weeks for pyritic tailings (5% sulfide) containing 1.4% calcite (Lapakko and Wessels 1995).

In mitigation design the balance between acid production and acid neutralization is affected by the amount of alkaline solids added relative to the amount of iron sulfide present. This is often expressed as the neutralization potential:acid production potential ratio, or NP:AP. The alkaline solids requirement can be estimated based on theory or empirical evidence. Calculation of the acid-producing sulfur content should be based on sulfur associated with iron sulfide minerals (and alunite-jarosite minerals, if present). The theoretical alkalinity requirement can be calculated assuming that each mole of sulfur associated with iron sulfides produces two moles of acid (H^+, reaction 1). It can also be assumed that each mole of calcium carbonate consumes one or two moles of acid. It is necessary to assume how much of the AP and NP will react. The neutralization provided by host rock minerals has also been used to calculate the loading of alkaline solids required (Lapakko et al. 1997).

$$CaCO_3(s) + 2H^+(aq) = H_2CO_3(aq) + Ca^{2+}(aq) \qquad [6]$$

$$CaCO_3(s) + H^+(aq) = HCO_3^-(aq) + Ca^{2+}(aq) \qquad [7]$$

Analysis of field data from coal mining areas, in conjunction with consideration of aqueous carbonate equilibria, suggests that one mole of calcium or magnesium carbonate will neutralize one mole of acid (reaction 7; diPretorio and Rauch 1988; Cravotta III et al. 1990; Brady et al. 1990). diPretorio and Rauch (1988) found that neutral drainage was consistently produced by coal seams containing "greater than 40 tons $CaCO_3$ equivalent of total NP per thousand tons of overburden." This value was subsequently modified to 30 tons/1000 tons "with fizz" by Brady and Hornberger (1990). The "with fizz" provision was added to ensure than the NP was present as calcium and magnesium carbonates as opposed to iron carbonates.

Numerous studies have been conducted on the application of alkaline materials to neutralize acid released from reactive mine wastes. With fine-grained mine wastes, such as tailings, and alkaline solids a homogeneous mixture can be more readily attained and, due to more uniform particle sizing, flow tends to be more uniform. These factors may be more conducive to neutralization of acid generated by sulfide-bearing mine wastes.

Studies have been conducted to examine the effectiveness of adding limestone (Lapakko et al.1997) and rotary kiln fines (Lapakko et al. 2000) to fine-grained ($0.053 < d \leq 0.149$ mm) acid producing Duluth Complex rock. Addition of limestone elevated drainage pH and alkalinity and reduced the rate of iron sulfide oxidation during the 397-week period of record. Drainage remained circumneutral even following the depletion of limestone because host rock mineral dissolution was adequately rapid to neutralize acid produced at the slower rate of iron sulfide oxidation. Addition of rotary kiln fines also elevated drainage pH and alkalinity and reduced the rate of iron sulfide oxidation. However, once these alkaline solids were depleted, drainage acidified and sulfate concentrations increased.

Factors other than NP:AP ratios may determine if mine waste drainage is maintained in the neutral range. With waste rock, the blending and layering of acid-neutralizing solids are reported to be of minimal mitigative success, due to problems such as inadequate homogeneity of mixtures and preferential flow through acid-generating layers (Mehling et al. 1997). The large particle sizes of waste rock (the dimensions of which can reach several feet) and the acid-neutralizing solids most likely contribute to these problems. Analyses by Kempton et al. (1997) and Morin and Hutt (2000) indicate that preferential flow has a dominant influence on the effectiveness of waste rock blending. The latter publication indicated that waste rock drainage acidity is dependent on the flow path length within acid neutralizing rock separating zones of acid generating rock. The authors' analysis indicated that waste rock with a bulk NP:AP ratio of 300:1 could release acidic drainage if appropriate neutralizing rock flow path length was not attained.

Day (1994) concluded that limestone ($d < 0.6$ mm) mixed with acid producing rock (2.1% sulfur) should provide neutralization potential at least twice the acid-producing potential of the rock in order to ensure neutral drainage. (It should be noted that MEND (1994) indicates that 60 percent of the limestone was finer than 0.6 mm, and that 81.9 percent of the rock was finer than 3.35 mm.) Day (1994) further noted that iron precipitate coatings did not reduce the availability of the limestone during the 5-year column study.

In column experiments lasting a total of 24 weeks, O'Hagan (1986) found that a 5 percent $CaCO_3$ addition was required to neutralize drainage from shale with 1 percent sulfur and 0.7 percent pyritic sulfur. The 2.0 to 5.6 mm limestone and shale particles were well blended. Rose and Daub (1994) conducted a 15-week column experiment, and concluded that the 2 to 5 mm limestone particles mixed with 7.0%-sulfur pyritic shale ($d < 1$ cm; NP/AP = 1) were ineffective because they did not impart adequate alkalinity to the pore water. This ineffectiveness was hypothesized as being due to their large size and observed coating by iron precipitates.

Donovan and Ziemkiewicz (1994) added limestone layers to 400-ton piles of sandstone and shale coal overburden roughly one to eight inches in diameter, to produce limestone contents of 0.46, 1.07, and 1.26% ($0.56 < NP/AP < 2.38$). The authors concluded that these and other layered alkaline additions did not consistently affect drainage quality during the year after construction "due to their inhomogeneous distribution, to heterogeneity in NP or MPA [Maximum Potential Acidity] within the piles, to hydroxide armoring of the amendment layers, or to time lag in reaching the outflow." The site was resampled 11 years later and drainage from the two higher limestone additions was "circumneutral" (Ziemkiewicz and Meek 1994).

In summary, the main problem in the field has been achieving a good mixture of the alkaline material with the waste rock and problems of preferential flow within large waste rock stockpiles. Most applications at metal mines have either layered acid producing with acid consuming rocks, or tried to blend materials by dumping alternate loads of acid consuming and acid producing material. The problem is that with the layered approach, acid is generated within the acid producing layer and due to preferential flow is not completely neutralized by the acid consuming layer. Similar problems occur in the approach where the loads are dumped in an alternate manner. The challenge is to develop an approach where the acid consuming material is well distributed throughout the pile and in intimate contact with the acid producing material.

Adding limestone to each haul truck as the truck leaves the pit may provide the correct limestone loading and an acceptable level of mixing. This could be accomplished by the truck driving under a hopper where the limestone would be added directly to the top of the load. This type of system is currently used at the Gold Quarry Mine in Nevada to add lime (CaO) to gold bearing sulfide rock to maintain neutral conditions in the leach pad (Bolin et al. 2000). The limestone would begin to mix with the waste rock as the truck drives to the waste dump and then would be further mixed as the material is dumped.

Although visually most stockpiles appear to consist solely of large particles, the interior of these piles contain substantial quantities of fine grained materials. For underground operations, based on the material removed from the AMAX exploration shaft near Babbitt, MN, 38% of the material was less than 1 inch; silt and clay size material comprised about 3% of the mass of the pile (Lapakko et al. 1986). Specific surface area increased from 0.6 $m^2 g^{-1}$ for the coarse sand fraction to 2.6 to 4.7 $m^2 g^{-1}$ for the silt and clay fraction. Sulfur content increased from 0.67% for coarse sand to 1.65-1.94% for the silt and clay sized material. As a result, most of the reactive sulfide surface area of the pile was contained within this fine grained material and generated the majority of the acid in the stockpile. Incorporating a fine grained limestone, in intimate contact with acid producing fines, into the stockpile may provide sufficient contact to neutralize a substantial fraction of the acid production.

4. METHODS

4.1. Prediction Test Piles

4.1.1. Experimental Apparatus

Four 20 ft. x 20 ft. bins to house the rock for the field waste characterization study were constructed using 8 in. x 8 in. x 20 ft. treated timbers stacked two high (Figure 1). The timbers were placed on a compacted sand pad. A one piece 36 mil Reinforced Polypropylene (RPP) liner was placed in the bin and covered with 2 to 4 inches of sand followed by a second one piece 36 mil RPP liner, sloped to one end of the bin, which was covered with six inches of sand (Figures 1, 2). A 11/2 in. slotted PVC pipe covered with a geotextile sleeve was installed between the two liners for use as a leak detection system. A 11/2 in. slotted PVC leachate collection pipe with a geotextile sleeve was placed on the top of the top liner. The pipe ran the entire length of the bin and exited in the center of the bin to a collection sump.

The collection sump as well as flow instrumentation was housed in a 60-gallon polyethylene plastic tank (Figures 3, 4). The leachate flowed into a 7-gallon polyethylene plastic sump equipped with two Madison Co. polypropylene hinged liquid level sensors. When the flow reached the upper sensor, a MARCH model LC-SCP-MD pump was triggered on and pumped the sump down until the water level reached the lower level sensor. The water was pumped through a JLC International Inc. IR-Opflow flow meter and flow was recorded on a Precision Digital model 94788 flow totalizer. A portion of each pump cycle was collected in a 2-liter sample bottle for analyses and the remainder of the flow was pumped to a treatment plant.

Before the rock was loaded into the bins a temperature and oxygen sampling apparatus was placed on the top sand layer (Figure 5). Rock was hand placed over the apparatus to prevent any damage while filling the bins (Figure 6). Test piles 2, 3, and 4 also had the apparatus installed at mid-pile (approximately 3 feet up). The apparatus consisted of a 2 in. PVC pipe ten feet long, which housed a temperature probe. For oxygen sampling a 3/16 inch I.D. plastic Tygon tubing with a 1/4 inch I.D. slotted PVC pipe attached to the end was secured to each side of the pipe. The slotted pipe was covered with a geotextile fabric to prevent plugging from fine rock particles. On one side of the pipe the sampling port was placed at 10 feet and the other at 5 feet.

4.1.2. Materials

4.1.2.1. Excavation

The University of Minnesota initiated a project to enlarge its underground physics laboratory at the Soudan Mine, which resulted in excavation of approximately 22,000 cubic yards of greenstone rock. Prior to excavation a drill hole was bored through the center of the cavern to characterize the rock. The rock was then blasted and removed in four lifts. The explosives used were 75% ANFO, a commercially-prepared combination of ammonium nitrate and fuel oil, and 25% Mine Rite, an ammonium nitrate based water gel. As the rock was removed the walls of the cavern were sealed with shotcrete, a mixture of portland cement containing 11% silica fume and –1/2" aggregate. Rock designated for field dissolution testing was trucked to the MN DNR research site in Hibbing, MN.

During the removal of the top lift of rock at the Soudan Mine, several drill cuttings samples were collected and along with the drill core were analyzed for percent sulfur. Based on these analyses, areas within the bottom three lifts were selected as target zones for obtaining a range of sulfur contents to be used for the field waste characterization tests at the DNR's field research site. Once an identified area had been blasted, approximately 50 cubic yards of rock was removed from the mine in approximately 1.5 cubic yard muck boxes.

4.1.2.2. Pile Construction and Sample Collection

Three types of samples were collected for characterization of rock placed into the prediction bins. First, as each muck box was emptied into a pile a random sample was taken and placed in one gallon plastic containers. Each time an identified area was removed from the shaft, 25 samples were collected and analyzed at Lerch Brothers Inc. (Hibbing, MN) to determine if they would produce a test plot of the desired sulfur content. If the results were suitable the rock was loaded into 10 cubic yard dump trucks and hauled to the research site. The 25 samples were retained and analyzed for total sulfur, sulfate, evolved carbon dioxide, and whole rock chemistry. Thirteen of the samples were analyzed for trace metal content. These analyses were conducted by ACTLABS.

A second sample was collected to determine particle size distribution and the variation of chemistry with particle size. The bins were loaded by placing the rock onto a conveyer, which piled the rock in the center of the bin (Figure 7). The rock was then leveled using a backhoe, forming a truncated pyramid (Figure 8). Based on the dimensions of the truncated pyramid it was determined that the piles contained approximately 39 cubic meters. Based on the bulk density determined for the limestone addition tanks the mass of the piles was estimated to be 63 metric tons. As the rock was loaded onto the conveyer, a random sample (approximately 1 cubic yard) was set aside for analyses of particle size distribution.

A third set of 20 samples was collected to further assess compositional variability, including modes of sulfide mineral occurrence, of rock in test piles 2, 3, and 4. Samples were not collected from test pile 1 since analyses of muck box samples indicated sulfur contents wee relatively uniform. Furthermore, visual examination of the rock revealed no concentrated pyrite occurrences.

These samples were collected as the bins were being loaded. For test piles 2 and 3, four samples were taken from the top of the pile after each 10 yards was added and leveled off, one from each side of the pile. For test pile 4, two samples were collected while the first three feet of rock was being added, eight random samples when the first three feet of rock had been leveled off, six random samples after an additional foot of rock had been added, and four samples when the pile was completed. These samples had not yet been analyzed at the time of this report.

4.1.3. Analytical Methods

4.1.3.1. Solid Phase Analyses

Particle size distribution of the one-cubic meter sample taken during bin construction was determined at the MN DNR. The +12 inch and -12 in./+6 in. fractions were manually measured, removed from the pile and weighed. The remaining sample was shoveled through two stacked screens to remove the -6in./+2.5 in. and -2.5 in./+0.75 in. fractions. Rock passing the 0.75 in. screen was collected in five-gallon buckets. For all four piles this fraction did not exceed three buckets.

One of the buckets was randomly selected, placed on a sheet of plastic and split using the four corners method (Scott 1942). One fourth of the sample (approximately one gallon) was used to determine the size distribution of the -0.75 inch rock using a Gilson Ro-Tap equipped with Tyler standard sieves. Sulfur, sulfide, sulfate, evolved carbon dioxide, whole rock and trace metal chemistry of the various size fractions were determined by ACTLABS using methods described below.

Chemical analyses of rock samples were conducted either by Lerch Brothers Inc. or ACTLABS. Lerch Brothers Inc. (Hibbing, MN) performed the initial sulfur determination on the 25 muck box samples using a LECO combustion furnace (method ASTM E395-95A). The mean of the sulfur determination conducted by Lerch Brothers was used to identify the test piles. The remaining chemical analyses were conducted by ACTLABS Inc. Sulfur, sulfate (sulfide was determined by difference), and evolved carbon dioxide were determined in Tucson, AZ using ASTM E-1915-97 (ASTM 2000). A 10 percent hydrochloric acid solution was used to solubilize the carbonate minerals, and the carbonate present was quantified as the difference between total carbon in the initial sample and that in the residue. The remaining solid-phase constituents were determined by ACTLABS Inc. in Ancaster, ON. Whole rock constituents were determined using a lithium tetraborate fusion modified from ASTM E886-94 (ASTM 2000) and analysis by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) using a Thermo Jarrell-Ash ENVIRO II ICP. Concentrations of Ag, Cd, Cu, Ni, Pb, Zn, and Bi were determined using a total digestion method modified from Crock et al. (1983), with analysis by ICP-AES. Other trace elements were determined using instrumental neutron activation analysis (Hoffman 1992).

Mineralogical analyses are presently being conducted by McSwiggen & Associates in St. Paul, MN and were not completed in time for the present report and will be presented in the future. Analyses includes determining the mineral content of the four piles, chemistry of individual minerals, and the degrees of sulfide and carbonate mineral liberation.

4.1.3.2. Test Pile Drainage

Water input to and output from the test plots were determined. Water input to the piles consisted entirely of precipitation (Tables A2.1, A2.2). Precipitation was collected in a US Standard rain gage at the Hibbing field research site. Flow was recorded on a bi-weekly basis once the piles began to flow. Flow was measured using an IR-Opflow flow meter and was recorded using a Precision Digital model 94788 flow totalizer. During the initial startup of the experiment the flow meters were not functioning due to electrical problems. As a result, flow from 21 July, 2000 to 09 November, 2000 had to be estimated (see attachment A2.2 for details).

Composite **drainage quality** samples were collected on a bi-weekly basis once the piles began to flow. An additional grab sample on the first water that flowed into the sumps of test piles 1 and 4 was also analyzed. Samples were analyzed for specific conductance, pH, alkalinity, and acidity at the MN DNR lab. Specific conductance was analyzed using a Myron L conductivity meter, and an Orion SA720 meter, equipped with a Ross combination pH electrode (8165), was used for pH analyses. Alkalinity (for pH ≥ 6.3) and acidity were determined using standard titration techniques for endpoints of 4.5 and 8.3, respectively (APHA et al. 1992). The remaining sample was filtered for metals and sulfate analysis at MDA. Metal samples were acidified with 0.2 mL of Baker Instra-

Analyzed nitric acid per 50 mL. An additional 500 mL sample acidified with 1.0 mL of Baker Analyzed sulfuric acid was taken for nutrient analyses.

Ca, Mg, Na, and K were determined with a Varian 400 SPECTRAA; inductively coupled plasma mass spectrometry (ICP-MS, Hewlett Packard HP4500 Series, model #G1820A) was used for the remaining metals analyses. Sulfate concentrations were determined using a Lachat QuickChem 8000 or, for $[SO_4] < 5$ mg/L, a Dionex ion chromatograph. Nutrients were analyzed at MDA using the Automated Cadmium Reduction Method (Wastewater Method 4500-NO_3 F) on a Technicon AA11 for Nitrate + Nitrite Nitrogen, the Ammonia-Selective Electrode Method (Wastewater Method 4500-NH_3 F) on an Accumet 950 pH/ion meter for Ammonia Nitrogen, the Ascorbic Acid Method (Wastewater Method 4500-P E) on a Perkin Elmer 552 Spectrophotometer for Total Phosphorus, and the Semi-Automated Colorimetric Method (EPA 351.2) with a Bran&Luebbe Traacs 800 for Total Kjeldahl Nitrogen.

4.1.3.3. Temperature and Oxygen within Test Piles

Temperature was determined using a Cole-Parmer model 8402-00 meter. Oxygen readings were determined using a GC Industries model GC-502 meter and a YSI model 57 as a comparison to verify results. (See attachment A9.3 for temperature and oxygen notes and comparisons.) The method for oxygen sampling consisted of inserting the probe into an oxygen chamber which was connected to a vacuum pump on one end and to the oxygen sampling port on the other. The pump was turned on and the valve to the oxygen port was opened. Oxygen measurements were read after a five minute purge time. Temperature was read at the same time as the oxygen readings. The sampling apparatus is illustrated in Figure 9.

4.1.4. Calculations

Yield coefficients were calculated to express the amount of flow as a fraction of the precipitation falling on the pile.

$$Y_{b,t} = V_{b,t}/[(P_t/12) \times A_b \times 28.2)], \text{ where} \qquad [8]$$

$Y_{b,t}$ = yield coefficient for pile b for flow period t, dimensionless;
$V_{b,t}$ = volume of flow from pile b during flow period t, L;
P_t = precipitation during flow period t, inches (division by 12 converts to feet);
A_b = horizontal cross-sectional area of pile b, ft^2; and
28.2 = factor to convert cubic feet to liters.

Since the base of each pile was 20 feet square, the area A_b can be calculated and inserted into equation 8.

$$Y_{b,t} = V_{b,t}/[940\ P_t] \qquad [9]$$

For periods flow during which flow was not measured from a specific pile (e.g. due to failure of equipment), flow was estimated as the product of the yield coefficient for the pile and the volume of precipitation onto the pile during the period of unmeasured flow.

Mass release during individual flow periods was calculated as the product of the volume of flow and the concentration at the end of the flow period. Mass release during the entire year was calculated as the sum of the releases from the individual flow periods. Rates of release were calculated by dividing mass release for a period by its duration. To determine rates over a longer time frame, the time-weighted average release rate of periods during the time frame was determined.

4.2. Limestone Addition Tanks

4.2.1. Materials

The 0.67% sulfur rock used in test pile 4 of the prediction study was selected for use in the alkaline mixing experiment (see sections 4.1.1. and 4.1.3 for sample collection details). The rock was screened to pass a 1.5 inch screen at Casper Construction Inc. in Grand Rapids, MN (Figures 10 and 11). A bobcat loader was used to fill the tanks with the exception of tank 5 which could not be reached with the loader and was filled using five gallon buckets. Three bucket loads were placed in each tank, the loader positioned the bucket just above the tank and the rock was randomly shoveled into the tanks (Figure 12).

For the tanks that had the rock mixed with limestone, the loader scooped a bucket of rock and then the limestone (1/3 of the total addition), which had been weighed, was added to the bucket (Figures 13, 14 and 15). A sample of rock was taken from each loader bucket, prior to adding the limestone for the alkaline mixing tanks, for a total of 3 samples per tank. A total of 55 pounds of limestone was added to the 1:1 ratio tanks and 165 pounds to the 3:1 ratio tanks.

4.2.2. Experimental Apparatus

The limestone mixing tests are being conducted in six polyethylene plastic tanks (d = 48 in., h = 42 in.). The tanks are housed in a 20' x 20' lined bin that serves as a double containment (Figures 16 and 17). Two control tanks (tanks 1 and 6), two tanks with limestone mixed at a 1:1 ratio (tanks 2 and 5), and two tanks with limestone mixed at a 3:1 ratio (tanks 3 and 4). The tanks were fitted with 2 -inch slotted PVC outlet pipe on the bottom, which drained into a 22 gallon polyethylene plastic sample collection sump (Figure 18). The bottom of the outlet pipe was installed approximately 2 inches above the bottom of the tank which created a zone of saturation, so as not to allow the waste rock to be within this zone three inches of silica sand was placed in the bottom of each tank. The tanks were then filled to a depth of approximately 31 inches with either rock (control tanks) or rock mixed with limestone, yielding a bed volume of 32.4 cubic feet. Bulk density of the rock was subsequently determined as 108.2 lbs/ft^3, yielding a bed mass of 3506 pounds. The limestone had a bulk density of 86.6 lbs/ft^3. The tanks were filled on 24 October, 2000 and input to the tanks is limited to precipitation.

4.2.3. Analytical Methods

4.2.3.1. Solid Phase Analyses

The three rock samples from each tank were composited. A representative split and a sample of the limestone were sent for analyses. Samples were analyzed for total sulfur, sulfate, evolved carbon dioxide, as well as whole rock and trace element concentrations at ACTLABS. Total sulfur for the six samples ranged from 0.40% to 0.56%. The limestone used as described by the company was "manufactured sand" and was obtained from CAMAS, Shiely Division in Eagan, MN. Particle size distribution for the rock samples and limestone was determined by Lerch Brothers. Percent moisture of the limestone (5 %) was determined at the MN DNR. See section 4.1.4.1. for analytical methods. The mineralogical composition and pyrite liberation were determined for splits of samples from the two control tanks. Analyses were conducted by Mineralogical Consulting Service, Pengilly, MN (Appendix 1, Attachment A1.1.).

4.2.3.2. Aqueous Analyses

The sample schedule was designed to collect samples on a bi-weekly basis and after selected large rain events. Water input to the tanks will consist entirely of precipitation. The collection sump was calibrated in five liter increments and total flow was measured with a ruler. One inch of precipitation is about the equivalent to 30 liters of input water. A grab sample for analyses was collected directly from the sump and the sump was then emptied. A 250 mL sample was taken for pH, specific conductance, alkalinity (if pH exceeded 6.30) or acidity, metals, and sulfate analysis. These samples were analyzed for pH and specific conductance directly in the bottle. A 20 mL sample was then taken for analysis of alkalinity or acidity. The remaining sample was filtered for metals and sulfate analysis. Metal samples were acidified with 0.2 mL of Baker Instra-Analyzed nitric acid per 50 mLs. Periodic samples for nutrients (500 mLs) were also taken. Nutrient samples were acidified with 2 mLs of Baker Analyzed sulfuric acid per 500 mLs. See section 4.1.4.2. for analytical methods.

5. RESULTS

5.1. Prediction Test Piles

5.1.1. Introduction

Four field test piles were constructed to examine the variation of the quality of drainage from Archean greenstone rock as a function of sulfur content. Construction of individual piles was completed from 21 July to 19 September 2000. These piles provide data for only four sulfur contents, as opposed to the 14 different samples examined in the laboratory.

However, the field tests are more representative of waste rock dissolution under operational conditions. Relative to the laboratory phase, the rock size used in this phase is more representative of that generated during mining and, therefore, more accurately simulates movement of air and water within the rock. In addition, it is being subjected to dissolution under actual environmental conditions. The data generated will be used to aid in extrapolating data from the more intensive laboratory study to field conditions.

5.1.2. Solid-Phase Analyses

Roughly 75% of the rock in test piles 1 and 2 was coarser than 3/4-inch, as compared to about 55% of the rock in test piles 3 and 4 (Table 1). The -100 mesh fraction for the four piles ranged from 0.8% to 1.9%. The respective mean sulfur analyses for test piles 1 - 4 were 0.02%, 0.20%, 0.39%, and 0.67% (Table 2). The major whole rock components (and approximate range of average values) were SiO_2 (52-68%), Al_2O_3 (13-20%), FeO (9-11%), MgO (3-6%), and K_2O (1.7-2.5%). Contents of CO_2 (0.02-0.5%), CaO (0.23-0.77%), and Na_2O (0.2-0.4%) were low (Table 3).

As was the case with laboratory solids, most trace metal concentrations in the field rock were less than 20 mg kg^{-1}. Elements with concentrations above 20 mg kg^{-1} (and their range in mg kg^{-1}) were La (13-30), Nd (15-35), Co (20-40), Ce (30-70), Rb (60-75), Cu (20-110), Zn (80-160), Ni (70-190), and Cr (100-400). Additional data on trace metal contents for all bins and Sobek NP values for Bin 4 are presented in Appendix 1.

The mass-weighted average compositions determined for the particle size samples were typically in close agreement with compositions determined by analysis of the 25 muck box samples (Table 4). This suggests that the one-ton particle size sample was fairly representative of the piles. Notable exceptions to this agreement were the sulfur contents from the two low sulfur bins. In both cases the mass-weighted average compositions for the particle size samples yielded sulfur concentrations more than twice those for the muck box samples. In both cases the sulfur content of each particle size fraction was higher than that of the muck box sample average. It is possible that some anomalously high sulfur rock was included in the random sample collected for particle size analysis.

There were no consistent trends in the variation of sulfur content with particle size. For the 0.02% and 0.39% sulfur piles, sulfur content tended to increase as particle size decreased (Table A1.12). In contrast, the sulfur content in the 0.67% sulfur pile tended to decrease as particle size decreased. For the 0.20% sulfur pile, sulfur content was elevated in the +1/4-inch fractions and fairly stable in the finer fractions.

For all four piles carbon dioxide content tended to increase with decreasing particle size, and the CO_2 content of the -100 fraction was roughly an order of magnitude higher than the mass-weighted mean. In fact, almost all fractions finer than 0.25 inches had CO_2 contents at least three times the mass-weighted mean. Calcium concentrations also increased with decreasing particle size, suggesting (although not conclusively) that a calcium carbonate phase may be present. Consequently, the effectiveness of the fine fraction for neutralizing acid would be enhanced not only by the greater degree of carbonate mineral liberation and elevated specific surface area, but also by the preferential concentration of carbonates in this fraction.

Analyses are presently in progress to determine the mineral content of the four piles, the chemistries of the individual minerals, the variation of mineral content with particle size, and the variation of sulfide and carbonate mineral liberation with particle size.

5.1.3. Temperature and Oxygen Profiles

Variations in temperature and oxygen affect the rate of sulfide mineral oxidation. Temperature and oxygen content within piles 1, 3, and 4 were measured two to four times from 2 August to 26 September 2000. All four piles were sampled eight to thirteen times from 27 March to 17 October 2001 and three times between 15 May and 26 August 2002. Start-up problems were encountered with both sampling and measuring oxygen content (appendix 2, attachment A2.3). Some sampling problems due to obstructed tubing also occurred in test piles 3 and 4 late in 2001 (see appendix 2, attachment A2.3. for field notes).

Temperature was measured from March to December and ranged from approximately -2°C to 23°C. Temporal trends were similar in all piles, with temperatures lowest in March and highest in July and August (Table 5). Temperatures at the bottom of the piles typically ranged from approximately 0°C to 18°C. Piles 2-4 were sampled both at the bottom and approximately three feet from the bottom. The high and low temperatures for the upper sampling ports were roughly 2-4 degrees more extreme than those from the lower ports. The greater degree of insulation at the bottom of the piles probably resulted in more moderate variations in temperature.

Oxygen contents in the gas phase were measured 6 to 15 times at the 14 ports. At two of the ports only six measurements were made because the tubing used for measurements became obstructed. Of the167 measurements, 78% (130 of 167) of the values were in the range of 16% to 21% of the gas phase, as compared with 21% for the oxygen content of the atmosphere. Of the 37 values out of the typical range, 21 were determined on two days. Ten values determined on 27 March 2001 ranged from approximately 7% to 12%, and 11 values determined on 17 October 2001 ranged from roughly 23% to 26%. It is conceivable, if not likely, that these measurements are in error.

Average oxygen concentrations at the 12 ports that functioned throughout the study ranged from 18.1% to 19.8%. Average oxygen concentrations were examined as a function of vertical depth in the pile (top vs bottom port for five and ten foot distances into pile), horizontal distance into pile (five vs ten foot distance for top and bottom port) and sulfur content (top port five feet into pile, top port ten feet into pile, bottom port five feet into pile, bottom port ten feet into pile). Since the range in concentrations was fairly small and some problems were encountered in measurement, the following comparisons are tentative.

In three of four cases, average oxygen concentrations at the top of the pile were 0.1% to 1.1% higher than at the top of the pile. In all four cases assessing horizontal distance into the pile, average oxygen concentrations five feet into the pile were 0.1% to 0.8% higher than those 10 feet into the pile. There was no consistent dependence of oxygen concentrations on sulfur content. Considering the data collected to date it appears oxygen concentrations in gas within all four piles are near atmospheric and the variation of these concentrations within the pile is small. It is unlikely that possible variations of this magnitude will have a substantial effect on rates of sulfide mineral oxidation within the pile. The fact that oxygen concentrations are near atmospheric indicates that rates of sulfide mineral oxidation (per unit sulfide mineral surface area) should be close to those observed in the laboratory.

5.1.4. Flow

The four test piles were constructed late in 2000, and the periods of flow were roughly two to four months. Flow for the first partial year was assumed to cease on 20 November 2000, although a small amount of flow occurred subsequently (Attachment A2.1). Due to equipment problems flow was not determined until November 1 (piles 1-3) or 9 (pile 4), 2000, providing only one month of measured flow for the two to four month records for that year. Yield coefficients (the ratio of drainage volume to input precipitation volume) of 0.50 to 0.63 were calculated for one- to three-week periods after flow meters were installed in 2000. The short period of record over which these values were determined must be considered when evaluating their merit. Flows for the remaining one to three months were estimated using the observed precipitation during the period of unmeasured flow and yield coefficients determined for each pile for the period from August to November 2001 (see Attachment A2.2). The estimated flows ranged from 3700 to 7000 liters for 2000.

In 2001, precipitation was 26.06 inches (Table A2.2) and the four piles produced drainage from the middle of April to the middle of December. Total flows ranged from approximately 17,500 to 20,400 liters. Yield coefficients of 0.73 to 0.85 were calculated and these values are considerably higher than yield coefficients of 0.44 and 0.58 reported by Eger and Lapakko (1985) and 0.55 reported by Smith and Beckie (2003) (Table 6). The yield coefficients for piles 1,3 and 4 from 2 August - 28 November 2001 ranged from 0.50 to 0.63. These yields are in good agreement with previously reported values. The yield coefficient for pile 2 from August to November 2001 was higher (0.81) (Appendix 2, Attachment A2.2).

In 2002, precipitation was 27.21 inches and the four piles produced drainage from the middle of April to the end of November. Total flows ranged from approximately 13,000 to 17,500 liters, representing 51% to 67% of the precipitation input to the piles (yield coefficients of 0.51 to 0.67). The yield coefficients determined for 2002 are more consistent with previously reported values (Eger and Lapakko 1985; Smith and Beckie 2003).

The yield coefficients determined for 2001 seem unusually high when compared to the 2002 values and those reported previously. It is possible that the apparently high yields in 2001 are reasonable because the size of the piles are so small. If so, then a problem exists with the low coefficients observed in 2002. The reason for the large variation in drainage yields between 2001 and 2002 is unclear, especially considering the variation was observed for all four piles. As is disscussed in a later section, this large variation was also observed for the six limestone addition tanks.

Error in the determination of yield coefficients could be the result of errors in 1) measuring precipitation, 2) measuring drainage volume, or 3) error in calculation. Precipitation measurements at the site were in reasonable agreement with those reported for the Hibbing airport. It seems unlikely that errors in measuring drainage volume would occur uniformly at all 10 measurement locations. The same calculation was used for both years. Yield coefficients calculated in the future may lend insight into the large variation observed over the present two-year period of record.

5.1.5. Drainage Quality and Chemical Mass Release

In 2000, three to six drainage quality samples were collected from each pile between 14 August and 20 November. In 2001 (9 April - 28 November) and 2002 (28 April - 28 October), 11 and 10 samples per pile, respectively, were collected. These samples were composites that represented the flow weighted mean drainage quality over a typical period of two to three weeks. Chemical mass release was calculated based on concentrations in test pile drainage and the drainage volume. Rates of release were calculated for 2001 and 2002 by dividing chemical mass release by the time over which release occurred and the mass of the pile.

Actual flows in 2001 were 20 to 30 percent higher than those used to calculate rates. Consequently, chemical mass release and rates of release in 2001 were approximately 20 to 30 percent higher than those presented in this report. In the upcoming year, estimates will be made to incorporate all flow into the 2001 rates of release. The flow volumes used to calculate rates in 2001 were roughly equal to those measured in 2002. Therefore, changes in rates between the two years reflect change in drainage concentrations.

Drainage pH values typically ranged from 7.5 to 8.4 and **alkalinities** from roughly 40 to 80 mgL^{-1} as $CaCO_3$. Drainage pH values from the two lower sulfur piles tended to oscillate in the approximate range of 7.5-8.5, and exhibited no distinct temporal trend over the course of the study (Figures 19, 20). Typical drainage pH ranges for the 0.39% (7.5-7.9) and 0.67% (7.4-8.2) sulfur piles were lower and both displayed a slightly decreasing trend over the 2001 and 2002 field seasons (Figures 21, 22). Alkalinities from the 0.02% and 0.20% sulfur piles tended to oscillate within respective ranges of 40-75 and 60-80 mg $CaCO_3$ L^{-1}, with no distinct temporal trend over the course of the study (Tables A3.1, A3.2, respectively). Alkalinities from the 0.39% and 0.67% piles typically ranged from 45-70 and 40-85 mg $CaCO_3$ L^{-1}, respectively, and tended to be lower during 2002 than in the earlier part of the study (Tables A3.3, A3.4).

Sulfate release reflects acid production (equation 1). Sulfate concentrations from the four piles typically ranged from 20 to 300 $mgL^{-1}$and generally increased as the sulfur content of the pile increased. All piles exhibited a sulfate concentration peak in 2000, probably due to the release of oxidation products accumulated after the rock was blasted. Concentrations from the 0.02% and 0.20% piles tended to decrease slightly over time and plateau during 2002 (Figures 19, 20). In contrast, sulfate concentrations in drainage from the 0.39% and 0.67% sulfur piles tended to increase over time (Figures 21, 22).

It was assumed that all chemical release was the result of reactions in the pile. Because sulfate concentrations in precipitation can be elevated, data from precipitation monitoring stations in the region were checked to determine their contribution to drainages. For the 2001 calendar year, average sulfate concentrations in precipitation at Marcel, Ely, Wolf Ridge and Fond du Lac were in the range of 0.59 to 0.97 mg L^{-1} (http://nadp.sws.uiuc.edu/nadpdata/state.asp?state=MN). Drainage from the piles was approximately 60 percent of precipitation (Table 6). Assuming sulfate was conserved in solution, the aforementioned concentrations would increase to the range of 1.0 to 1.6 mg L^{-1}. Sulfate concentrations in drainage from the 0.02% S pile were the lowest of the four piles, typically ranging from 17 to 21 mg L^{-1} in 2002. Comparing adjusted sulfate concentrations in the precipitation with those in the drainage, precipitation contributed roughly five to nine percent of the sulfate release from the pile (100 x 1/21 ~ 5, 100 x 1.6/17 ~ 9). The fraction of sulfate release contributed by precipitation for the remaining three piles would be less than this value because sulfate concentrations in drainages from these piles was higher. Sulfate concentrations from precipitation are not considered further in the discussion of sulfate release.

Sulfate release rates calculated for discrete time intervals during 2001 and 2002 ranged over about one order of magnitude for each of the piles (Table 7). These variations were due to variations in drainage volume (Tables A4.1-A4.4) and sulfate concentrations. From 2001 to 2002, rates of sulfate release from the 0.02% and 0.20% sulfur piles decreased by roughly 25%, and this reflects a corresponding decrease in sulfate concentrations (Figures 19, 20). Rates from the 0.39% and 0.67% sulfur piles in 2002 were approximately 65% higher than those in 2001 (Table 8). These increases were largely the result of sulfate concentrations increasing over time (Figures 21, 22).

Rates of sulfate release in 2002 increased linearly with the sulfur content of the rock (Figure 23). The slope of the line presented in Figure 23 was determined to be 32.2 μmol (kg week)$^{-1}$ (pct S)$^{-1}$ (r^2 = 0.98). The slope for a similar graph depicting laboratory data was reported as 224 μmol (kg week)$^{-1}$ (pct S)$^{-1}$ (Lapakko et al. 2002, Figure 21). The ratio of the field slope to that from the laboratory data suggests that sulfate release rates in the field were 0.14 times those in the laboratory.

Retardation factors were also calculated using sulfate release rates from the individual piles. In 2001 and 2002, these values ranged from 0.055 to 0.55 (Table 7), in comparison with values of 0.096 to 0.33 reported for Duluth Complex rock (Lapakko 1994). The retardation factor for the 0.02% S pile was unusually high, particularly because it was compared to a sample with a sulfur content of 0.04% S. It should be noted that the 0.02% S content for this pile was determined based on analysis of 25 muck box samples (Table 2). Sulfur concentrations reported for size fractions of the bulk sample suggest the sulfur content of the pile may actually be in the neighborhood of 0.04% (Table 4, Table A1.12).

Calcium, magnesium, sodium and potassium were released from minerals that dissolved and neutralized acid. Release of one mole of calcium or magnesium represents neutralization of two moles of acid and release of one mole of sodium or potassium represents neutralization of one mole of acid. Concentrations of these metals peaked in 2000 and generally tended to decrease with time (Figures 19-22). Concentrations of calcium, magnesium and potassium tended to increase as the sulfur content of the pile increased, and the opposite trend was observed for sodium.

Molar concentrations generally decreased in the order Ca > Na > Mg ~ K. In contrast, solid-phase concentrations (and their approximate ranges) decreased in the order MgO (3 - 6%) > K_2O (1.5 - 3.5%) > CaO (0.2 - 0.8%) ~ Na_2O (0.2 - 0.5%) (Table 4). High aqueous phase calcium concentrations relative to solid-phase calcium concentrations indicates the solid phase in which calcium was present dissolved relatively rapidly. Conversely, magnesium and potassium concentrations in drainages were relatively low and their solid-phase concentrations were relatively high. These elements were apparently present in mineral phases that dissolved relatively slowly.

Calcium release rates tended to increase with increasing sulfur content. This trend was also observed for sulfate release rates and suggests that calcium release rates were driven by the rate of acid production. Rates of calcium release from the 0.02%, 0.20%, and 0.39% S piles in 2002 were roughly 50% to 75% of those in 2001 (Table 8), reflecting the previously mentioned decrease of calcium concentrations over time (Figures 19, 20). The rate of calcium release from the 0.67% S pile in 2002 was roughly 1.2 times that in 2001, and this indicates calcium concentrations increased slightly from 2001 to 2002. Sulfate release from this pile also increased in 2002, and the increase in calcium release may have been the result of increased acid production.

The decreasing calcium rates observed for the 0.02% and 0.20% S piles suggests there may have been a small amount of a more reactive phase containing calcium, such as fine-grained carbonate minerals or residue from shotcrete used in the Soudan Mine cavern. The carbon dioxide contents of the rock ranged from 0.054 to 0.46, which is higher than values typically observed for the laboratory samples ($CO_2 < 0.05\%$).

Although magnesium release rates in 2001 exhibited no distinct dependence on solid-phase sulfur content, release rates in 2002 strictly increased with sulfur content. Release rates for the 0.02%, 0.20% and 0.39% piles in 2002 were roughly 40 to 60 percent of those in 2001 (Table 8), reflecting a decrease in magnesium concentrations from 2001 to 2002. The rate of magnesium release from the 0.67% S pile in 2002 was the same as that in 2001. The rate of sulfate release from this pile increased in 2002, and magnesium release may have increased, in part, due to increased acid production (as was suggested previously for calcium release).

Sodium release tended to decrease with increasing sulfur content. The average annual sodium release rates in 2002 were roughly 30 to 50 percent of those in 2001 and indicate a pronounced decrease in sodium concentrations. The extent to which sodium release decreased over this period was greater than or equal to that for calcium, magnesium and potassium.

Potassium release demonstrated a mild tendency to increase with increasing solid-phase sulfur content. Annual potassium release from the piles in 2002 ranged from approximately 60 to 90 percent of those in 2001. The extent to which potassium release decreased over this period was generally lower than that for calcium, magnesium and sodium.

Concentrations of **trace metals** (Cu, Ni, Co, Zn) were generally very low. Only copper was detectable (> 0.002 mgL^{-1}) in more than half the cases. Concentrations in 2002 typically did not exceed 0.006 mgL^{-1} and exhibited no distinct dependence on sulfur content of the pile (Tables A3.1-A3.4).

In 2002, iron concentrations were generally below 0.01 mgL^{-1} and tended to increase as the sulfur content of the piles increased (Tables A3.1-A3.4). Manganese concentrations were typically below detection (0.002 mgL^{-1}). Aluminum concentrations were generally below 0.01 mgL^{-1} and were highest in the 0.02% sulfur pile. Ammonia and nitrate concentrations were elevated in 2000, most likely due to the presence of residual blasting agents in the rock, and showed a decreasing trend over time (Tables A3.1-A3.4). This trend suggests the ammonia and nitrate were being removed from the piles and that concentrations would approach zero in the fairly near future.

5.1.6. Comparison of Field and Laboratory Sulfate Release Rates

Rates of sulfate release in 2002 increased linearly with the sulfur content of the rock (Figure 23). The slope of the line presented in Figure 23 was determined to be 32.2 μmol (kg week)$^{-1}$ (pct S)$^{-1}$ ($r^2 = 0.98$). The slope for a similar graph depicting laboratory data was reported as 224 μmol (kg week)$^{-1}$ (pct S)$^{-1}$ (Lapakko et al. 2002, Figure 21). The ratio of the field slope to that from the laboratory data suggests that sulfate release rates in the field were 0.14 times those in the laboratory. Retardation factors calculated using sulfate release rates from the individual piles in 2001 and 2002 ranged from 0.055 to 0.55 (Table 7). These values, as would be expected, are in reasonable agreement with the 0.14 value.

Assuming sulfate release was not limiting in either the laboratory or field and ignoring effects of temperature on oxidation rates, the difference between laboratory and field rates would be due to differences in pyrite surface area. (Note that field data indicate the oxygen content of the gas phase in the piles was near atmospheric concentrations.) A rough estimate of the relative pyrite surface areas in the laboratory and field can be made by assuming the variation of pyrite liberation as a function of particle size in the field was similar to that in the laboratory. For the laboratory solids, the degree of pyrite liberation increased with decreasing particle size, and the average degree of liberation particles in the -100/+150 size fraction ($105 < d < 149$ μm) was 81% (range of 67% - 90%). The percentage of laboratory solids in the -100 mesh fraction averaged 9.5%, ranging from 7.6% to 11.2% (Lapakko et al. 2002, Table 2). The percentage of field solids in this size fraction averaged 1.4%, ranging from 0.8% to 1.9% (Table 1). The ratio of the -100 mesh percentage in the field to that in the laboratory can be approximated using the quotient of average values, or 1.4/9.5 = 0.15.

Given the assumptions stated at the beginning of the previous paragraph, the sulfate release rate in the field would be 0.15 times that in the laboratory. This is reasonably close to the 0.14 retardation factor determined based on slopes of graphs depicting sulfate release rates vs percent solid-phase sulfur. Furthermore, this suggests that available pyrite surface area is the dominant controlling factor in both the laboratory and field. Temperature differences between the field and laboratory and reduced sulfate removal in the field would also be expected to affect rates of sulfate release. The extent of pyrite liberation in the field solids is presently being determined and will provide additional insight on the pyrite surface area in the field relative to that in the laboratory. The influence of available surface area on observed sulfate release rates will be further assessed when these data are available.

The calcium retardation factors for 2001 and 2002 were near one, except for values from the 0.20%

S pile. These factors indicate the field rates were roughly equal to or greater than laboratory rates. In contrast a range of 0.14 to 0.46 was reported for calcium retardation factors for Duluth Complex rock (Lapakko 1994). The high values are partly due to a higher range of CaO contents in the field rock than in the laboratory rock (0.23%-0.76% vs 0.04%-0.29%). The very high retardation factors also suggest the presence of a highly soluble calcium phase present in the field rock but absent in the laboratory samples. As noted above, the CO_2 content of the field rock was higher than that typically observed in the laboratory, indicating the possibility of a calcium carbonate phase in the field rock.

Retardation factors for magnesium ranged from 0.008 to 0.6. The extremely low Mg retardation factor of 0.008 was strongly influenced by the elevated magnesium release rate from the corresponding laboratory sample which had a siderite content of 17.9%. Retardation factors for the remaining three piles (0.1-0.6) compare favorably to the 0.053 to 0.36 range reported for Duluth Complex rock (Lapakko 1994).

Release rates for sodium in the field were higher than those observed in the laboratory, as reflected by retardation factors ranging from approximately 3 to 30 (Table 7). This suggests the presence of a rapidly dissolving solid-phase form of sodium in the field that was not present in laboratory solids. Based on the large decrease in sodium release from 2001 to 2002, the amount of the reactive sodium-bearing phase may be relatively small.

Potassium release rates in the field ranged form roughly 0.1 to 0.9, with values for the 0.20%, 0.39% and 0.67% S piles ranging from 0.6 to 0.9 (Table 6). This indicates that potassium release rates in the field were similar to those in the laboratory.

5.2. Limestone Addition Tank Results

5.2.1. Introduction

Six field tanks were used to determine, as a function of limestone loading, the effectiveness of blending limestone with waste rock in controlling acid generation. The experiment began on 24 October 2000. In addition to two controls, duplicate tanks with limestone additions producing NP:AP ratios of 1:1 and 3:1 were examined. The average sulfur content of rock in the six tanks was 0.49%.

5.2.2. Solid Phase Analyses

Particle size distribution for rock in tanks 1 - 5 was determined using a dry screening method and a wet screening method was used for tank 6. Although 40% to 60% of all samples were finer than 0.5 inches, the wet screening produced a finer particle size distribution. The wet screening yielded 10.4% finer than 100 mesh as opposed to approximately 5% for the dry screening. This was considerably finer than the 0.8% to 1.9% finer than 100 mesh reported for dry screening of rock in the prediction piles. The limestone was 57% -20 mesh and 4.5% -100 mesh (Table 9).

The respective averages for total sulfur, sulfate, and CO_2 contents of the rock were 0.49%, 0.019%, and 0.39%, respectively. The approximate averages for major whole rock components for the tank samples were SiO_2 (66%), Al_2O_3 (13%), FeO (9%), MgO (3%), and K_2O (2%). CaO and Na_2O contents were both about 0.3% (Table 10). All values were within the range reported for the prediction piles. Copper, nickel, cobalt and zinc concentrations were similar to those reported for the 0.67% S prediction pile (Table A1.17. vs Table A1.10). The CO_2 content of the limestone was 41.56% (estimated as LOI), slightly less than the 44% expected for pure calcite.

Mineralogical analysis of two samples from the tanks indicated that the major minerals present in the rock were quartz (~50%), chlorite (~25%), and sericite (~20%). The samples contained roughly 1% pyrite and 1.2% siderite. The pyrite was reported to be fine grained and liberated only in rocks finer than 28 mesh (600 μm). Most of the liberated pyrite occurs in fractions finer than 48 mesh (300 μm). The total pyrite liberation is approximately 12% (Appendix 1, Attachment A1.1).

5.2.3. Flow

Drainage volumes from the limestone tanks in 2001 ranged from roughly 550 to 640 liters. These volumes represented 85% to 98% of the precipitation input of 649 liters (Table 11). Drainage volumes in 2002 were lower, ranging from approximately 360 to 390 liters. The yields, relative to input precipitation, in 2002 were considerably lower than in 2001. All values were near 50% (Table 11) and this is consistent with values reported in previous studies (Eger and Lapakko 1985; Smith and Beckie 2003). The decrease of yields was similar to that observed for the field piles. This behavior is difficult to explain and suggests an error in measurement of precipitation or flow, or a calculational error. No error was found and additional effort will be directed toward resolving this anomaly in the upcoming year.

5.2.4. Drainage Quality and Chemical Mass Release

Each tank was sampled once in 2000, thirteen times in 2001, and nine times in 2002. Drainage pH typically ranged from 7.5 - 8.5, peaked from June to August, and was in essentially the same range for all tanks to which limestone was added. The pH of drainage from the control tanks was at the lower end of this range and several values were below 7.5.

Alkalinity from all tanks decreased over the course of the study and tended to increase with increasing limestone loading (Tables A3.5-A3.10). Concentrations from the controls reached the range of 10 to 25 mg L^{-1} as $CaCO_3$ during June 2002. Concentrations from the 1:1 and 3:1 limestone additions stabilize in approximate respective ranges of 40-60 and 50-70 mg L^{-1} as $CaCO_3$ after September 2001.

Sulfate concentrations displayed no obvious, consistent temporal trends (Figures 24-29). Concentrations from the controls were higher than those from the tanks to which limestone was added (Tables A3.5-A3.10). In 2002, the average sulfate concentration from the controls was around 350 mg L^{-1} compared to and average of 290 mg L^{-1} from the treated tanks. These differences in sulfate concentration were reflected in the rates of sulfate release (Table 12), because the volume of drainage did not vary greatly among the tanks. The elevated sulfate concentrations from the controls suggest that there may be areas of accelerated pyrite oxidation within the tank. These could be areas in which acidic conditions have developed and pyrite oxidation is accelerated by bacterial mediation.

After elevated concentrations in the first three samples, calcium and magnesium concentrations typically ranged from 100 - 200 mg L^{-1} and 10 - 20 mg L^{-1}, respectively. Rates of calcium release were typically slightly higher than rates of sulfate release (Table 12). Although the average calcium release rate from the controls was slightly higher than that from the treated tanks, differences in both calcium and magnesium release rates among the tanks were relatively small (Table 12). The calcium release from the controls may have been slightly accelerated by the elevated rate of acid production in these tanks, as indicated by higher sulfate release rates.

Nitrate concentrations were elevated in 2000, likely due to the presence of residual blasting agents in the rock but showed a decreasing trend throughout the 2001 field season (Tables A3.5 - A3.10). Concentrations during 2002 typically ranged from 10 to 15 mg L^{-1}.

5.2.5. Comparison of Field and Laboratory Chemical Release Rates

Rates of chemical release from the limestone addition tanks were determined for sulfate, calcium and magnesium and compared to rates of release observed for a greenstone sample containing 0.50% S in the laboratory. For weeks 60-100, rates of sulfate, calcium and magnesium release were 116, 6.37, and 72.6 μmol (kg rock week)$^{-1}$ (Lapakko et al. 2002, Table 9). Although sulfate release rates from the controls were higher than those from the treated tanks, rates did not vary greatly among the various tanks. The observed range was 27 to 41 μmol (kg rock week)$^{-1}$, yielding retardation factors of 0.23 to 0.35. These factors are similar to those calculated for the field piles.

The -100 mesh fraction was about 5% for the controls and 11.2% for the 0.50% S sample in the laboratory. Normalizing the retardation factors for the difference in -100 mesh fractions (see section 5.1.6) yields adjusted normalized retardation factors of 0.52 and 0.78. This indicates that after an estimated adjustment for available pyrite surface area the rates of sulfate release from the field tank controls were roughly 50% to 75% of laboratory rates.

Sulfate release rates from the alkaline addition tank controls were also compared to those observed from the test piles. The average sulfur content of the six tanks was 0.49% (Table 10) and five percent of the rock in control tanks 1 and 2 was finer than 100 mesh (Table 9). Using the slope of the line presented in Figure 23, a sulfate release rate of 16 μmol (kg rock week)$^{-1}$ was calculated ($32.2 \times 0.49 = 16$). Accounting for the difference in the -100 fraction (5% for the tanks vs 1.4% for the field piles) yields a predicted rate of $(5/1.4) \times 16 = 56$ μmol (kg rock week)$^{-1}$. This is roughly 40% higher than the average value of 40 μmol (kg rock week)$^{-1}$ observed for the controls.

Calcium release rates also fell into a fairly small range of 33 to 43 μmol (kg rock week)$^{-1}$, and appeared to be independent of limestone loading (Table 12, p. 2). Retardation factors of 5.2 to 6.8 indicated the field rates were higher than those in the laboratory. This suggests a soluble calcium phase, as well as the limestone added, was present in the field rock but not in the laboratory sample. The average Ca and CO_2 contents of the field rock were 0.39 and 0.38 percent (Table 10), indicating that some calcium may be present as a carbonate. The corresponding values for the laboratory rock were 1.76 and 0.03 percent (Lapakko et al. 2002).

Magnesium release rates ranged from 6.3 to 7.8 μmol (kg rock week)$^{-1}$ and demonstrated no strong dependence on limestone loading. Retardation factors ranged from 0.087 to 0.11. These factors were relatively low due to the high rates of magnesium release from the siderite-bearing sample in the laboratory.

6. PLANS

The following tasks have been identified for completion in the upcoming biennium.

1. Extend data collection and interpretation through the 2004 field season.
2. Determine the chemistry of additional samples collected from field piles to assess compositional variability within individual piles.
3. Determine the Sobek NP values for suites of samples from piles 1, 2, and 3.
4. Determine the variation in modes of occurrence of sulfide and carbonate minerals within individual test piles.
5. Determine the mineralogical composition of rock used in field tests.
6. Determine the composition of carbonate minerals in field tests.
7. Determine the extent of NP depletion from test piles and tanks.
8. Investigate possible reasons for the large change from 2001 to 2002 in yield coefficients from both test piles and limestone addition tanks.
9. Make estimations to consider flow not included in mass release rate calculations for test piles in 2001.
10. Determine the relationship between field rates of chemical release and flow.
11. Continue the comparison of field and laboratory rates and rates reported in the literature.

7. ACKNOWLEDGMENTS

Funding for the construction of the field test piles was provided by the MN DNR Division of Lands and Minerals. Funding for the remainder of the project was provided by the Minnesota Minerals Coordinating Committee and the Minnesota Environmental Cooperative Research Fund. Paul Wannarka and Dan Hestetune from Soudan Underground State Park, Guy Larson from Lametti and Sons, Lee Peterson and Bob Martin from CNA Consulting Engineers, and Bill Miller from the University of Minnesota provided valuable assistance in obtaining the rock for the field test piles. Rick Ruhanen provided geological expertise on Minnesota greenstone terranes. and provided input on sample selection for the field tests. Doug Rosnau, Mike Lubotina, Pat Geiselman, Al Dzuck, and Tom Anderson assisted in the construction of the field test piles. John Folman conducted laboratory dissolution experiments, with assistance from Anne Jagunich and Patrick Geiselman. Andrea

Johnson, with assistance from Doug Rosnau, was responsible for collection and analyses of field test pile samples. Andrea was also responsible for producing appendix tables and generating tables and figures throughout the report. Sue Backe and Sue Saban provided data input. Lyn Leopold assisted in obtaining silicate mineral dissolution literature.

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Table 1. Particle size distribution of rock used in field test piles (percent passing).

SIZE FRACTION	TEST PILE 1	TEST PILE 2	TEST PILE 3	TEST PILE 4
+ 12"	12.2	8.7	3.0	7.9
- 12" / +6"	10.6	8.9	6.2	6.1
- 6" / +21/2"	21.4	23.3	12.5	11.1
- 21/2" / +3/4"	33.0	32.7	30.9	32.7
-3/4" / +1/4"	11.4	10.5	22.1	19.3
-1/4" / +10 mesh	5.2	6.2	12.1	11.7
-10 / +35 mesh	3.8	6.2	8.4	6.9
-35 / +100 mesh	1.5	2.3	3.1	2.4
-100 / +200 mesh	0.3	0.4	0.7	0.7
-200 mesh	0.5	0.8	1.0	1.2

Note: All size fractions were dry sieved.

Table 2. Sulfur analyses of muck box samples for field test piles 1 – 4 (n = 25). Analyses by Lerch Bros.

TEST PILE 1 MEAN % S = 0.02, SD = 0.019	TEST PILE 2 MEAN % S = 0.20, SD = 0.095	TEST PILE 3 MEAN % S = 0.39, SD = 0.226	TEST PILE 4 MEAN % S = 0.67, SD = 0.223
0.005	0.08	0.20	0.29
0.006	0.10	0.20	0.33
0.01	0.13	0.22	0.42
0.01	0.13	0.23	0.45
0.01	0.13	0.23	0.46
0.01	0.13	0.24	0.47
0.01	0.14	0.24	0.48
0.01	0.18	0.25	0.50
0.01	0.18	0.28	0.56
0.01	0.19	0.29	0.58
0.01	0.20	0.29	0.59
0.01	0.20	0.30	0.64
0.01	0.21	0.32	0.66
0.02	0.21	0.33	0.69
0.02	0.21	0.34	0.74
0.02	0.21	0.36	0.75
0.02	0.22	0.36	0.76
0.02	0.25	0.39	0.77
0.02	0.26	0.41	0.79
0.03	0.32	0.49	0.80
0.03	0.32	0.50	0.94
0.04	0.33	0.51	0.94
0.05	0.37	0.61	1.02
0.07	0.40	0.81	1.04
0.08	0.46	1.47	1.09

Table 3. Average whole rock composition of field test piles. Analyses by ACTLABS.

Sample	0.02% S[1]	0.20% S[1]	0.39% S[1]	0.67% S[1]
%S	0.012	0.222	0.374	0.634
SO_4 as S	0.016	0.025	0.028	0.032
CO_2	0.124	0.239	0.054	0.462
S_iO_2	52.05	60.76	67.92	65.99
Al_2O_3	19.74	14.96	13.01	12.85
Fe_2O_3	11.27	10.10	8.66	10.48
MnO	0.133	0.092	0.073	0.089
MgO	6.35	5.26	3.25	3.38
CaO	0.723	0.765	0.378	0.226
Na_2O	0.402	0.283	0.394	0.203
K_2O	2.54	1.83	1.70	1.90
T_iO_2	0.870	0.667	0.538	0.515
P_2O_5	0.403	0.411	0.257	0.132
LOI	5.80	4.78	3.53	4.02
Total	100.28	99.89	99.78	99.78

1 - Average sulfur content of the 25 muck box samples determined by Lerch Brothers.

Table 4. Average whole rock composition from 25 muck box samples and of the particle size sample from each field test pile. Analyses by ACTLABS.

PARAMETER	Pile 1 (0.02 %S)		Pile 2 (0.20 %S)		Pile 3 (0.39 %S)		Pile 4 (0.67 %S)	
	Average value	Mass weighted average	Average value	Mass weighted average	Average value	Mass weighted average	Average value	Mass weighted average
%S	0.012	0.04	0.222	0.532	0.374	0.363	0.634	0.548
SO_4 as S	0.016	0.043	0.025	0.025	0.028	0.030	0.032	0.051
CO_2	0.124	0.119	0.239	0.255	0.054	0.132	0.462	0.082
S_iO_2	52.05	51.839	60.76	67.010	67.92	68.149	65.99	71.423
Al_2O_3	19.74	19.663	14.96	13.123	13.01	12.004	12.85	11.830
Fe_2O_3	11.27	11.627	10.10	9.205	8.66	8.982	10.48	7.834
MnO	0.133	0.130	0.092	0.081	0.073	0.063	0.089	0.041
MgO	6.35	6.526	5.26	3.198	3.25	3.937	3.38	2.822
CaO	0.723	0.596	0.765	0.591	0.378	0.559	0.226	0.187
Na_2O	0.402	0.491	0.283	0.236	0.394	0.281	0.203	0.222
K_2O	2.54	2.294	1.83	2.010	1.70	1.383	1.90	1.896
T_iO_2	0.870	0.842	0.667	0.483	0.538	0.507	0.515	0.417
P_2O_5	0.403	0.305	0.411	0.201	0.257	0.312	0.132	0.093

NOTE: The mass weighted values do not include the +12" and -12" / + 6" size fractions. These two size fractions were not analyzed.

Table 5. Page 1 of 4. Dissolved oxygen and temperature data for field piles.

Date	0.02% Sulfur (Piles 1) Lower sampling port		
	Temperature (C)	5' DO (%)	10' DO (%)
8/2/00	18.1	22.0	20.4
8/15/00	18.0	16.8	17.3
8/18/00	17.1	19.1	19.1
9/26/00	11.3	15.6	15.7
3/27/01	-0.5	9.6	9.4
6/21/01	11.8	20.2	19.5
7/11/01	14.6	23.5	19.9
7/24/01	18.1	21.0	21.1
8/02/01	17.7	18.6	16.6
8/23/01	16.7	18.2	13.9
9/25/01	13.8	20.5	20.4
10/17/01	11.7	24.2	24.5
5/15/02	0.7	19.1	19.4
7/11/02	17.0	17.2	17.2
8/26/02	15.6	17.4	17.4
Average	12.7	18.9	18.1

Table 5. Page 2 of 4. Dissolved oxygen and temperature data for field piles.

Date	0.20% Sulfur (Pile 2)					
	Lower sampling port			Upper sampling port		
	Temperature (C)	5' DO (%)	10' DO (%)	Temperature (C)	5' DO (%)	10' DO (%)
3/27/01	-0.1	16.9	8.1	-1.6	19.3	19.1
6/21/01	12.4	20.5	20.1	14.4	21.5	20.6
7/11/01	14.7	19.9	19.9	17.6	20.2	19.9
7/24/01	17.4	21.4	21.4	21.4	21.3	21.3
8/02/01	17.1	16.6	16.6	19.0	17.1	16.8
8/23/01	17.4	13.9	18.2	18.6	18.2	18.0
9/25/01	14.4	20.5	20.5	12.9	20.7	20.2
10/17/01	11.5	24.2	24.2	9.2	24.5	24.2
5/12/02	0.9	18.9	19.4	3.0	20.1	18.9
7/11/02	16.8	16.7	17.2	19.9	17.4	16.9
8/26/02	16.4	16.1	15.6	17.8	17.9	17.4
Average	11.9	18.7	18.3	12.8	19.8	19.4

Table 5. Page 3 of 4. Dissolved oxygen and temperature data for field piles.

Date	0.39% Sulfur (Pile 3)					
	Lower sampling port			Upper sampling port		
	Temperature (C)	5' DO (%)	10' DO (%)	Temperature (C)	5' DO (%)	10' DO (%)
9/26/00	14.6	8.8	16.5	12.2	16.4	13.6
3/27/01	-0.1	6.7	NA[1]	-1.6	12.0	11.8
6/21/01	12.8	16.9	19.2	14.5	20.8	20.2
7/11/01	15.1	20.2	20.1	17.6	20.4	20.5
7/24/01	17.7	21.7	21.9	21.4	21.6	21.7
8/02/01	17.6	15.3	16.8	19.3	19.4	18.4
8/23/01	17.8	NA[2]	NA[2]	18.8	18.2	22.2
9/25/01	15.1	NA[2]	20.9	12.9	20.7	20.5
10/17/01	11.8	NA[2]	24.5	9.2	25.2	25.5
5/15/02	1.7	NA[2]	19.4	3.2	20.1	19.4
7/11/02	17.0	NA[2]	18.2	19.8	19.2	19.4
8/26/02	16.8	NA[2]	17.9	18.2	18.2	17.9
Average	13.2	14.9	19.5	13.8	19.4	19.3

[1] Oxygen not sampled due to water in tubing.
[2] Oxygen not sampled due to obstructed tubing.

Table 5. Page 4 of 4. Dissolved oxygen and temperature data for field piles.

Date	0.67% Sulfur (Pile 4)					
	Lower sampling port			Upper sampling port		
	Temperature (C)	5' DO (%)	10' DO (%)	Temperature (C)	5' DO (%)	10' DO (%)
8/2/00	19.6	20.5	20.9	23.9	19.7	19.6
8/15/00	18.7	8.5	15.2	21.2	15.7	15.5
8/18/00	18.2	16.9	19.1	19.8	19.2	22.8
9/26/00	14.5	9.0	17.3	11.5	16.2	15.3
3/27/01	-0.1	10.3	8.6	-2.2	9.0	9.8
6/21/01	13.1	16.7	NA[1]	15.5	22.0	21.2
7/11/01	15.6	19.4	18.8	20.0	19.7	19.4
7/24/01	18.4	20.5	20.5	23.2	21.3	20.8
8/02/01	17.9	15.6	15.6	20.6	16.6	16.6
8/23/01	18.0	NA[2]	21.1	20.0	22.2	22.2
9/25/01	15.1	NA[2]	20.2	12.8	20.2	20.2
10/17/01	11.7	NA[2]	22.9	8.5	24.0	15.6
5/15/02	2.7	NA[2]	20.1	4.4	20.4	20.6
7/11/02	17.5	NA[2]	18.9	20.7	19.4	19.2
8/26/02	16.9	NA[2]	19.0	19.1	19.0	19.0
Average	14.5	15.3	18.4	15.3	19.0	18.5

[1] Oxygen not sampled due to water in tubing.
[2] Oxygen not sampled due to obstructed tubing.

Table 6. 2000, 2001, and 2002 total input and output flow volumes in liters and yield coefficients for prediction piles.

Pile	INPUT FLOW VOLUME	OUTPUT FLOW VOLUME	YIELD COEFFICIENT
2000			
1	11,392	7,029	NA
2	5,254	3,808	NA
3	6,617	3,660	NA
4	11,534	7,021	NA
2001			
1	24,023	20,383	85 %
2	24,023	20,029	83 %
3	24,023	17,486	73 %
4	24,023	19,606	81 %
2002			
1	25963	16337	63%
2	25963	15772	61%
3	25963	13237	51%
4	25963	17360	67%

Table 7. Page 1 of 5. Sulfate, calcium, magnesium, sodium, and potassium release rates from greenstone prediction field piles (μmol (kg rock week)$^{-1}$).

Sulfate Release 2001					
Date	Weeks	0.02% S	0.20% S	0.39% S	0.67% S
4/25/01	4	2.95	13.8	6.10	15.5
5/10/01	2	4.83	11.1	4.81	14.2
5/23/01	2	3.67	9.73	5.88	18.3
6/15/01	3	3.00	14.7	9.62	19.4
8/02/01	7	0.858	4.38	2.92	4.31
8/20/01	2	2.29	20.1	7.26	12.9
9/12/01	3	0.430	5.02	1.39	2.63
10/11/01	4	3.01	10.5	9.95	17.7
10/30/01	2	2.11	7.45	12.7	23.2
11/28/01	4	1.12	3.45	5.71	10.8
Average rate		2.43	10.0	6.64	13.9
Lab[1]	60-100	4.46	66.6[2]	120[2]	98.3
Retardation Factor[4]		0.545	0.150	0.055	0.141
Sulfate Release 2002					
4/28/02	2	1.52	4.08	7.98	13.3
6/4/02	6	0.485	1.63	1.96	3.99
6/24/02	3	4.63	17.3	21.0	55.1
7/8/02	2	1.98	11.1	12.9	22.8
7/29/02	3	1.18	4.04	6.11	12.5
8/13/02	2	3.66	18.2	25.8	44.6
9/3/02	3	1.89	5.61	13.0	25.9
9/19/02	2	1.17	3.60	6.31	12.9
10/7/02	3	1.41	5.98	11.3	20.6
10/28/02	3	0.481	0.896	5.49	10.2
Average rate		1.84	7.24	11.2	22.2
Lab[1]	100-154	3.94	58.4[3]	111[3]	89.9
Retardation Factor[4]		0.467	0.124	0.101	0.247

[1] Data from laboratory reactors with 0.04%, 0.20%, 0.39% and 0.72% sulfur.

[2] Median pH values for 0.20% S and 0.39%S rock for weeks 60-100 were 4.15 and 3.97.

[3] Median pH values for 0.20% S and 0.39%S rock for weeks 100-154 were 4.09 and 3.91

[4] Field rate/lab rate.

Table 7. Page 2 of 5. Sulfate, calcium, magnesium, sodium, and potassium release rates from greenstone prediction field piles (μmol (kg rock week)$^{-1}$).

Calcium Release 2001					
Date	Weeks	0.02% S	0.20% S	0.39% S	0.67% S
4/25/01	4	13.8	46.3	31.7	28.7
5/10/01	2	21.9	36.4	24.9	23.7
5/23/01	2	8.71	28.7	23.2	27.6
6/15/01	3	6.95	37.0	29.1	29.4
8/02/01	7	2.12	11.8	5.07	5.68
8/20/01	2	5.64	49.7	12.8	14.9
9/12/01	3	1.07	11.3	2.38	3.01
10/11/01	4	7.30	24.5	14.9	20.2
10/30/01	2	5.02	14.7	17.3	25.7
11/28/01	4	2.43	7.06	7.49	11.9
Average rate		7.50	26.7	16.9	19.1
Lab[1]	60-100	6.79	3.32	16.1	16.8
Retardation Factor[2]		1.10	8.04	1.05	1.14
Calcium Release 2002					
4/28/02	2	3.84	7.87	10.8	13.9
6/4/02	6	1.41	2.67	2.63	4.33
6/24/02	3	10.4	34.8	26.6	57.1
7/8/02	2	3.88	17.1	14.2	23.4
7/29/02	3	2.85	8.15	7.90	13.5
8/13/02	2	8.19	29.2	26.6	44.5
9/3/02	3	3.90	10.2	14.0	26.6
9/19/02	2	2.97	6.31	6.39	13.0
10/7/02	3	3.22	10.4	12.2	20.4
10/28/02	3	1.38	1.34	5.86	10.2
Average rate		4.21	12.8	12.7	22.7
Lab[1]	100-154	4.98	2.51	12.7	20.5
Retardation Factor[2]		0.845	5.10	1.00	1.11

[1] Data from lab reactors with 0.04%, 0.20%, 0.39% and 0.72% sulfur.

[2] Field rate/lab rate.

Table 7. Page 3 of 5. Sulfate, calcium, magnesium, sodium, and potassium release rates from greenstone prediction field piles (μmol (kg rock week)$^{-1}$).

Magnesium Release 2001					
Date	Weeks	0.02% S	0.20% S	0.39% S	0.67% S
4/25/01	4	3.13	8.38	6.57	3.89
5/10/01	2	4.85	6.26	4.87	3.56
5/23/01	2	2.12	4.65	4.27	3.64
6/15/01	3	1.30	4.88	4.85	3.34
8/02/01	7	0.397	1.69	0.873	0.696
8/20/01	2	1.19	7.43	2.38	1.96
9/12/01	3	0.223	1.71	0.438	0.398
10/11/01	4	1.70	4.08	3.08	2.93
10/30/01	2	1.05	2.21	3.27	3.42
11/28/01	4	0.580	1.15	1.51	1.65
Average rate		1.67	4.24	3.21	2.55
Lab[1]	60-100	9.68	6.83	18.0	241
Retardation Factor[2]		0.173	0.621	0.178	0.011
Magnesium Release 2002					
4/28/02	2	0.769	1.16	1.76	1.74
6/4/02	6	0.285	0.455	0.451	0.529
6/24/02	3	1.96	4.99	4.26	6.45
7/8/02	2	0.726	2.59	2.33	2.72
7/29/02	3	0.499	1.08	1.21	1.45
8/13/02	2	1.43	3.90	4.09	4.90
9/3/02	3	0.668	1.31	2.18	2.87
9/19/02	2	0.491	0.831	0.952	1.41
10/7/02	3	0.568	1.40	1.95	2.24
10/28/02	3	0.248	0.230	0.938	1.06
Average rate		0.764	1.79	2.01	2.54
Lab[1]	100-154	7.73	7.72	13.9	321
Retardation Factor[2]		0.099	0.232	0.145	0.008

[1] Data from lab reactors with 0.04%, 0.20%, 0.39% and 0.72% sulfur.
[2] Field rate/lab rate.

Table 7. Page 4 of 5. Sulfate, calcium, magnesium, sodium, and potassium release rates from greenstone prediction field piles (μmol (kg rock week)$^{-1}$).

Sodium Release 2001					
Date	Weeks	0.02% S	0.20% S	0.39% S	0.67% S
4/25/01	4	32.0	30.9	33.8	22.6
5/10/01	2	66.6	29.5	32.6	16.9
5/23/01	2	42.1	30.3	32.2	22.0
6/15/01	3	38.9	32.1	26.0	17.0
8/02/01	7	8.31	7.01	3.44	2.30
8/20/01	2	19.0	31.4	8.46	5.12
9/12/01	3	3.17	6.93	1.37	0.863
10/11/01	4	18.1	13.4	6.81	4.72
10/30/01	2	13.9	7.55	6.55	4.38
11/28/01	4	5.96	3.43	2.64	1.97
Average rate		24.8	19.3	15.4	9.78
Lab[1]	60-100	0.728	0.837	0.887	0.622
Retardation Factor[2]		34.1	23.1	17.4	15.7
Sodium Release 2002					
4/28/02	2	9.94	3.53	3.83	2.51
6/4/02	6	3.20	1.24	0.964	0.703
6/24/02	3	29.5	18.8	10.3	10.4
7/8/02	2	14.7	10.3	5.53	3.67
7/29/02	3	7.70	4.12	2.62	1.91
8/13/02	2	24.4	14.7	8.04	5.85
9/3/02	3	10.5	4.92	3.47	2.63
9/19/02	2	6.38	2.58	1.35	1.47
10/7/02	3	6.28	3.90	2.23	1.66
10/28/02	3	2.88	0.554	1.10	0.792
Average rate		11.6	6.47	3.94	3.16
Lab[1]	100-154	0.583	0.857	0.894	0.915
Retardation Factor [2]		19.9	7.55	4.41	3.45

[1] Data from lab reactors with 0.04%, 0.20%, 0.39% and 0.72% sulfur.

[2] Field rate/lab rate.

Table 7. Page 5 of 5. Sulfate, calcium, magnesium, sodium, and potassium release rates from greenstone prediction field piles (μmol (kg rock week)$^{-1}$).

Potassium Release 2001					
Date	Weeks	0.02% S	0.20% S	0.39% S	0.67% S
4/25/01	4	2.42	3.81	4.53	2.36
5/10/01	2	3.89	3.78	3.82	2.98
5/23/01	2	3.35	4.50	4.64	4.85
6/15/01	3	3.18	5.10	5.10	5.30
8/02/01	7	0.933	1.42	0.956	1.09
8/20/01	2	1.83	5.73	2.24	2.44
9/12/01	3	0.341	1.58	0.397	0.457
10/11/01	4	1.89	2.55	2.06	2.32
10/30/01	2	1.25	1.59	2.02	2.37
11/28/01	4	0.826	0.694	0.824	0.997
Average rate		1.99	3.08	2.66	2.52
Lab[1]	60-100	12.4	3.35	4.51	3.67
Retardation Factor [2]		0.160	0.919	0.590	0.687
Potassium Release 2002					
4/28/02	2	0.902	0.920	1.13	1.12
6/4/02	6	0.325	0.335	0.319	0.349
6/24/02	3	3.58	4.82	4.06	5.97
7/8/02	2	2.15	3.13	2.60	3.22
7/29/02	3	1.42	1.34	1.35	1.70
8/13/02	2	3.05	4.77	4.07	5.00
9/3/02	3	1.59	1.84	2.17	2.68
9/19/02	2	1.36	1.10	1.46	1.37
10/7/02	3	0.955	1.33	1.26	1.51
10/28/02	3	0.802	0.194	0.597	0.706
Average rate		1.61	1.98	1.90	2.36
Lab[1]	100-154	8.31	2.25	3.19	2.81
Retardation Factor [2]		0.194	0.880	0.596	0.840

[1] Data from lab reactors with 0.04%, 0.20%, 0.39% and 0.72% sulfur.
[2] Field rate/lab rate.

Table 8. Ratio of drainage volumes[1] and chemical releases in 2002 to those in 2001. The drainage volume in 2002 approximated that in 2001. Rates of chemical release in 2002 were typically lower than those in 2001, reflecting decreasing concentrations in the drainage. Rates of sulfate release from the two piles of highest sulfur content increased from 2001 to 2002. This may indicate that acid conditions may be developing in some areas of these two piles.

Pile, Pct S	Drainage Volume[1]	SO_4	Ca	Mg	Na	K
0.02	0.99	0.76	0.56	0.46	0.47	0.81
0.20	1.01	0.72	0.48	0.42	0.34	0.64
0.39	0.96	1.69	0.75	0.63	0.26	0.71
0.67	1.06	1.60	1.18	1.00	0.32	0.94

[1] The drainage volume used for 2001 was that used to determine mass release rates. The actual drainage volume from the piles was approximately 20 to 30 percent higher than this value. This discrepancy will be rectified in the next report.

Table 9. Particle size distribution for rock and limestone used in field limestone addition tanks (percent passing). Analysis by Lerch Brothers, Inc.

FRACTION	Tank 1	Tank 2	Tank 3	Tank 4	Tank 5	Tank 6	Limestone
2"	100.0	100.0	100.0	100.0	100.0	100.0	100.0
1 ½"	97.1	97.3	91.3	90.1	88.9	95.3	100.0
1"	68.2	77.4	80.2	72.6	77.5	82.4	100.0
1/2"	43.3	40.5	53.2	52.4	61.7	54.8	100.0
1/4"	31.5	27.2	37.5	36.2	43.8	42.0	100.0
4M	27.1	22.9	32.4	31.1	37.8	37.8	100.0
10M	16.7	14.2	19.6	18.7	23.1	25.3	87.9
20M	12.6	10.8	14.4	13.6	16.9	19.5	57.1
28M	10.8	9.3	12.0	11.4	14.1	17.0	41.8
35M	9.5	8.2	10.2	9.9	12.1	15.3	30.2
48M	7.8	6.7	6.9	7.9	9.6	13.3	18.5
65M	6.2	5.5	5.1	6.3	7.6	11.6	9.0
100M	5.4	4.6	4.7	5.2	6.3	10.4	4.5
200M	3.4	2.8	2.5	3.1	3.7	8.2	1.4

NOTE: All samples were dry screened with the exception of Tank 6 which was wet screened for comparison.

Table 10. Whole rock chemistry (percent) of field limestone addition tanks. Analyses by ACTLABS, Inc.

Parameter	Tank 1	Tank 2	Tank 3	Tank 4	Tank 5	Tank 6	Limestone
S	0.56	0.40	0.50	0.46	0.55	0.48	0.01
S^{2-} [2]	0.54	0.34	0.48	0.44	0.53	0.46	0
SO_4^{2-} as S	0.016	0.06	0.02	0.016	0.02	0.02	0.016
CO_2	0.40	0.37	0.22	0.44	0.44	0.48	41.56[3]
Al_2O_3	13.86	13.09	12.53	13.12	13.28	13.00	0.47
CaO	0.41	0.37	0.26	0.46	0.32	0.43	27.63
Fe_2O_3	10.65	8.83	8.61	9.38	10.30	9.31	0.87
K_2O	1.86	2.03	1.95	1.91	1.85	2.09	0.29
MgO	3.59	2.96	2.91	3.26	3.41	2.89	18.82
MnO	0.068	0.065	0.053	0.089	0.065	0.059	0.081
Na_2O	0.36	0.38	0.30	0.39	0.34	0.38	<0.01
P_2O_5	0.15	0.12	0.10	0.12	0.13	0.21	0.03
SiO_2	64.70	68.40	69.30	65.96	65.38	67.32	9.68
TiO_2	0.587	0.458	0.452	0.522	0.519	0.514	0.026
LOI	4.19	3.73	3.62	3.89	4.02	3.72	41.95
TOTAL[2]	100.42	100.44	100.08	99.11	99.60	99.92	99.78

1 - Determined by difference. Less than values are assumed to be 0.

2 - For parameters from Al_2O_3 through LOI2.

3 - Analysis by Lerch Brothers Inc. and determined by LOI.

Table 11. 2001 and 2002 total input and output flow volumes in liters and yield coefficients for limestone tanks.

TANK	RATIO	INPUT FLOW VOLUME	OUTPUT FLOW VOLUME	YIELD COEFFICIENT
2001				
1	Control	649	635	98 %
6	Control	649	558	86 %
2	1:1	649	599	92 %
5	1:1	649	570	88 %
3	3:1	649	554	85 %
4	3:1	649	555	86 %
2002				
1	Control	737	371	50%
6	Control	737	387	53%
2	1:1	737	375	51%
5	1:1	737	363	49%
3	3:1	737	357	48%
4	3:1	737	363	49%

Note: Due to a heavy rainfall on 6/23/02, flow volumes for 6/24/02 were estimated based on the total flow and precipitation for the field season and the rainfall for the heavy rain event.

Table 12. Page 1 of 3. Sulfate, calcium and magnesium release rates (μmol(kg rock week)$^{-1}$) from limestone tanks.

Date	Week	Sulfate Release					
		Control Tank 1	Control Tank 6	1:1 Ratio Tank 2	1:1 Ratio Tank 5	3:1 Ratio Tank 3	3:1 ratio Tank 4
4/25/01	4	21.3	16.3	15.8	15.2	19.0	15.5
5/10/01	2	17.3	8.52	8.02	8.87	7.24	8.01
5/23/01	2	34.1	35.6	29.8	43.3	36.4	33.2
6/15/01	3	51.5	36.0	32.3	44.8	41.8	33.9
8/02/01	7	9.61	6.47	9.77	13.7	13.1	7.11
8/20/01	2	32.1	32.8	28.0	36.5	39.3	32.8
9/12/01	3	9.75	9.72	4.99	9.31	9.10	9.40
9/28/01	2	30.9	30.5	26.7	36.9	35.8	28.4
10/11/01	2	63.5	57.0	45.6	66.5	63.0	51.4
10/30/01	2	43.9	28.2	20.6	39.8	39.3	36.5
11/26/01	4	44.8	151	20.2	32.1	32.7	26.7
4/10/02	1	54.4	24.6	60.3	66.4	54.1	74.6
5/10/02	4	16.4	18.4	10.9	12.3	15.4	8.32
6/4/02	4	6.84	6.92	3.69	5.74	4.64	6.21
6/24/02	3	112	203	76.6	105	99.3	88.9
7/8/02	2	44.8	28.7	30.8	34.2	30.7	33.4
7/29/02	3	19.1	32.5	13.0	18.5	15.6	17.0
8/12/02	2	92.6	43.8	59.7	81.8	49.3	64.3
9/19/02	5	48.0	39.4	31.7	44.2	39.1	28.7
10/28/20	6	22.5	1.85	11.2	15.5	15.8	14.4
Average Rate		38.7	40.6	27.0	36.6	33.0	30.9

Table 12. Page 2 of 3. Sulfate, calcium and magnesium release rates (μmol(kg rock week)$^{-1}$) from limestone tanks.

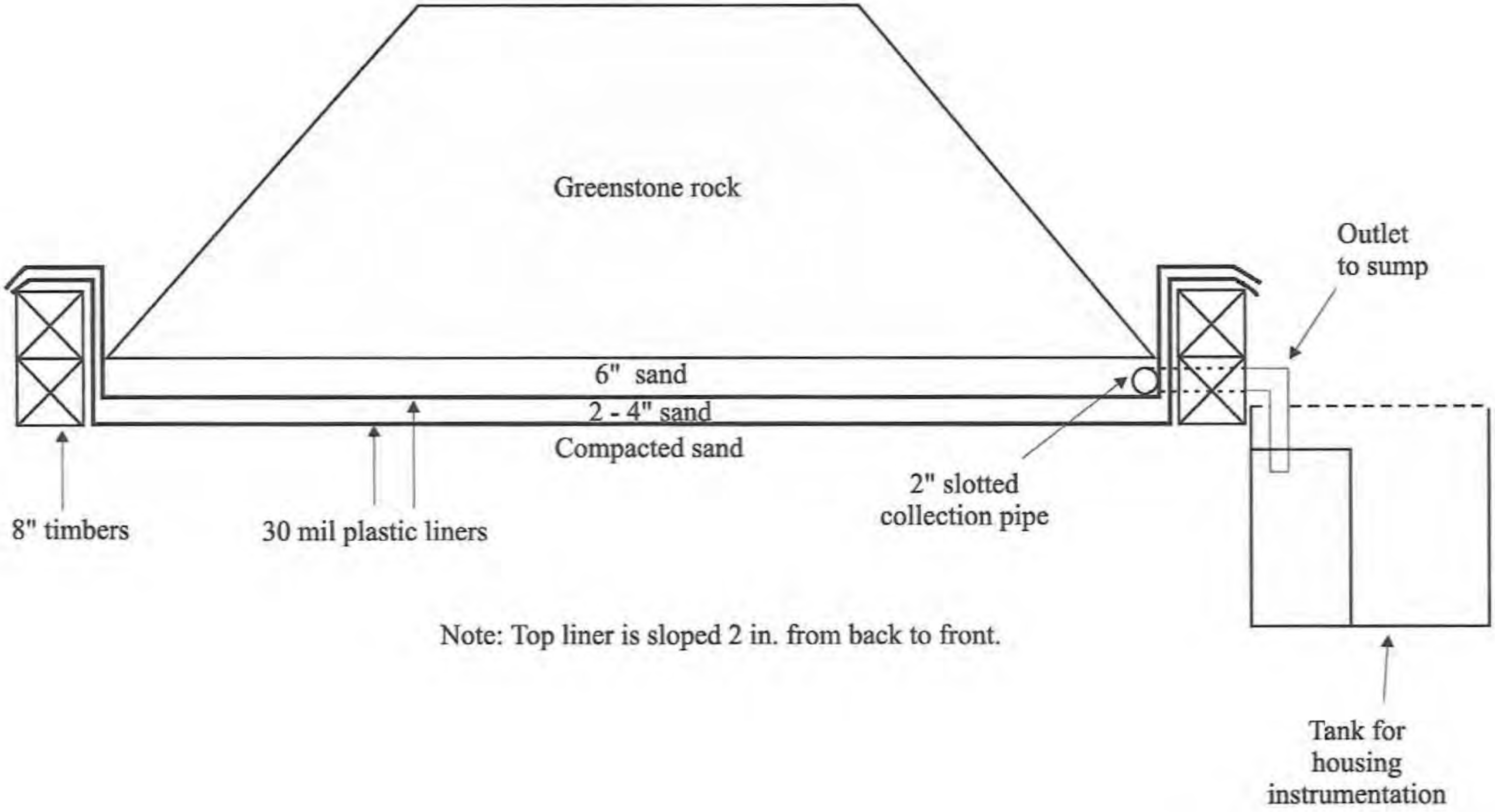
Date	Week	Calcium Release					
		Control Tank 1	Control Tank 6	1:1 Ratio Tank 2	1:1 Ratio Tank 5	3:1 Ratio Tank 3	3:1 ratio Tank 4
4/25/01	4	65.1	34.9	42.5	40.2	42.9	43.2
5/10/01	2	37.5	12.9	19.9	21.5	12.4	15.9
5/23/01	2	62.7	50.0	47.4	54.8	50.0	52.0
6/15/01	3	57.4	42.3	42.7	55.0	53.2	45.2
8/02/01	7	12.2	8.40	12.0	17.9	14.3	8.67
8/20/01	2	32.3	33.9	29.0	42.9	42.7	34.7
9/12/01	3	10.4	9.75	5.53	9.00	9.17	9.50
9/28/01	2	32.5	28.9	27.4	37.0	36.1	27.6
10/11/01	2	62.3	53.4	49.7	66.3	63.8	49.7
10/30/01	2	43.2	25.7	25.3	38.5	38.5	34.3
11/26/01	4	43.9	142	20.9	31.8	33.0	25.7
4/10/02	1	53.6	23.0	66.9	69.9	61.4	83.4
5/10/02	4	16.5	18.0	11.6	12.8	15.8	8.65
6/4/02	4	5.89	6.67	3.23	5.43	4.30	5.51
6/24/02	3	114	188	88.8	115	110	94.0
7/8/02	2	43.2	27.0	34.2	36.1	34.4	34.1
7/29/02	3	18.6	30.2	13.4	20.0	17.0	17.8
8/12/02	2	89.6	40.9	66.2	83.3	52.8	68.7
9/19/02	5	45.8	39.3	34.6	44.9	40.6	29.0
10/28/02	6	20.6	1.71	11.4	15.6	16.4	15.1
Average Rate		43.4	40.8	32.6	40.9	37.4	35.1

Table 12. Page 3 of 3. Sulfate, calcium and magnesium release rates (μmol(kg rock week)$^{-1}$) from limestone tanks.

Date	Week	Magnesium Release					
		Control Tank 1	Control Tank 6	1:1 Ratio Tank 2	1:1 Ratio Tank 5	3:1 Ratio Tank 3	3:1 ratio Tank 4
4/25/01	4	10.4	6.27	7.77	7.17	8.30	8.51
5/10/01	2	6.52	2.12	3.60	3.85	2.44	3.13
5/23/01	2	9.74	8.17	7.89	9.04	9.29	10.1
6/15/01	3	8.60	6.41	7.03	8.41	9.08	7.88
8/02/01	7	1.69	1.27	2.01	2.77	2.73	1.59
8/20/01	2	4.40	4.97	4.95	6.21	7.73	6.40
9/12/01	3	1.50	1.49	0.954	1.44	1.74	1.81
9/28/01	2	4.78	4.65	4.97	5.87	7.33	5.71
10/11/01	2	9.45	8.69	9.18	10.5	12.9	10.3
10/30/01	2	6.61	4.40	4.61	6.49	8.38	7.36
11/26/01	4	6.91	24.5	4.19	5.38	7.05	5.51
4/10/02	1	7.82	4.14	12.3	11.9	12.4	17.9
5/10/02	4	2.62	3.03	2.40	2.12	3.56	1.84
6/4/02	4	0.972	1.16	0.68	0.934	0.994	1.22
6/24/02	3	18.0	31.0	16.6	18.6	22.8	19.9
7/8/02	2	7.02	4.52	7.08	6.28	7.56	7.51
7/29/02	3	3.42	5.77	3.27	3.78	4.19	4.40
8/12/02	2	16.1	8.36	16.2	16.6	13.0	17.3
9/19/02	5	8.56	6.88	7.74	8.05	9.35	6.54
10/28/02	6	3.97	0.363	2.78	3.15	4.08	3.61
Average Rate		6.96	6.91	6.31	6.93	7.75	7.42

Figure 1. Bin construction.

Figure 2. Side view of bin construction for greenstone field experiment.



Note: Top liner is sloped 2 in. from back to front.

Figure 3. Leachate collection system for greenstone field experiment.

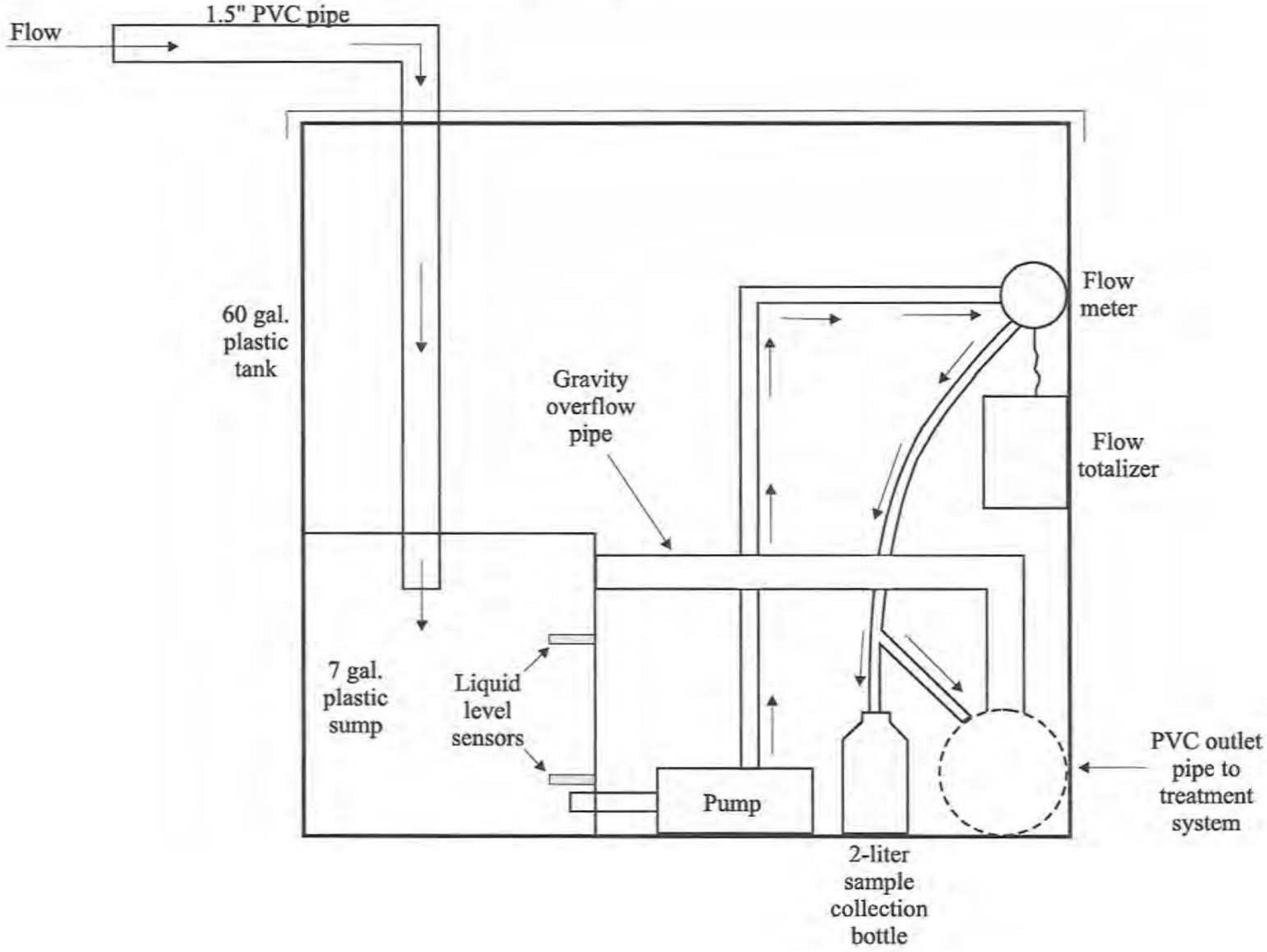


Figure 4. Leachate collection system.

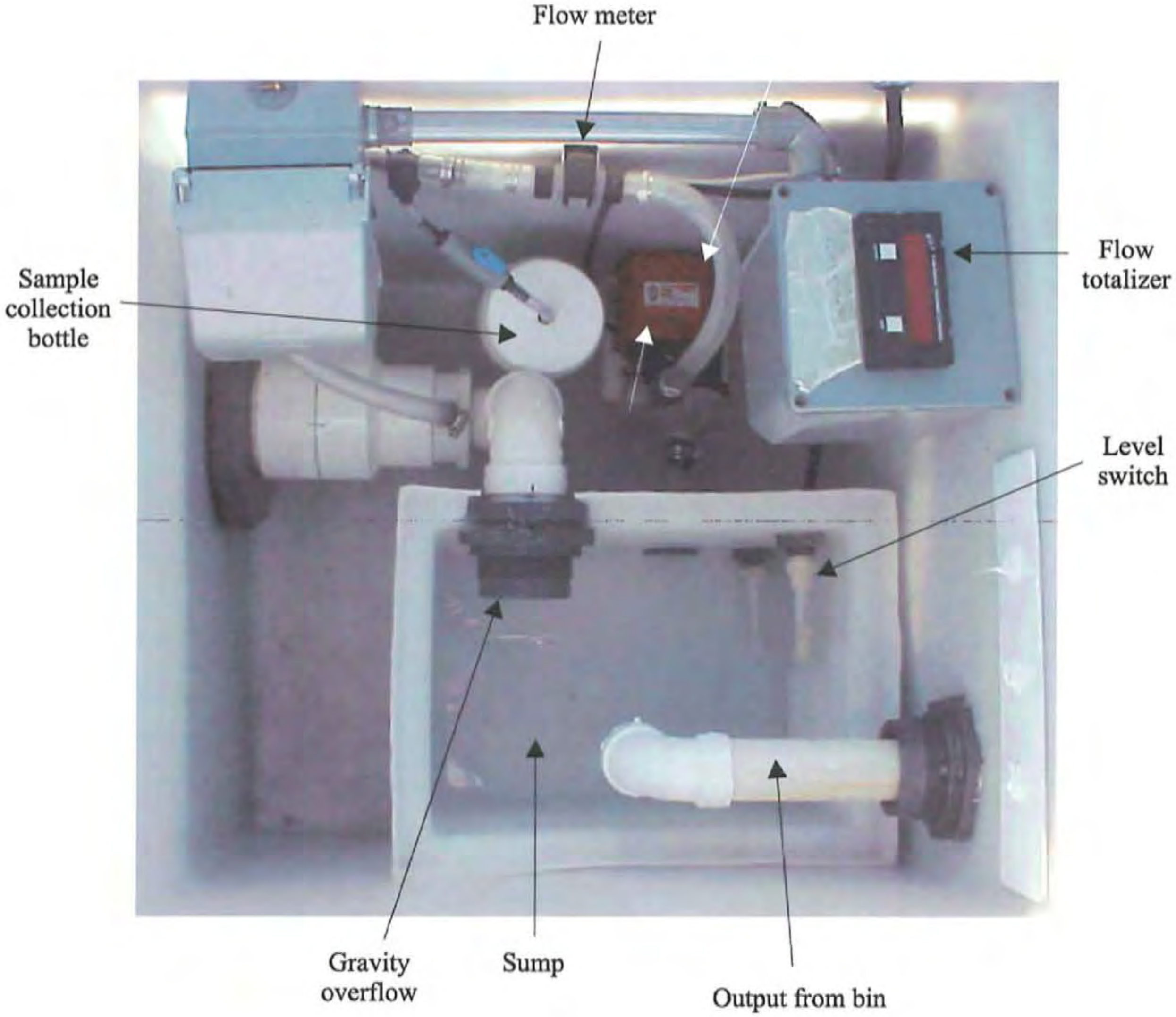
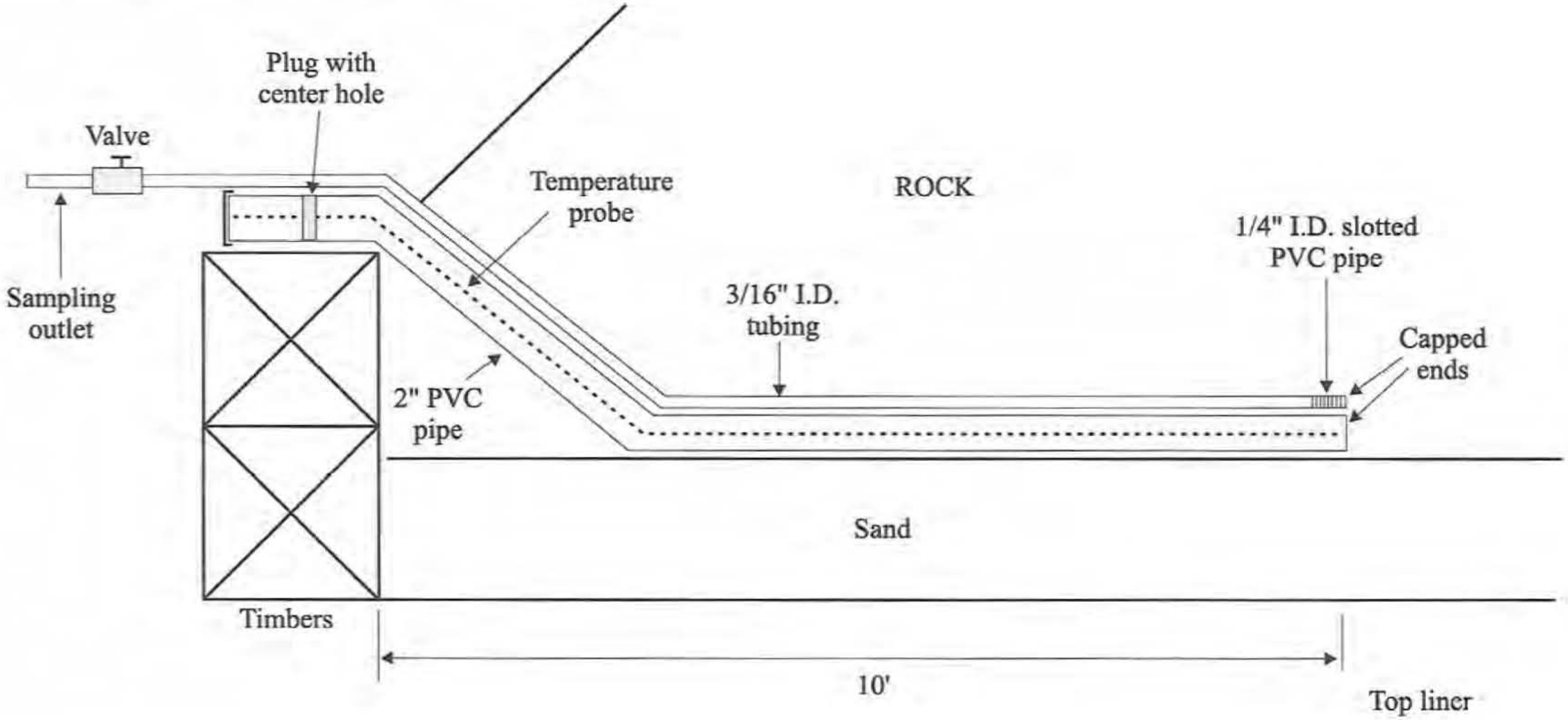


Figure 5. Temperature and oxygen sampling setup.



Note: Not illustrated is a second oxygen sampling port that extends 5 feet into the pile.

Figure 6. Initial rock addition and oxygen sampling setup.

Figure 7. Photograph of test pile construction.

Figure 8. Rock pile design for greenstone field experiment (not to scale).

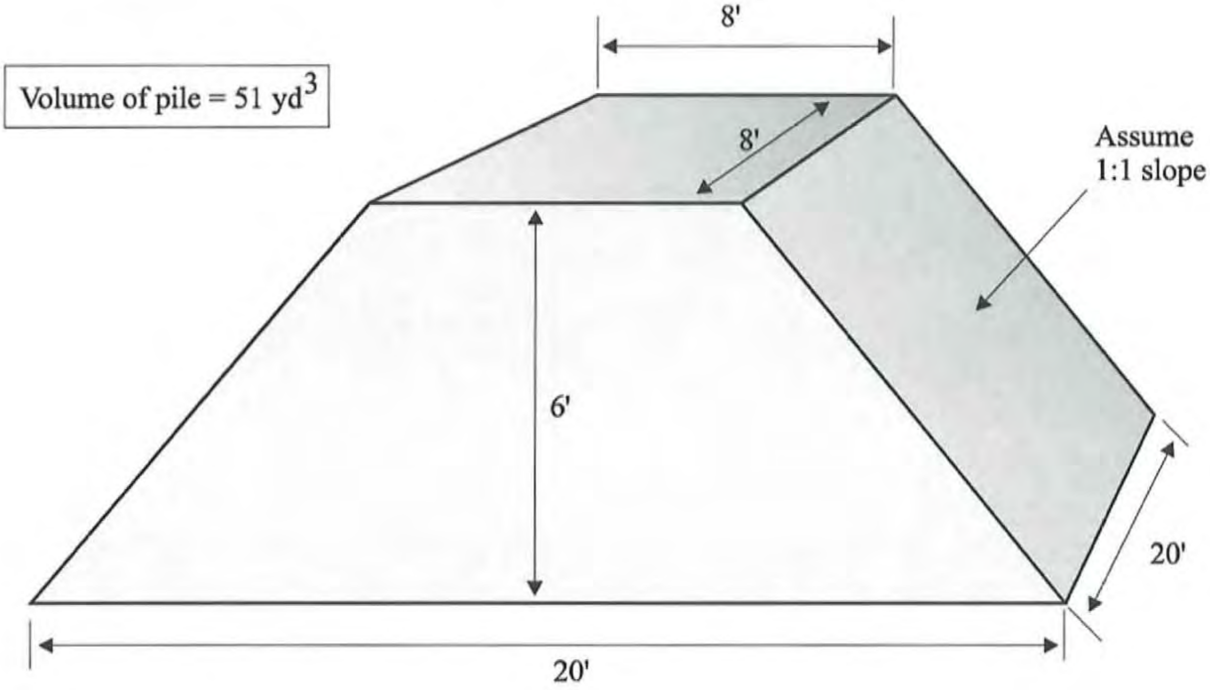


Figure 9. Temperature and oxygen sampling design (not to scale).

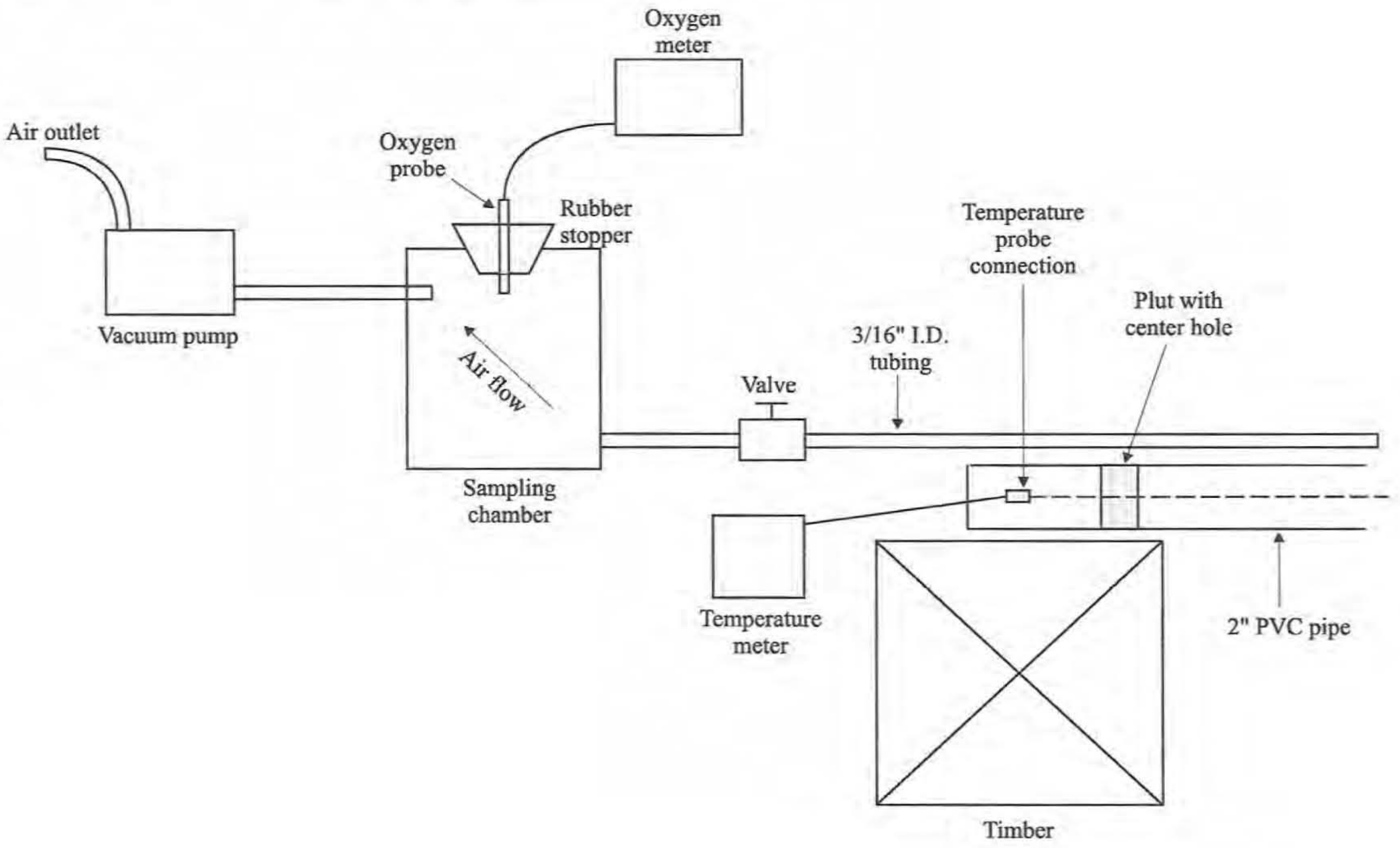


Figure 10. Greenstone rock used for the limestone addition experiment.

Figure 11. Rock in tank, 2001.

Figure 12. Adding rock and limestone to tanks. The material was scooped from the bucket into the tank.

Figure 13. Limestone used for the alkaline mixture experiment. The limestone product was purchased from Agrrerate Resources' Larson Mine on Grey Cloud Island and is called a manufactured sand

Figure 14. Adding limestone to the loader bucket. Limestone was added to the top and distributed over the material.

Figure 15. Limestone in loader after addition.

Figure 16. Limestone addition tanks set up with double containment.

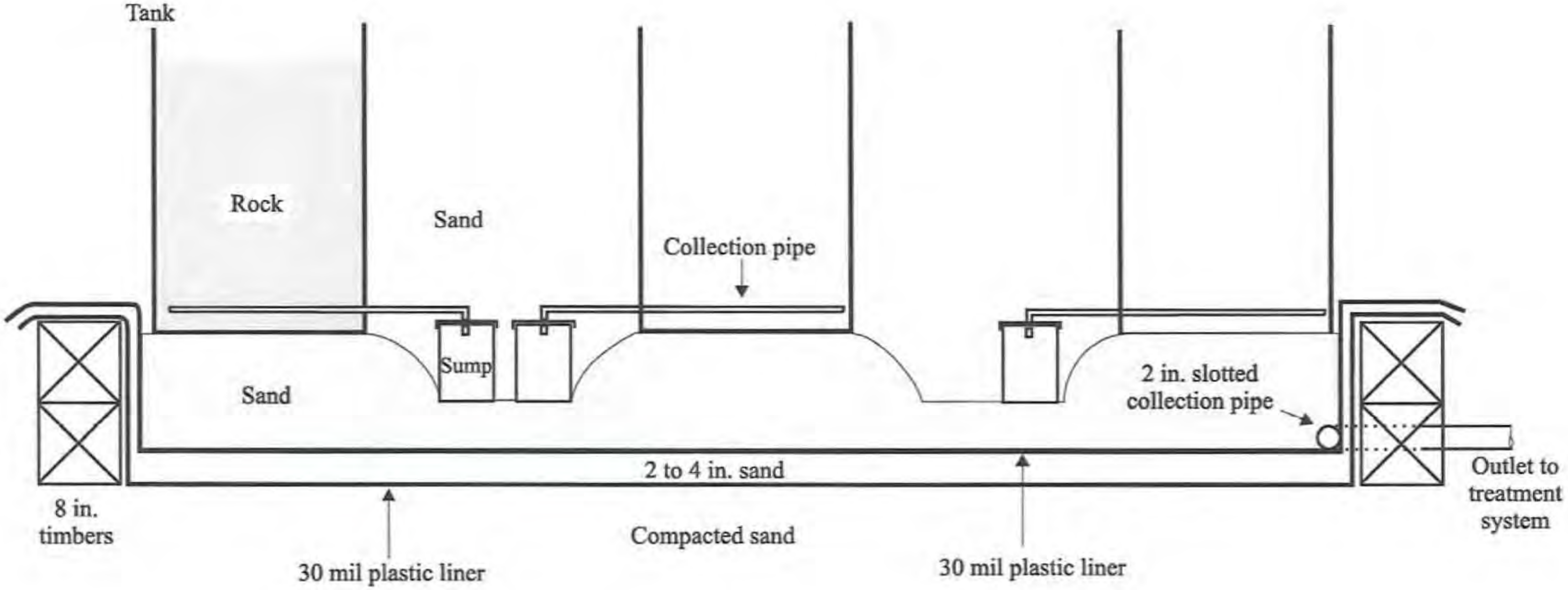


Figure 17. Alkaline mixture, experimental setup, 2001.

Figure 18. Details of limestone addition tank setup.

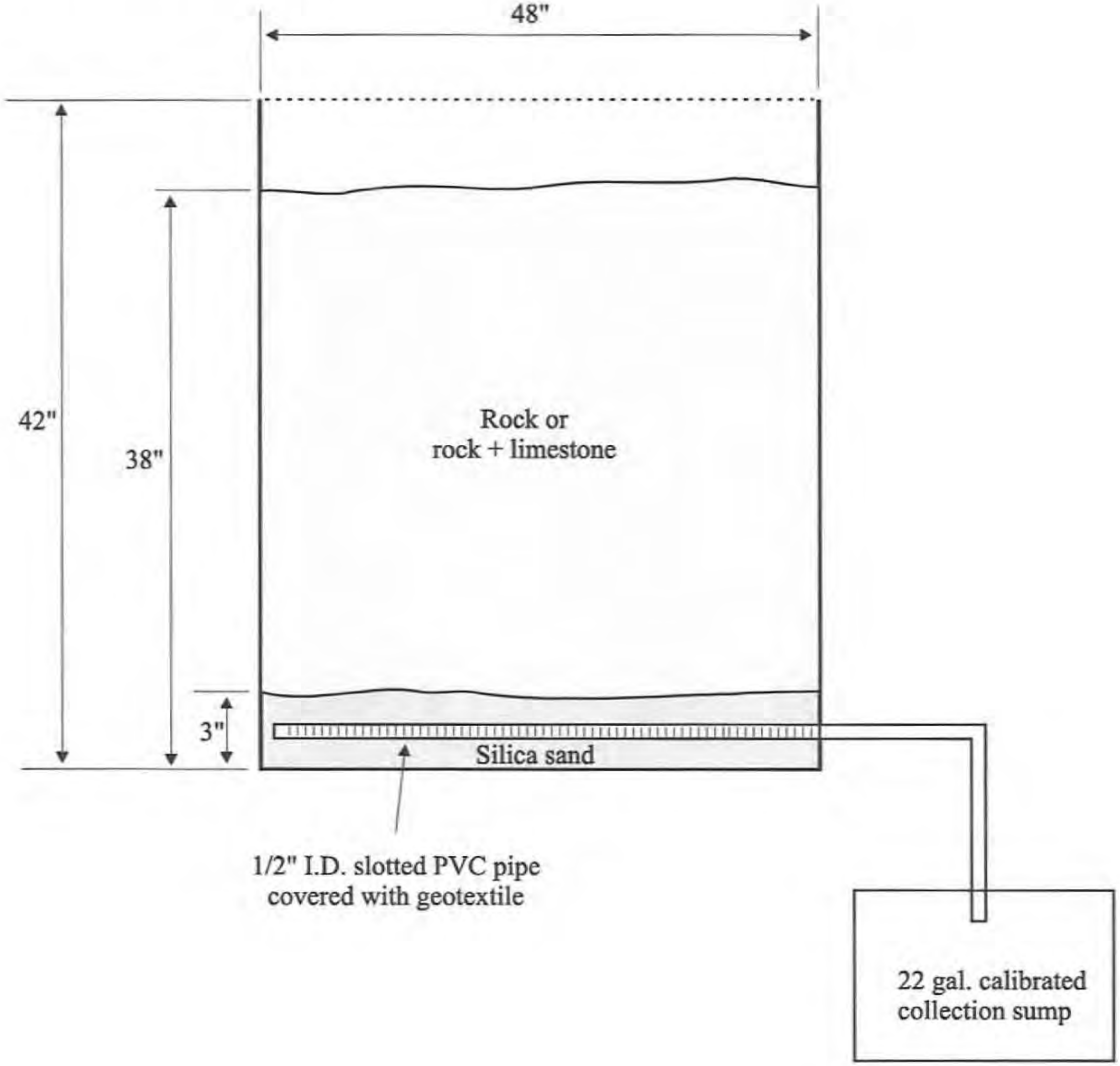


Figure 19. Drainage quality vs. time for the 0.02% S prediction field pile 1.

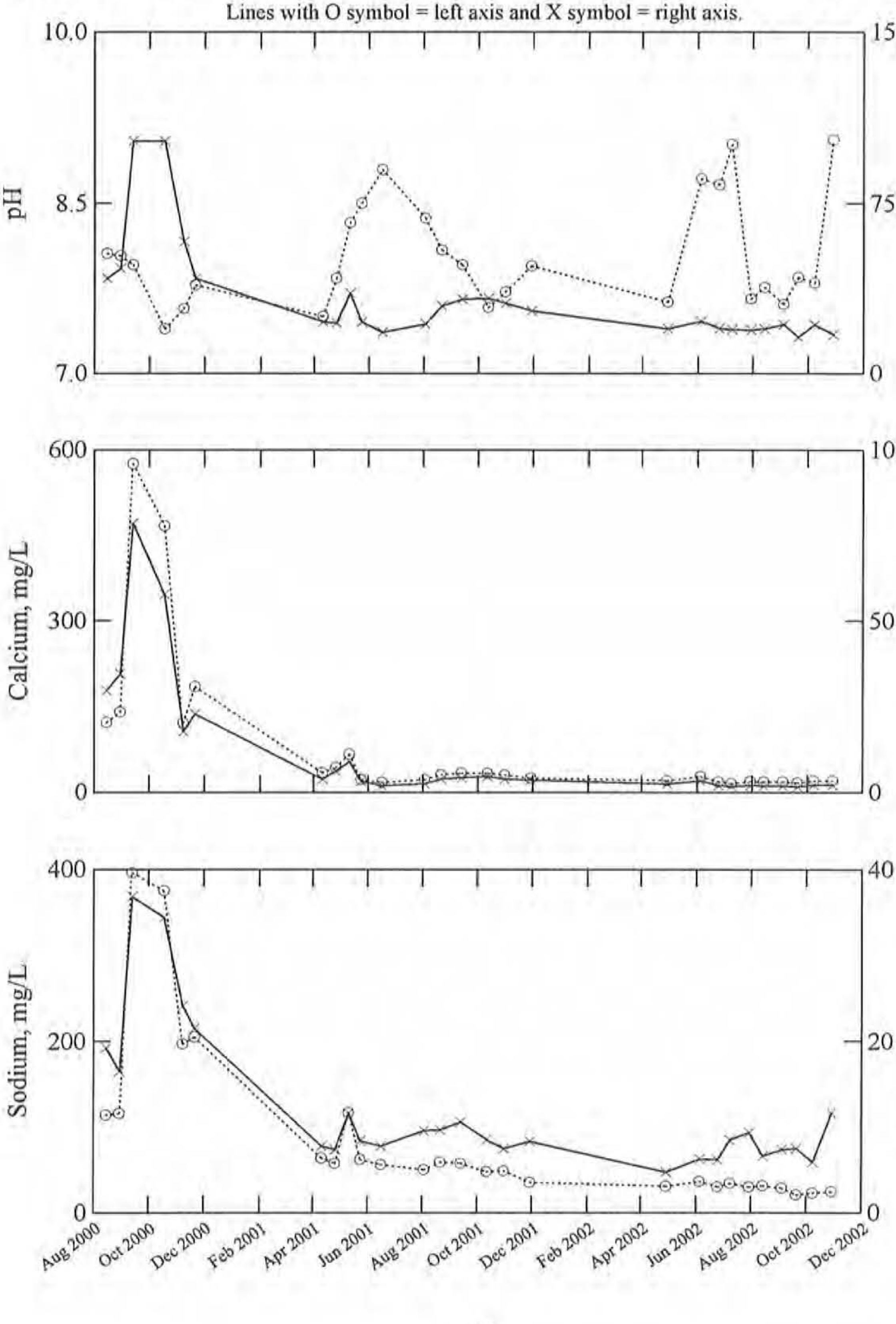


Figure 20. Drainage quality vs. time for the 0.20% S prediction field pile 2.

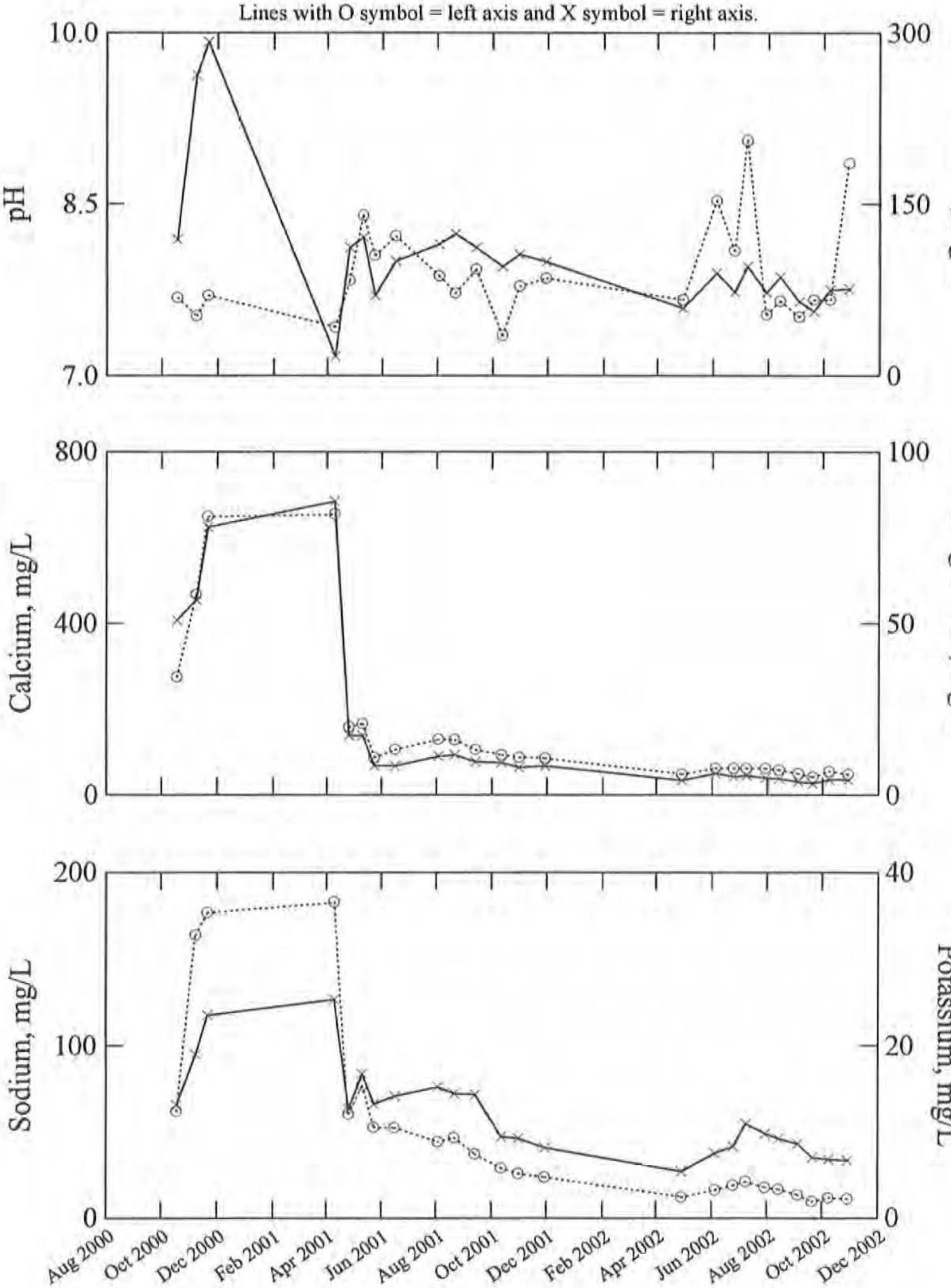


Figure 21. Drainage quality vs. time for the 0.39% S prediction field pile 3.

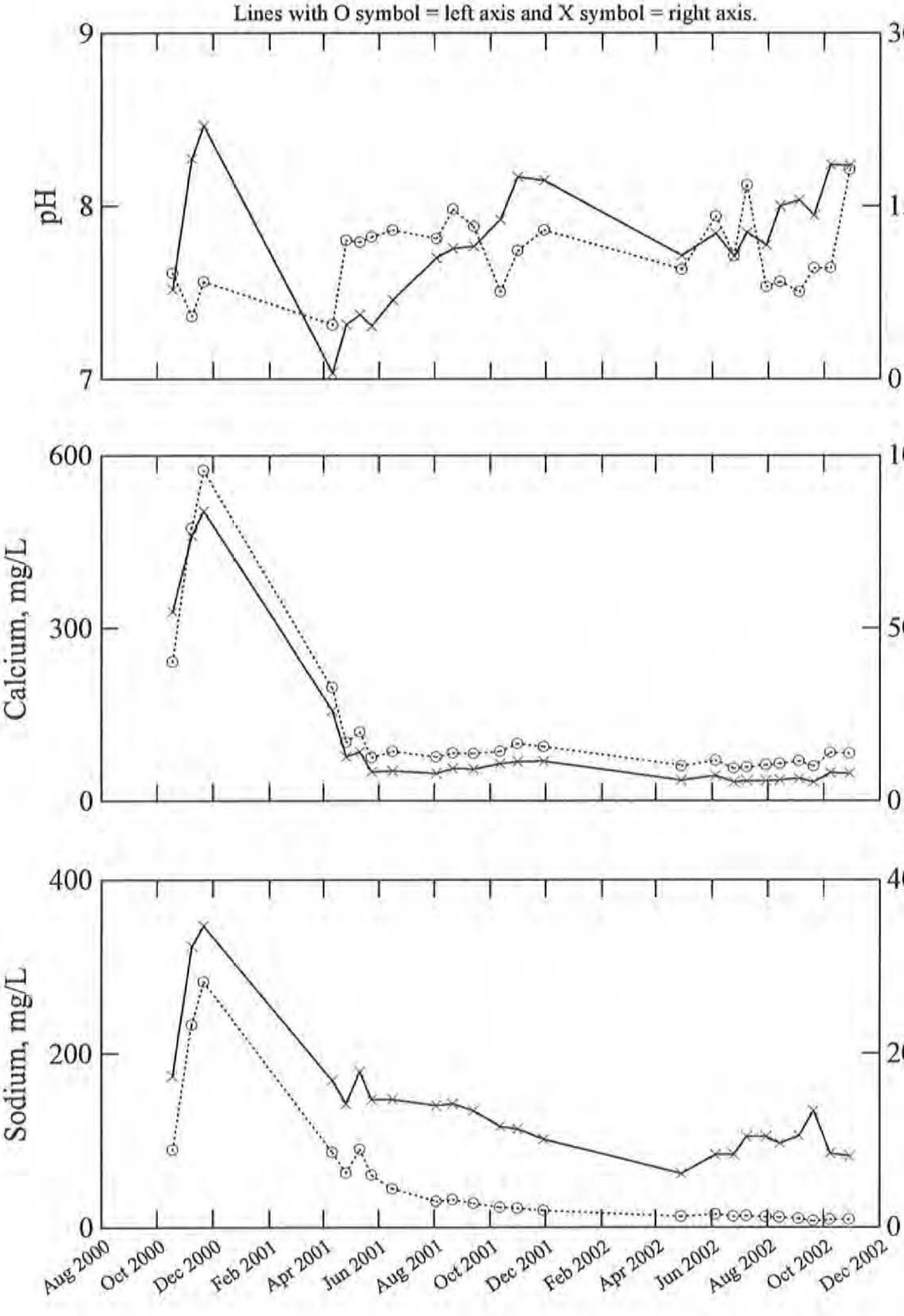


Figure 22. Drainage quality vs. time for the 0.67% S prediction field pile 4.

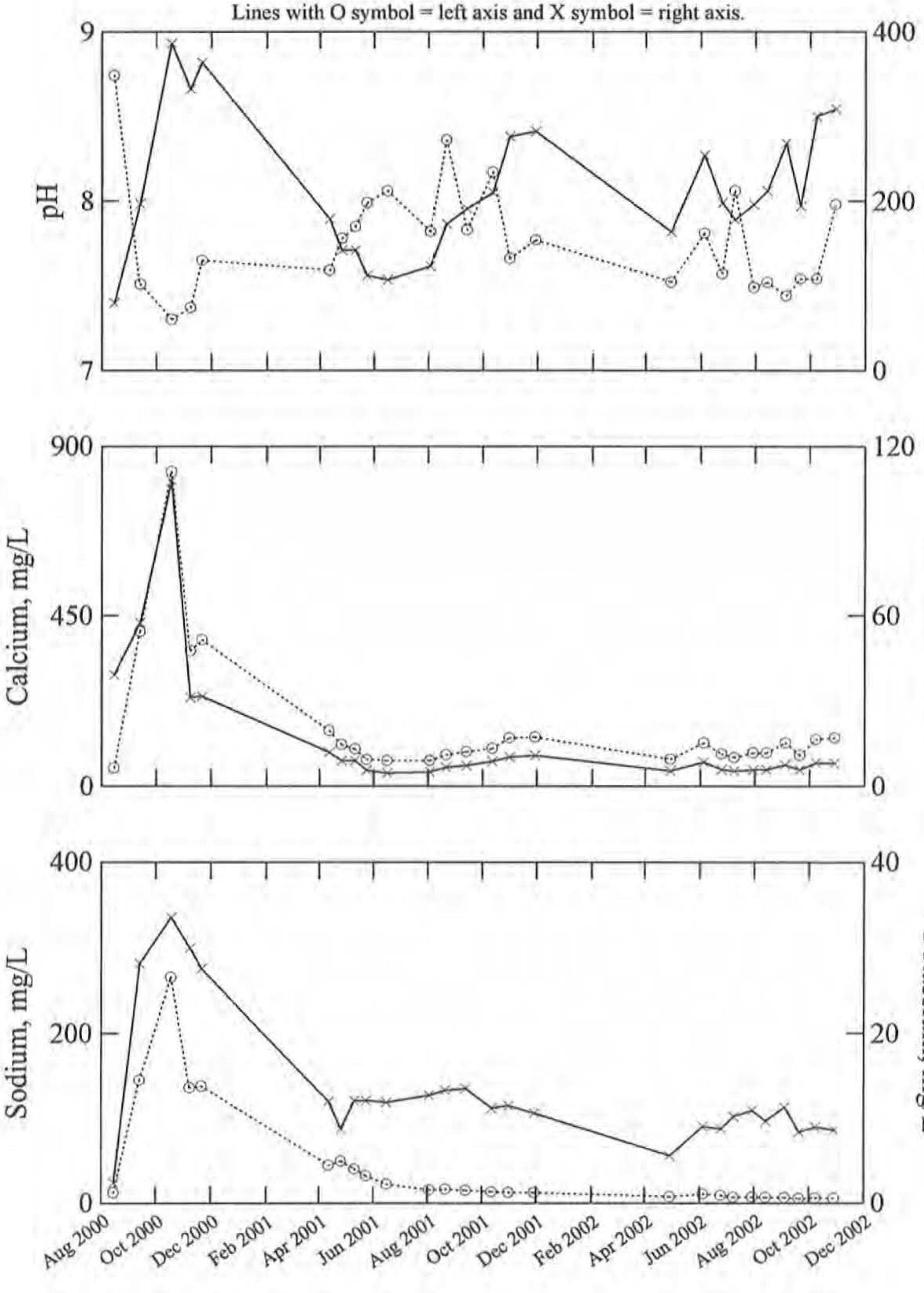


Figure 23. Average 2002 sulfate release rates increased linearly with solid phase sulfur content.

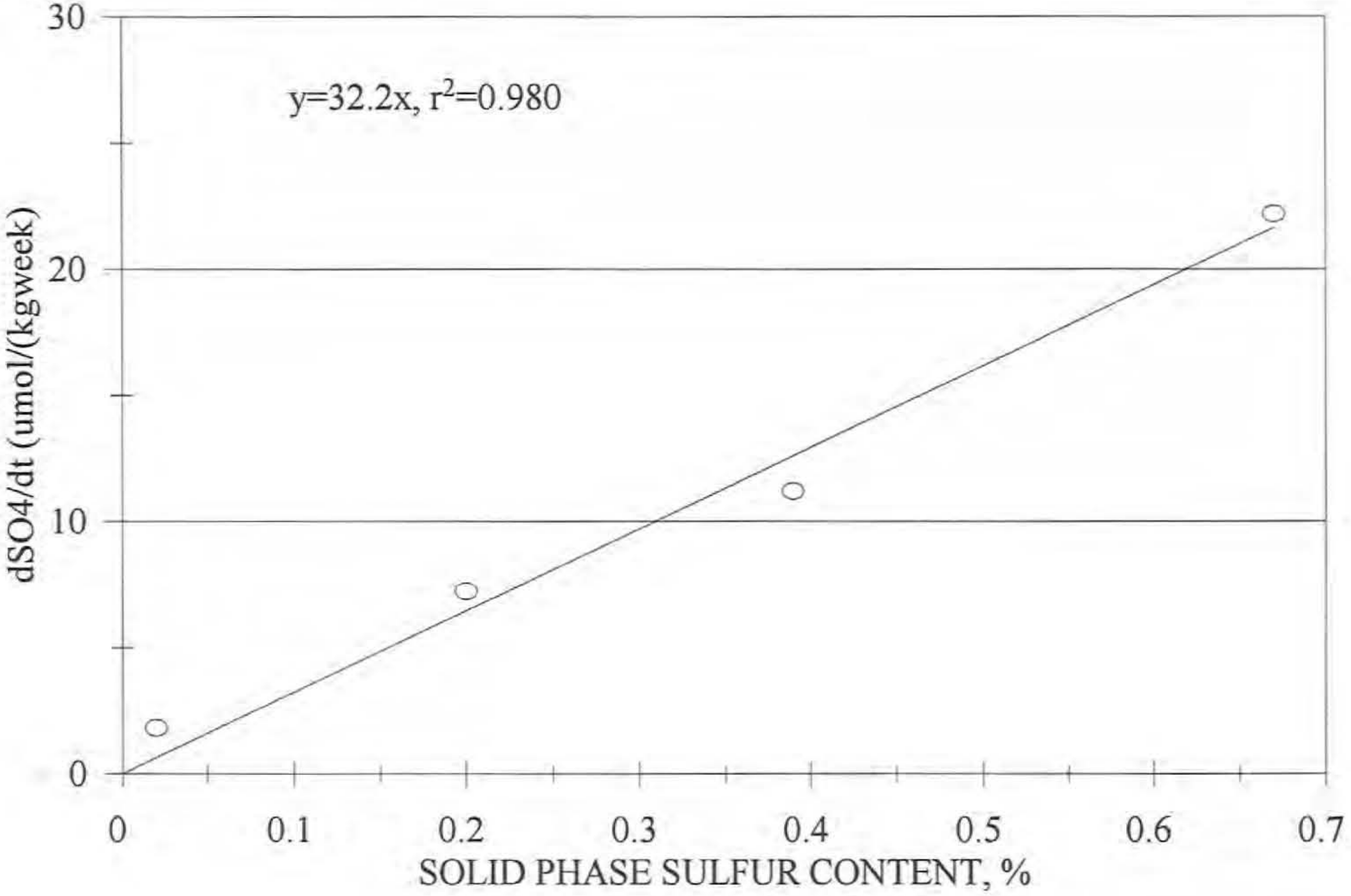


Figure 24. Drainage quality vs. time for the limestone addition control tank 1.

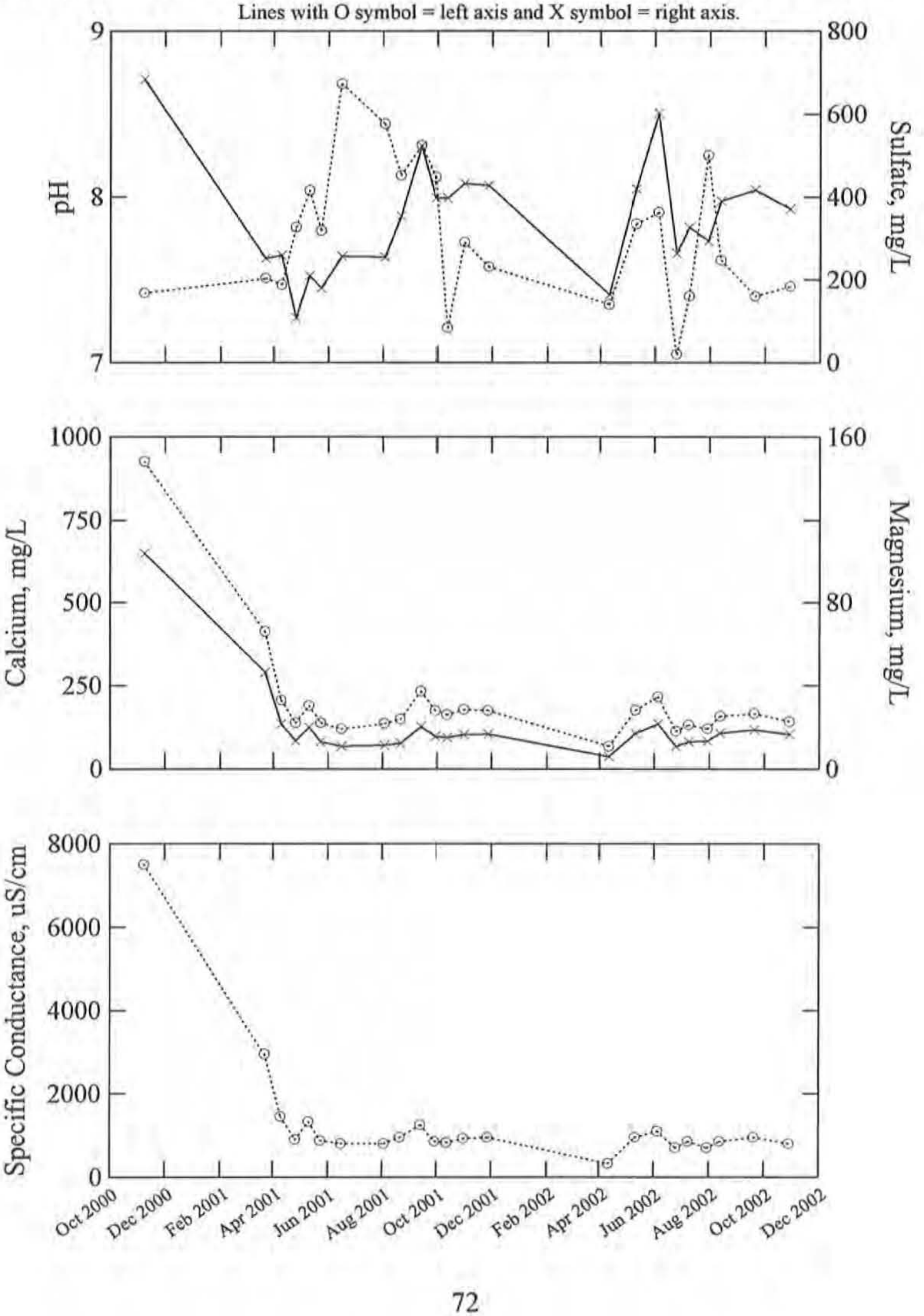
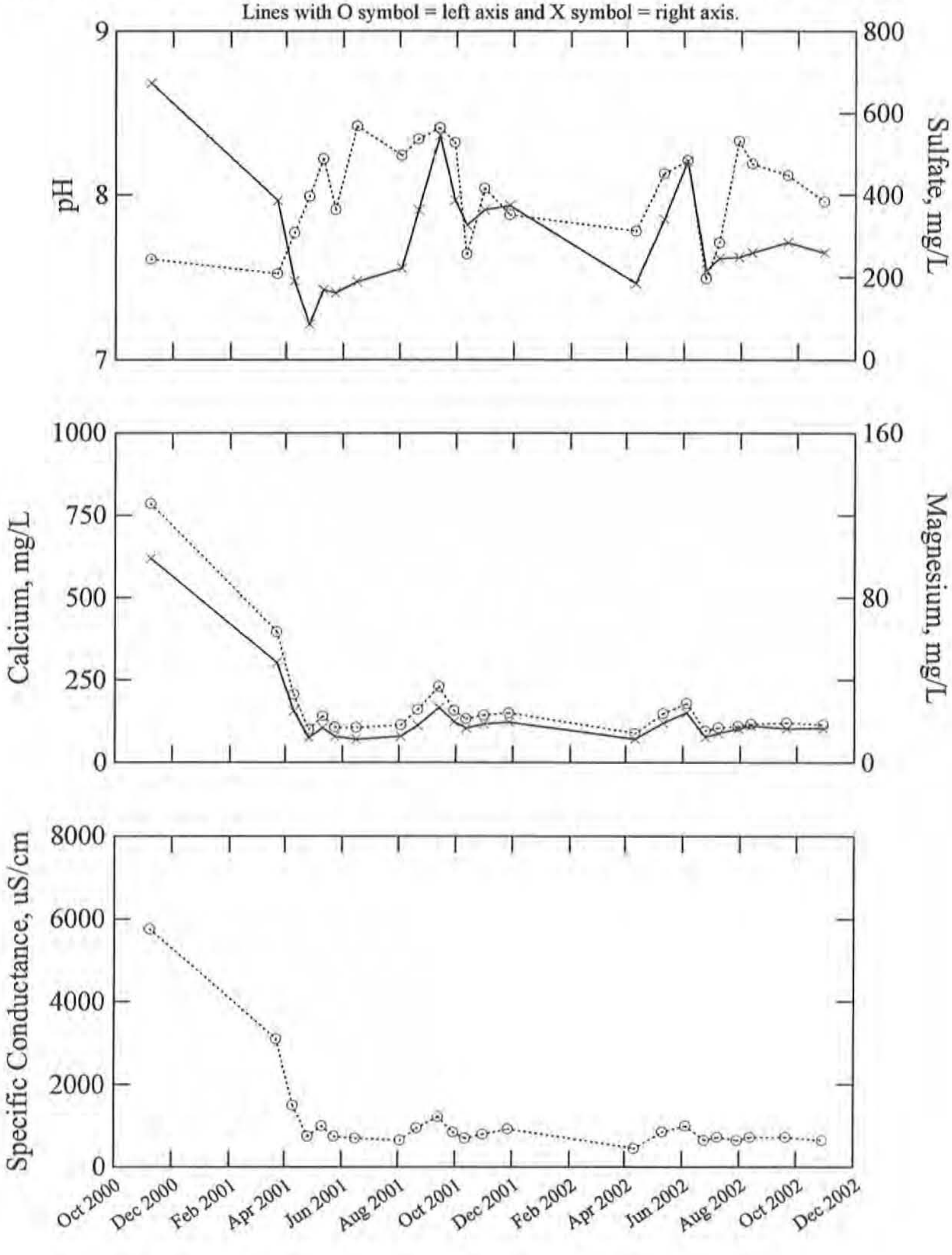


Figure 25. Drainage quality vs. time for the limestone addition control tank 6.



Lines with O symbol = left axis and X symbol = right axis.

Figure 26. Drainage quality vs. time for the limestone addition 1:1 ratio tank 2.

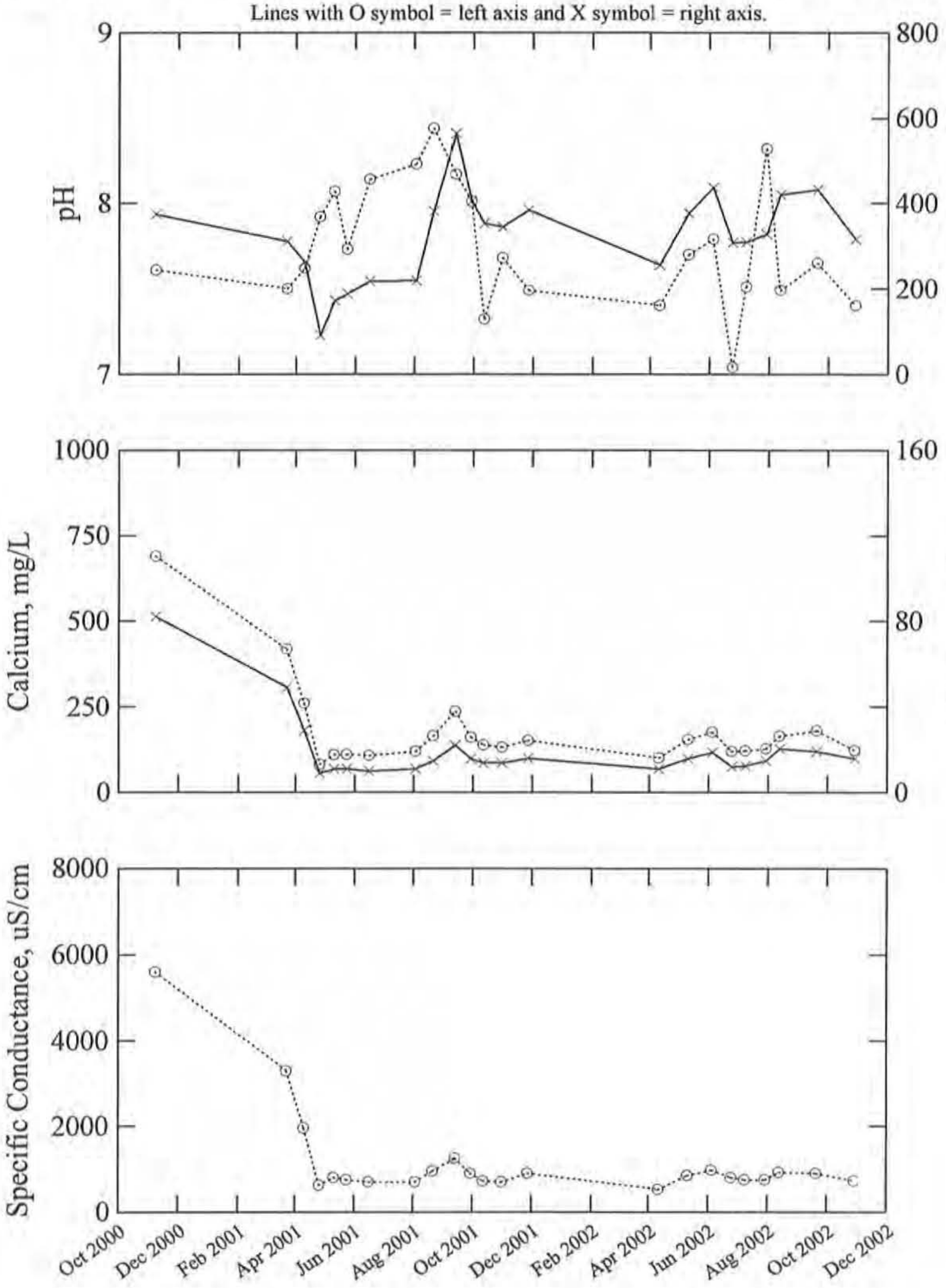


Figure 27. Drainage quality vs. time for the limestone addition 1:1 ratio tank 5.

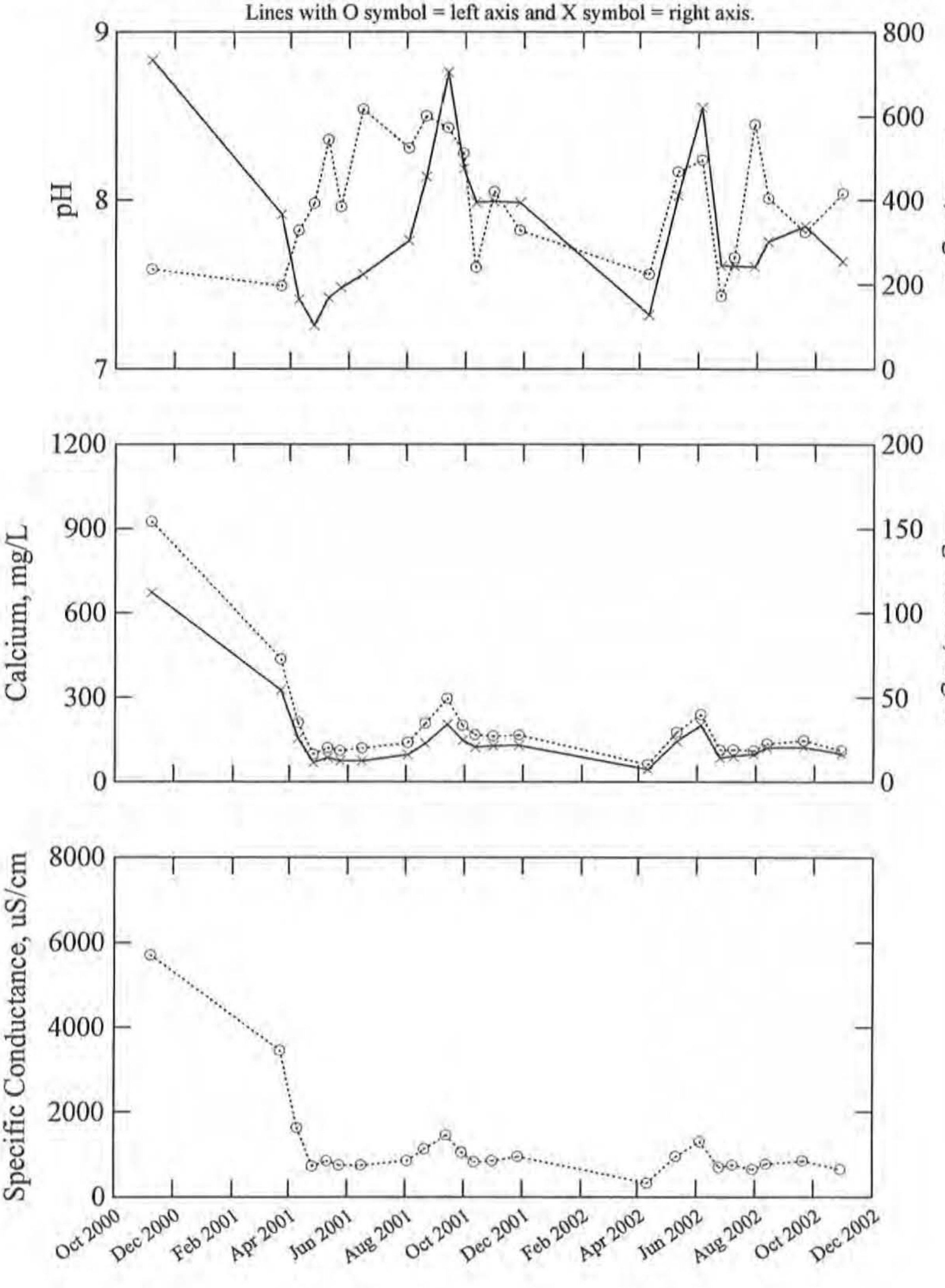


Figure 28. Drainage quality vs. time for the limestone addition 3:1 ratio tank 3.

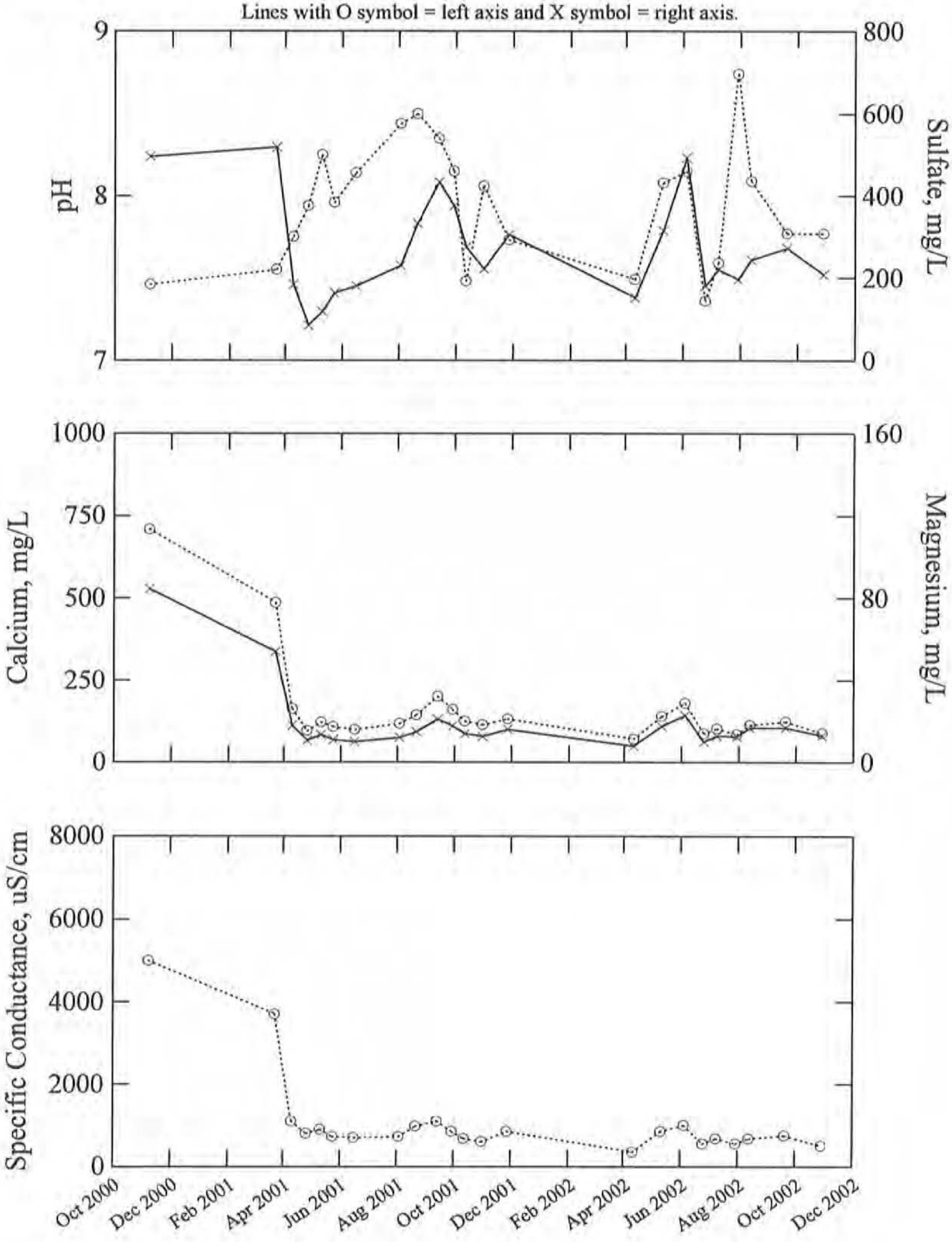


Figure 29. Drainage quality vs. time for the limestone addition 3:1 ratio tank 4.