Evaluation of selected phosphate sources for the control of acid production from pyritic coal overburden
by Edward Spotts

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Land Rehabilitation
Montana State University

Abstract:
Acid Mine Drainage (AMD) is a serious and pervasive threat to surface and groundwater quality in the eastern Appalachian coal regions and at surface area coal mines in the western United States. Recent research has indicated that the use of phosphate materials can be an effective treatment for the amelioration of AMD. Phosphate is effective at immobilizing iron and inhibiting the production of acid associated with the oxidation of FeS2.

A preliminary simulated weathering study was performed to evaluate the potential of several regional phosphate sources for controlling the production of acid from pyritic coal overburden. Sources deemed most effective were tested further for application rate determination utilizing a replicated soxhlet leaching technique described by Renton et al (1988a). Phosphate sources tested in this part of the study included two apatite ores (Cominco ore and Texas Gulf ore) at an application rate of 3% by weight apatite and two byproducts of the phosphate industry (Cominco waste and Stauffer sludge) at rates of 1%, 3% and 5% apatite by weight.

Results of leachate analyses indicate that all sources at all rates of application resulted in significant decreases in titratable acidity versus a control. Acidity reductions ranged from a low of 7% for samples treated with Cominco waste (1%) to a high of 67% for Texas Gulf ore-treated samples. Texas Gulf ore, Stauffer sludge (1%, 3% and 5%) and Cominco waste (1%, 3% and 5%) significantly reduced dissolved total iron (Fe) concentrations in leachate, with Stauffer sludge (5%) and Texas Gulf ore producing the most notable diminutions (62% and 63%, respectively). Maximum decreases in sulfate (SO42-) concentrations of 26%, 20% and 25% were achieved by applications of Texas Gulf ore and Stauffer sludge (3% and 5%), respectively. The more effective overall performance of the Stauffer sludge and Texas Gulf ore can be attributed to the considerably greater relative surface area and P solubility of these amendments. Results of a scanning electron microscope examination of amendments corroborate these findings.

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A thesis submitted in partial fulfillment
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APPROVAL

of a thesis submitted by

Edward Spotts

This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

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ABSTRACT

Acid Mine Drainage (AMD) is a serious and pervasive threat to surface and groundwater quality in the eastern Appalachian coal regions and at surface area coal mines in the western United States. Recent research has indicated that the use of phosphate materials can be an effective treatment for the amelioration of AMD. Phosphate is effective at immobilizing iron and inhibiting the production of acid associated with the oxidation of FeS_2.

A preliminary simulated weathering study was performed to evaluate the potential of several regional phosphate sources for controlling the production of acid from pyritic coal overburden. Sources deemed most effective were tested further for application rate determination utilizing a replicated soxhlet leaching technique described by Renton et al (1988a). Phosphate sources tested in this part of the study included two apatite ores (Cominco ore and Texas Gulf ore) at an application rate of 3% by weight apatite and two byproducts of the phosphate industry (Cominco waste and Stauffer sludge) at rates of 1%, 3% and 5% apatite by weight.

Results of leachate analyses indicate that all sources at all rates of application resulted in significant decreases in titratable acidity versus a control. Acidity reductions ranged from a low of 7% for samples treated with Cominco waste (1%) to a high of 67% for Texas Gulf ore-treated samples. Texas Gulf ore, Stauffer sludge (1%, 3% and 5%) and Cominco waste (1%, 3% and 5%) significantly reduced dissolved total iron (Fe) concentrations in leachate, with Stauffer sludge (5%) and Texas Gulf ore producing the most notable diminutions (62% and 63%, respectively). Maximum decreases in sulfate (SO_4^{2-}) concentrations of 26%, 20% and 25% were achieved by applications of Texas Gulf ore and Stauffer sludge (3% and 5%), respectively. The more effective overall performance of the Stauffer sludge and Texas Gulf ore can be attributed to the considerably greater relative surface area and P solubility of these amendments. Results of a scanning electron microscope examination of amendments corroborate these findings.

INTRODUCTION

Acid mine drainage (AMD) is a serious and pervasive threat to surface water and groundwater quality as well as the riparian resources of the United States. It is a common problem in the Appalachian coal mining regions of the eastern U.S. and at surface area mines in the western U.S.

Acid mine drainage forms when pyrite (FeS_2) or its orthorhombic polymorph, marcasite, which is found in coal and associated overburden lithologies, is exposed to weathering conditions (oxidation and hydrolysis) as a result of mining. Oxidation and hydrolysis of FeS_2 results in the formation of a series of soluble hydrous iron sulfates (Nordstrom 1982) and the production of acid in the form of hydrogen ions (H^+). The dissolution of these sulfate salts results in an effluent characterized by elevated levels of dissolved iron (Fe), sulfate (SO_4^{2-}), total dissolved solids (TDS) and low pH.

Drainages affected by AMD often have pH values as low as 2.0 and dissolved SO_4^{2-} and Fe concentrations of 400 ppm to 12,000 ppm and 50 ppm to 500 ppm, respectively (Corbett and Growitz 1967, Caruccio et al 1977, Nordstrom 1982). In addition, the low pH of the effluent can solubilize metals from rocks over which it flows and result in serious water quality degradation and elevated levels of Al^{3+}, Cu^{2+}, Mn^{2+}, Ni^{2+}, Zn^{2+} and other trace metals (Chen 1982).

Oxidation of free ferrous iron (Fe^{2+}) to ferric iron (Fe^{3+}) and the subsequent hydrolysis of Fe^{3+} leads to the production of more acidity and the formation of a

series of iron oxyhydroxides, which impart to AMD its characteristic red and yellow colors (Corbett and Growitz 1967). If the pH falls below approximately 3.5 and the ratio of Fe^{3+}:Fe^{2+} becomes great enough (10^{-6}:1) (Stiller 1980), oxidation of FeS_2 by Fe^{3+} becomes dominant and the FeS_2 oxidation cycle becomes synergetic and self-perpetuating (Singer and Stumm 1970).

Traditional methods for the treatment of AMD are often costly and ineffective. Recent research indicates that the addition of phosphate to acid producing materials may be an effective control for AMD. Phosphate is effective at immobilizing iron and inhibits the oxidation of FeS_2 by Fe^{3+}, thereby interrupting the autocatalytic nature of the FeS_2 oxidation cycle. In addition, acid production from the hydrolysis of Fe^{3+} is considerably reduced.

In this study, several sources of phosphate from southwestern Montana and southeastern Idaho, including industry byproducts, were evaluated for their effectiveness at controlling acid production from FeS_2-rich coal overburden. Those sources which proved most successful were chosen for rate application determination using a soxhlet leaching procedure described by Renton et al (1988a). Specific objectives of the study are defined in the OBJECTIVES chapter.

LITERATURE REVIEW

Pyrite Genesis and Morphology

It is commonly recognized that the weathering of FeS_2 is primarily responsible for the production of AMD. Iron disulfide (FeS_2) may be grouped into two general categories: 1) primary or 2) secondary. These categories can be further classified and discussed on the basis of genesis and morphology (Caruccio 1968, Grady 1977, Greer 1978 and Caruccio et al 1988).

Primary FeS_2 forms contemporaneously with diagenesis and lithification of sediment or coal. It can occur massively, as discrete grains or clusters of euhedral crystals, or as a replacement (primary) in plant cell walls. Massive FeS_2 and plant replacement FeS_2 typically are found in the size range 150 - 600 micrometers and primary euhedral FeS_2 crystals commonly range between 0.5 and 2.0 micrometers.

Framboidal FeS_2 is another class of primary FeS_2 that may occur as agglomerated spheres of small crystals or finely disseminated particles scattered throughout a coal seam or rock unit (Caruccio et al 1988). It is believed to form contemporaneously with sediment deposition under strongly reducing conditions where enriched levels of organic matter, iron and hydrogen sulfide gas (H_2S_2) are present. Individual crystals are less than 0.5 micrometers in diameter.

Of importance to note is the effect of particle size on acid production. While all classes of FeS_2 will produce some acid upon being exposed to oxidizing

conditions, the small size of the framboidal FeS_2 manifests itself in the form of tremendous surface area. This in turn results in more surface oxidation sites and a subsequent increase in reactivity and the rate of acid production (Pugh et al 1981).

Secondary FeS_2 is emplaced subsequent to diagenesis as sulfide components mobilized during weathering are redeposited as secondary FeS_2. It may replace plant material or be found along cracks and partings in the coal or associated lithologies and may have a massive appearance (Caruccio et al 1988). It is typically found in sizes between 0.5 and 600 micrometers and can range from anhedral to euhedral crystal form.

In addition to the crystal size and morphology of FeS_2, other factors affecting the oxidation and subsequent acid production of FeS_2 include oxygen content, amount and pH of water, ambient air and water temperature, the Fe^{2+}/Fe^{3+} ratio, the presence of chemoautotrophic bacterium and the mineralogy of the host and proximal lithologies (Caruccio 1973).

Chemistry of AMD

Although the exact sequence of reactions involved in the oxidation of FeS_2 and the production of acid have not been well established, the following reactions are commonly accepted as being representative of FeS_2 weathering (Barnes and Romberger 1968, Stumm and Morgan 1970).

When FeS_2 is exposed to oxygen, the following initial reaction occurs.

$$FeS_{2(s)} + 7/2\ O_2 + H_2O = Fe^{2+} + 2\ SO_4^{2-} + 2\ H^+ \quad [1]$$

Oxidation of 1 mole of FeS_2 by ambient oxygen results in the production of 1 mole of ferrous iron (Fe^{2+}), 2 moles of sulfate (SO_4^{2-}) and 2 moles of acidity (H^+). The rate of this reaction accelerates as the pH rises (Smith and Shumate 1970), increasing slowly to pH 3.0 and rapidly as pH exceeds 6.0.

The Fe^{2+} in solution becomes available for further oxidation to ferric iron (Fe^{3+}) by oxygen in the ambient environment. The rate of this reaction is very slow (Singer and Stumm 1970) and has been determined to be the rate limiting step in the perpetuation of acid production associated with the FeS_2 oxidation cycle.

Role of Bacteria

Colmer and Hinkle (1947), Leathen et al (1953) and Norris et al (1978) have shown that the presence of aerobic chemoautotrophic bacteria Thiobacillus ferrooxidans can catalyze and greatly accelerate the oxidation of Fe^{2+} to Fe^{3+}. These bacteria utilize CO_2 in water as a carbon source (Lundgren and Dean 1977) and derive energy for metabolic processes by utilizing an electron from Fe^{2+} during the conversion of Fe^{2+} to Fe^{3+} (Dugan 1975). The resultant increase in Fe^{3+} concentration can cause, at pH values below approximately 3.5, an acceleration of FeS_2 oxidation by Fe^{3+} and acid production by Fe^{3+} hydrolysis. Beck and Brown

(1968) and Arkestyn (1979) observed that T. ferrooxidans also catalyze the direct oxidation of FeS_2 by O_2.

The degree of T. ferrooxidans activity is controlled by the relationship between pH and Fe^{2+} activity and CO_2 concentrations. Optimum growth conditions and maximum biotic Fe^{2+} oxidation occur between pH 2.4 to 3.6 (Lundgren and Dean 1977) and a rapid decrease in biotic Fe^{2+} oxidation has been observed below pH 2.0 and above pH 3.6 (EPA 1971). Above a pH of approximately 4.0, Fe^{2+} levels in solution are not sufficient to allow for optimum growth of T. ferrooxidans

T. ferrooxidans are also capable of tolerating extremely high levels (up to 10,000 ppm) of Al^{3+}, Co^{2+}, Cu^{2+}, Mn^{2+}, Ni^{2+} and Zn^{2+} (Tuovinen et al 1971). The following reaction represents the oxidation of Fe^{2+} to Fe^{3+} in an AMD system.

$$Fe^{2+} + 1/4\ O_2 + H^+ = Fe^{3+} + 1/2\ H_2O \qquad [2]$$

Hydrolysis of Ferric Iron

The oxidation of Fe^{2+} to Fe^{3+} by either oxygen or T. ferrooxidans causes an increase in the activity of Fe^{3+}. The Fe^{3+} is then hydrolyzed and forms an initially amorphous iron hydroxide, $Fe(OH)_3$, often referred to as yellowboy, which can further decompose into the more thermodynamically stable iron oxide minerals goethite (*FeOOH) and hematite (Fe_2O_3) (Stumm and Morgan 1970, Van Breemen 1973). The complete hydrolysis of 1 mole of Fe^{3+} yields 3 moles of H^+ for every mole of $Fe(OH)_3$ formed.

$$Fe^{3+} + 3\ H_2O = Fe(OH)_{3(s)} + 3\ H^+ \quad [3]$$

The summary reaction for the sequence of reactions presented above can be written as follows.

$$FeS_{2(s)} + 15/4\ O_2 + 7/2\ H_2O = Fe(OH)_{3(s)} + 2\ SO_4^{2-} + 4\ H^+ \quad [4]$$

From this summary reaction it can be seen that a total of 4 moles of H^+ acidity is produced from the complete oxidation of 1 mole of FeS_2

Oxidation of FeS_2 by Ferric Iron

The sequence of reactions discussed above ,[1], [2], [3] and [4] are prevalent at pH values greater than approximately 3.5 (Singer and Stumm 1970). Thus the oxidation rate of FeS_2 is pH dependant above this value.

As acid production continues and the pH in the vicinity of the FeS_2 falls below pH 3.5, the formation of $Fe(OH)_3$ diminishes and the activity of free Fe^{2+} in solution increases (Singer and Stumm 1970). The lower pH and greater Fe^{2+} activity are conducive to the oxidation of Fe^{2+} to Fe^{3+} by T. ferrooxidans, resulting in an increase in Fe^{3+} activity to a point where Fe^{3+} becomes the primary oxidizer of FeS_2. This occurs when the Fe^{2+}:Fe^{3+} ratio reaches approximately $1:10^{-6}$ and the Fe^{2+}/Fe^{3+} voltage equilibrium falls below 0.41 V (Stiller 1980). At this point the oxidation of FeS_2 is no longer dependent upon pH but on the activity of Fe^{3+}, and the oxidation of FeS_2 by O_2 becomes unimportant (Singer and Stumm 1968).

Smith and Shumate (1970) reported that under abiotic conditions at pH 3, the rate of FeS_2 oxidation by Fe^{3+} is three to four orders of magnitude greater than oxidation by O_2. The oxidation of pyrite and production of acid via Fe^{3+} oxidation is shown in the reaction below.

$$FeS_{2(s)} + 14\ Fe^{3+} + 8\ H_2O = 15\ Fe^{2+} + 2\ SO_4^{2-} + 16\ H^+ \quad [5]$$

Two (2) moles of H^+ are produced for every mole of FeS_2 oxidized. The rate of this reaction is very fast (Singer and Stumm 1970) and once initiated, the acid producing mechanisms interact in a synergetic manner. The FeS_2 oxidation cycle becomes, in essence, autocatalytic and self-perpetuating.

Treatment of AMD

Several treatment methods for the abatement and control of AMD have been employed with varying degrees of success. It is possible to characterize these approaches into five general categories: 1) hydrologic and atmospheric isolation of acid producing material, 2) neutralization of acidity using various lime products, 3) reduction of the rate of acid production using bactericides, 4) passive treatment of AMD using constructed wetlands and 5) reduction of the rate of production of acid through the use of iron precipitating agents.

Isolation Approaches

Isolation approaches for controlling AMD include the use of impermeable synthetic or clay liners, clay caps and/or plugging or grouting of mine adits in an attempt to isolate the acid producing material from oxygen and infiltrating surface waters and groundwater (Moebs and Krickovic 1970, Kim et al 1982, Gallagher 1985, Geidel 1985). Flooding of adits via sealing (O_2 exclusion) and drainage wells have also been used to bypass overlying aquifer water through old mine workings and into aquifers underlying the mine workings. While these approaches have been successful in some instances, in general there is difficulty in achieving complete atmospheric and hydrologic isolation of the acid producing material. In many cases AMD will discharge from cracks and fractures connected and adjacent to a mine (Kim et al 1982). These cracks and fractures also act as conduits through which oxygen and water can reach the acid producing materials. Materials, construction and maintenance costs often render this approach economically unfeasible as a means for controlling AMD.

Neutralization

The use of liming agents ($CaCO_3$, $Ca(OH)_2$ and CaO) is one of the most common methods employed for the treatment of AMD (Thomas and Hargrove 1974, Barbar 1984, Carrucio et al 1988). The construction of limestone barriers, mine seals with impermeable $CaCO_3$ plugs, water treatment facilities and direct

incorporation into spoils are the most common applications of this technique (Deul 1984, Gleason and Russell 1976).

Liming agents neutralize acidity already produced and result in an increase in pH and concomitant decline in Fe and other metal levels. If the pH is raised to near neutral levels, the activity of T. ferrooxidans and the oxidation of pyrite will also be significantly inhibited (Dugan 1975). The use of neutralizing agents does not directly stop the production of acid. In addition, because the neutralization reaction between $CaCO_3$ and H^+ takes place at the surface of the limestone, coating of the lime with iron oxyhydroxides may occur, rendering the lime nonreactive. This can lead to a significant decrease in the neutralizing capacity of the lime through time, allowing reacidification to occur. Hence, materials with a high acid producing potential often require frequent reapplications of lime, significantly increasing the cost of this treatment.

Bactericides

The use of bactericides is an AMD treatment method aimed at reducing the production of acid by inhibiting the bacteria-catalyzed conversion of Fe^{2+} to Fe^{3+} [2], thus inhibiting the acid producing mechanisms associated with Fe^{3+} oxidation of FeS_2 [5] and Fe^{3+} hydrolysis [3].

Anionic detergents such as sodium lauryl sulfate or more commonly linear alkyl benzene sulfonate, and organics acids (benzoic, sorbic and others) are typically utilized (Erickson and Ladwig 1985) to treat AMD producing waste (Kleinmann

1978). Direct application into effluent or deep mine injection are also used to apply bactericides. Problems associated with the use of bactericides are related to proper placement and longevity. Kleinmann (1979) has noted the ability of bacteria to rapidly repopulate, thus requiring that the bactericide be reapplied frequently or continuously, significantly increasing the cost of the treatment. In addition, some bactericides have detrimental environmental side effects (Kleinmann 1979, Baker 1983).

Wetlands

An increasingly popular method of AMD treatment is the use of artificial wetlands. Early efforts in wetland construction were based on observations of natural wetlands affected by AMD. Design parameters such as wetland size, residence time and substrate type and thickness were often not incorporated into the design of early wetlands. As a result, many wetlands failed and there was difficulty in determining what causes and factors were responsible for wetlands which were successful at treating AMD. Even when successful at reducing Fe levels, many wetlands did nothing to improve the pH (Girts and Kleinmann 1986).

The predominant mechanism for iron removal in early constructed wetlands was the oxidation and hydrolysis of iron. This resulted in the formation of iron oxyhydroxides, thereby tying up much of the iron but also leading to the production of acid via Fe^{3+} hydrolysis [3] and accounting for the lack of a notable increase in pH.

Recent developments in the understanding of wetland processes have been made. The United States Bureau of Mines is currently working on ways to optimize dissimilatory sulfate reduction processes by anaerobic heterotrophs to improve wetland performance (Hedin et al 1988). In this process, microorganisms (Desulfovibrio spp.) reduce SO_4^{2-} to FeS and FeS_2. These reduction reactions consume H^+ and result in a significant increase in pH and Fe removal as opposed to wetlands of traditional design. Also, improvements in design and construction criteria have been made. Together, these developments may result in a more predictable, efficient future use of wetlands for the control of AMD.

Many AMD sites, however, such as those in steep, mountainous terrain, are not conducive to the construction of wetlands and there is difficulty in using wetlands at sites with significant flow volumes and highly elevated levels of Fe and Mn (Girts and Kleinmann 1986). It is therefore sometimes necessary to use a chemical water treatment system in conjunction with a wetland to meet regulatory effluent requirements at coal mines. Drying out of the wetland and subsequent reoxidation of sulfides is also a major concern.

Finally, at this point in time, wetlands are still largely experimental and sufficient temporal data need to be gathered before a conclusion as to their overall performance can be made and they can be implemented on a large scale.

Control of AMD Using Phosphates

An amendment which can effectively control the concentration of Fe^{3+} ions can halt the autocatalytic nature of the FeS_2 oxidation cycle. Research has indicated that the concentration of free Fe^{3+} and its ability to oxidize FeS_2 is dramatically reduced by the addition of a source of phosphate (PO_4^{3-}) ions (Flynn 1969, Stiller 1980, 1981, Baker 1983, Meek 1984, Renton et al 1988).

Phosphate is effective in this regard because it can precipitate the Fe^{3+} ion in a relatively insoluble form as $FePO_4$. It can also precipitate Fe^{2+} as $Fe_3(PO_4)_2$, rendering it unavailable for oxidation to Fe^{3+}, either by O_2 or bacteria. In addition, the iron phosphates can precipitate on the surface of FeS_2 crystals, further limiting FeS_2 reactivity (Baker 1983).

Stiller (1980) showed in a laboratory setting that the addition of phosphate to several different acid producing coal overburden samples in the form of crushed apatite ($Ca_5(PO_4)_3OH$) was effective at reducing the Fe^{2+}:Fe^{3+} ratio below $1:10^{-6}$, thus achieving an Fe^{2+}/Fe^{3+} voltage equilibrium of less than 0.41 volts. When this occurred the rate of FeS_2 oxidation by Fe^{3+} was significantly reduced. In a comparison of the effectiveness of sodium lauryl sulfate (bactericide), agricultural limestone and apatite at inhibiting the production of acid from coal plant waste weathered naturally in 35 gallon drums, Baker (1983) observed lowest concentrations of SO_4^{2-} in effluent from waste treated with apatite and concluded that apatite was more effective in controlling acid production than either sodium

lauryl sulfate or limestone. In addition, the rates of apatite required to effectively control acid production were approximately five times less by weight than the amount of limestone needed, indicating that the use of apatite for the control of AMD may be considerably less expensive than a similar use of limestone, assuming both sources are readily available.

To date few experiments have been performed to systematically evaluate the rate of application of a given phosphate source necessary to effectively control AMD. Meek (1984) found that regardless of the acid producing potential of a sample, an addition of 3% apatite by weight was effective at controlling acid production. Above this rate, no significant improvement in effluent water quality was observed.

Renton et al (1988b) conducted an experiment utilizing a soxhlet leaching procedure (Renton et al 1988a) which evaluated the effectiveness of various phosphate sources applied to several acid producing materials at different rates and particle sizes. He concluded that at an application rate of less than 1% by weight, apatite was ineffective at controlling the production of acid. However, at an application rate of 5%, the production of acid was decreased by greater than 90%. These results were obtained using a relatively pure source of apatite (code 31) from Texas Gulf Chemical in Aurora, North Carolina. Acid production was not significantly reduced (less than 30% vs. untreated control) by application of apatite

having a particle size larger than 1.6 mm (1/16 inch), regardless of the rate of application.

In the same study, the use of a phosphate industry byproduct, a slurry containing approximately 25% apatite with the remainder smectite clays, achieved only moderate reductions in acid production. However, when a fine-grained apatite "spike" was added to the slurry, acid production was substantially reduced.

Thus, the use of a source of PO_4^{3-} provides a mechanism for inhibiting the conversion of Fe^{2+} to Fe^{3+} as well as immobilizing Fe^{3+} already present. In this way, the rate limiting step in the FeS_2 oxidation cycle, the oxidation of Fe^{2+} to Fe^{3+}, is slowed and the acid producing mechanisms associated with the hydrolysis of Fe^{3+} and the autocatalytic nature of FeS_2 oxidation by Fe^{3+} is eliminated. In addition, the insolubility of apatite above a pH of approximately 4.5 insures that PO_4^{3-} ions will be available as an in-situ, point source control of AMD until the pH drops to this value. At this point the dissolution of apatite renders PO_4^{3-} ions available for the precipitation of iron. The dissolution of hydroxyapatite also liberates hydroxyl (OH^-) groups into solution, providing a source for H^+ neutralization.

Although the success of phosphate at controlling acid production from FeS_2 wastes has been established in the laboratory, specific rates have only been developed for a few sources of relatively pure apatite and a single byproduct from the eastern U.S. In addition, the feasibility of the exclusive use of an apatite processing waste product has not been fully examined.

The procurement of apatite can also present an obstacle to its use as an amendment for AMD. An economical source of apatite of proven effectiveness is not readily available in the Appalachian coal mining region of the eastern U.S. As a result, apatite must be shipped significant distances by truck or railroad from the southeastern U.S. This results in transportation costs which are often prohibitive to the large scale, widespread use of apatite for the treatment of AMD in the field (Renton 1989).

In the western U.S., however, apatite mined from the Permian Phosphoria Formation in southeastern Idaho and southwestern Montana is available and provides a relatively close source of phosphate for the coal mines of the Northern Great Plains. Several byproducts of the phosphate industry are also available which contain significant amounts of PO_4^{3-}. The low cost and availability of these byproducts in conjunction with their proximity to large area coal mines and other sources of AMD pollution (namely many hardrock mines located in the mountainous regions of the west) warrant the evaluation of these sources for their effectiveness at controlling AMD. An additional benefit will also be recognized in that a previously unwanted and potentially environmental threatening byproduct of the phosphate industry may be available for beneficial use in the control of AMD.

STUDY OBJECTIVES

The specific objectives of this study are listed below.

1) To evaluate the potential of several regional phosphate sources, including two industrial byproducts, for controlling acid production from coal overburden.

2) To develop specific application rates for those phosphate sources which proved to be most effective at controlling acid production.

3) To compare the effectiveness of regional phosphate sources with those used in previous studies and to verify and corroborate the results of those studies.

MATERIALS AND METHODS

Experimental Design

The study was conducted in two separate phases discussed below.

Phase I

The initial phase of the study was a nonreplicated, qualitative evaluation of four regional phosphate sources, one commercially available phosphate fertilizer and one previously studied phosphate source from North Carolina, for their ability to control acid production from FeS_2-rich coal overburden. This part of the study utilized a computerized automated rapid weathering apparatus (CARWA) to generate leachates from overburden treated with equal amounts of each phosphate source (by weight %P). Leachates were analyzed for pH, SO_4^{2-} and titratable acidity to evaluate each source's effectiveness at reducing acid production. Economic factors such as cost/benefit considerations and availability of each source were also taken into account when evaluating the effectiveness of a source.

Phase II

The second phase of the study consisted of the development of specific application rates for the phosphate sources deemed most successful at controlling acid production from the overburden sample. A soxhlet extraction apparatus was employed for this part of the study following a procedure outlined by Renton et al (1988). All treatments were run in triplicate.

In addition, amendment solubility versus pH, scanning electron microscopic (SEM) analysis and energy dispersive analysis of X-rays (EDAX) were performed on the amendments used in the soxhlet leaching experiment.

Acid Producing Overburden Sample

An acid producing sample of Wolf Creek coal overburden from the Peabody Coal Company's Seneca Mine near Hayden, Colorado was chosen for use in the experiment. A preliminary evaluation of several overburden samples from various western coal mines indicated that the Wolf Creek overburden would best fit the criteria deemed necessary for the experiment, namely that the sample have a saturated paste pH of less than 3.0 and contain enough pyritic sulfur to enable it to readily produce acid in a laboratory setting. The first criteria was deemed necessary because, theoretically, it is not until pH values fall below approximately 3.5 that Fe^{3+} levels become elevated enough that Fe^{3+} becomes the primary oxidizer of FeS_2 and the production of acid becomes a self-perpetuating cycle. These conditions were deemed essential because it is this component of the FeS_2 oxidation cycle which the use of phosphate is designed to inhibit.

The Wolf Creek overburden sample was disaggregated to pass a 2 mm screen and homogenized. Sulfur fractionation and particle size analyses were performed using an acid-base accounting method (EPA 1978, Schafer and Associates and Reclamation Research 1987) and the hydrometer method (Day

1965), respectively. In addition, a post-soxhlet leaching acid-base account/sulfur fractionation analysis was performed on a homogenized bulk sample derived from the three replicates of each treatment and the control.

A saturated paste extract was also obtained and analyzed for pH and EC. A 5 ml aliquot of the extract was filtered through a 0.45 micron cellulose nitrate filter and preserved with 7 N HNO_3 to pH < 2.0. Inductively Coupled Plasma (ICP) spectroscopy was employed for the analysis of the total concentration of all metals (Al, Ca, Fe), phosphorous (P) and sulfur (S) in solution. X-ray diffraction (XRD) analysis was also performed on the clay fraction (< .002 mm).

Amendment Materials

Four regional phosphate sources and a commercially available phosphate fertilizer (Triple Superphosphate) were evaluated for their ability to control acid production from the Wolf Creek overburden. A sixth source procured from Texas Gulf Chemical of Aurora, South Carolina, had been utilized in previous studies (Renton et al 1988b) and was used as a comparison against which the effectiveness of the regional sources could be evaluated.

All regional sources were crushed and sieved through a 60 mesh (0.25 mm) screen. Texas Gulf ore was received in a condition where > 90% passed through a 150 mesh (0.105 mm). Triple Super Phosphate (TSP) fertilizer was received and applied in prill form.

Each source was analyzed for total P (Horwitz 1980), total surface area using the BET N_2 adsorption isotherm technique (Mortland and Kemper 1965), crystallographic morphology and particle size range using a scanning electron microscope (SEM) (Kittrick 1965) and elemental chemical composition by energy dispersion analysis of X-rays (EDAX). Amendments (< 0.25 mm) were mounted on an aluminum stub and plated with Au prior to microscopic examination. Selected fields of view and individual amendment particles from the stub were subjected to EDAX analysis concurrent with SEM examination. Powder mount X-ray diffraction analysis was performed to indicate whether carbonates were present in the amendments. Solubility of P and S versus pH was also determined using potassium biphthalate-HCl and potassium biphthalate-NaOH buffer solutions at pH values of 2.2, 3.0, 4.0, 5.0 and 5.9. Total P and S were determined by ICP spectroscopy.

Phosphate Source Location

The Cominco *ore* sample is apatite ore mined from the Permian Phosphoria Formation by the Cominco fertilizer company near Garrison, Montana. Cominco *waste* is a byproduct of the washing of crushed ore (< 1.6 mm; 1/16 inch) and contains a relatively high percentage of aluminosilicate clays. Both products are available from the Cominco fertilizer plant near Garrison, Montana.

The Stauffer *ore* is apatite mined in southeastern Idaho from the Permian Phosphoria Formation and procured by the Stauffer Chemical Company (now

Rhone-Poulence). Stauffer *sludge* is a dried slurry material which is the byproduct of elemental phosphate production at the Stauffer (Rhone-Poulence) Plant in Silver Bow, Montana. Triple Super Phosphate (TSP) is a commercially available calcium phosphate fertilizer.

Texas Gulf phosphate is processed apatite rock crushed so that > 90 % is < 150 mesh (0.105 mm) and was procured from Texas Gulf Chemical in Aurora, North Carolina.

Experimental Procedure

Amendment Evaluation

Each regional phosphate source and the triple superphosphate was added to 200 grams of Wolf Creek overburden at a rate equivalent to 18.5% P by weight. This value represents the amount of P by weight in 1 mole of pure hydroxy apatite ($Ca_5(PO_4)_3OH$). To each sample was added 100 ml of distilled water and a few drops of AMD containing Thiobacillus ferrooxidans. The samples were stirred, covered and allowed to equilibrate for three days.

Following equilibration, another 100 ml of distilled water was added and the samples were placed in CARWA. This apparatus subjects the samples to 6 complete cycles of leaching, each consisting of wetting the sample with 200 ml of distilled water, 45 minutes of agitation, 45 minutes of aeration (oxidation) and a 30

minute extraction period. For a more complete description of CARWA and its operating procedures, refer to Harvey and Dollhopf (1986).

Leachates were collected after each cycle for a total of six leachates per sample. All leachates were analyzed for pH, titratable acidity and SO_4^{2-}. All samples were brought to a boil prior to determination of titratable acidity using 0.1 and 0.01 N NaOH. Concentrations of SO_4^{2-} were determined turbidimetrically (Rhoades 1982).

Phosphate Source Rate Determination

Based on the results of the phosphate source evaluation experiment, four sources were chosen for application rate determination utilizing the soxhlet leaching experiment: Cominco ore, Cominco waste, Stauffer sludge and Texas Gulf ore.

A 143 mm soxhlet extraction apparatus was utilized for this part of the study. The soxhlet apparatus consists of a round 500 ml pyrex flask into which a pyrex extraction chamber, which contains the sample, is fitted. A pyrex condenser is fitted to the top of the extraction chamber. Distilled water is added to the flask, which is placed in a heat mantle. The water is brought to a low, steady boil. Steam rising from the flask enters a vapor bypass tube on the side of the extraction chamber and rises into the condenser. The steam is condensed and drips back onto the sample in the extraction chamber. When the water (leachate) level in the extraction chamber reaches capacity, it drains via a syphon tube back into the flask

and the cycle is repeated. In this study, 300 ml of distilled water were placed in the flask prior to heating and initiation of the leaching cycle.

All phosphate sources (amendments) were added to 100 g samples of Wolf Creek overburden. The Cominco waste and Stauffer sludge were applied in three rates equivalent to 1%, 3% and 5% apatite (based upon 18.5 % P in apatite) by weight. Cominco ore was applied at 3% apatite by weight to allow comparisons between a waste product and the ore from which it was derived. Texas Gulf ore was also applied at 3% apatite by weight and, as mentioned earlier, would serve as a comparison for which data already existed and evaluations could be made against the regional sources. An unamended control was also established and all treatments were run in triplicate. Amendment application rates are shown below in Table 1.

Table 1. Application rates and phosphorous content of amendments.

Treatment	Application Rate % apatite	Amount Added (g/100g overburden)	Phosphorous %
Control	0	0.00	0.0
Cominco ore	3	5.04	11.0
Cominco waste	1	2.18[1]	8.5
Cominco waste	3	6.53	8.5
Cominco waste	5	10.90	8.5
Stauffer sludge	1	2.68	6.9
Stauffer sludge	3	8.04	6.9
Stauffer sludge	5	13.40	6.9
Texas Gulf ore	3	4.08	13.6

1. Amount Added = (%P in pure hydroxy apatite / %P in amendment) (Application Rate)
= (18.5 %P / 8.5 %P) (1) = 2.18

All amended overburden samples were thoroughly mixed and placed in 143 x 45 mm cellulose thimbles. The thimbles were placed in a soxhlet extraction apparatus and subjected to a 24 hour leach period. Previous work by Renton et al (1988a) had shown that greater than 90% of all leachable products are removed within 16 to 20 hours. A 24 hour period was chosen for convenience.

Leachate Analysis

After 24 hours of leaching, the leachates were collected and the thimbles containing the overburden were placed in 400 ml pyrex beakers. The beakers were then placed in a drying oven at 105 C for 14 days to allow the sample to reoxidize. Renton et al (1988a) had established that greater than 90% of oxidation had occurred within 12 days and a 14 day drying period was also chosen for convenience. After 14 days samples were again placed in the soxhlet apparatus and subjected to another 24 hour leaching period. This drying (oxidation)/leaching cycle was repeated 4 times, including an initial 24 hour leaching period. For a more detailed description of the procedure outlined above, refer to Renton et al (1988a).

Leachate volume was recorded after each leaching period and the leachate was gravity filtered with a Whatman #4 qualitative filter to remove any precipitates which may have formed. The leachate was allowed to cool to room temperature and was measured for EC and pH. A 20 ml aliquot was then drawn off and filtered through a 0.45 micron cellulose nitrate filter and preserved with 1 ml of 7 N HNO_3 to pH < 2.0. This aliquot was then analyzed for total dissolved Ca, Fe,

P and S using ICP spectroscopy. Dissolved S was taken to be a direct measurement of SO_4^{2-}-S and associated acid production [1], [4] (Renton et al 1988a) and would serve as a way of comparing the effectiveness of each treatment.

Preliminary analysis of selected subsamples using ion chromatography (IC) analysis was compared to ICP results and indicated that greater than 90% of total dissolved S was in the form of SO_4^{2-}. Therefore, ICP analysis for S was utilized for the remainder of the experiment.

Ion chromatography results for PO_4^{3-} were inconclusive due to the high concentrations of SO_4^{2-} and low concentrations of PO_4^{3-} in solution. However, ICP results indicated that levels of P in the amended samples were not substantially elevated with respect to the control or high enough to warrant concern and ICP was chosen for P analysis for all leachate samples.

A 30 ml aliquot of leachate was drawn off for determination of titratable acidity. To each aliquot was added 5 drops of 30% hydrogen peroxide (H_2O_2) to insure that all Fe would be in the Fe^{3+} form. Each sample was then boiled for 2 minutes to insure complete oxidation and to remove any excess H_2O_2.

After allowing the samples to cool, a 20 ml aliquot was drawn off and titrated to pH 7.0 endpoint with 0.01 N NaOH.

Phosphorous and Sulfur Solubility Determination

Two grams of each of Cominco ore, Cominco waste, Stauffer ore, Stauffer sludge and Texas Gulf ore were placed in potassium phthalate - hydrochloric buffer solutions of pH 2.2, 3.0 and 4.0 and potassium phthalate - sodium hydroxide buffer solutions of pH 5.0 and 5.9 and allowed to equilibrate for 2 days. The experiment was run with duplicate samples. The pH of each sample was recorded at 24 and 41 hours after the initiation of the experiment to verify equilibrium conditions. Buffer pH values had risen, possibly due to the liberation of OH^- associated with the dissolution of hydroxy apatite. Linear regressions were run to determine solubilities at the desired pH values [H^+] for P and S.

Solution from the samples was filtered through a 0.45 micron cellulose nitrate filter and preserved with 6 N HCl to pH < 2.0. Samples were then analyzed for total phosphorous and sulfur by the ICP method.

Calcium carbonate equivalents were determined for Texas Gulf ore. Twenty (20) ml of 6 N HCl were pipetted into a beaker. The beaker and solution were weighed. Two (2) grams of Texas Gulf ore were then added to the beaker, causing a violent fizzing. The resulting solution was covered to prevent evaporation and allowed to equilibrate for 24 hours. The beaker and its contents were then weighed again. The difference between the original weight, accounting for the 2 grams of ore added, and the final weight was attributed to loss of CO_2. This result was converted to calcium carbonate equivalents.

RESULTS AND DISCUSSION

Amendment Selection

The leachate chemistry resulting from the CARWA amendment selection experiment using the four regional phosphate sources and Triple Superphosphate fertilizer are summarized in Table 2. Values represent the sum of all six CARWA cycles for the Wolf Creek overburden sample.

Table 2. CARWA leachate chemistry from treated Wolf Creek overburden.

Treatment	SO_4^{2-}	Acidity(as $CaCO_3$)
	(mg/l)	
Cominco ore	27154	18423
Cominco waste	28260	23789
Stauffer ore	23402	20749
Stauffer sludge	17848	15807
Triple superphosphate	-----	32701

Based upon the results of the acidity determination, Triple Superphosphate was disqualified as a candidate for rate determination because of its poor performance relative to the other treatments. It was therefore not analyzed for SO_4^{2-}. The Cominco ore-treated sample resulted in the production of less acidity than the sample treated with Stauffer ore, but had considerably higher levels of SO_4^{2-}. The Cominco ore was nonetheless chosen for further study because of its greater phosphorous content (11 % vs. 9.2 % for the Stauffer ore).

The Stauffer sludge was chosen for further rate determination studies based on the merits of its ability to reduce both SO_4^{2-} and acidity production compared to the other treatments. The Cominco waste, though not as effective as the other treatments at reducing SO_4^{2-} and acidity levels, was chosen for further study because it is a waste product and should therefore be considerably less expensive to obtain than a phosphate ore. It might therefore prove to be a more economically feasible amendment.

The Texas Gulf ore was chosen, as mentioned previously, because its effects on the reduction of acid production from coal waste had been studied earlier (Renton et al 1988b). These results could be used as a measure against which the effectiveness of the regional sources could be compared.

Overburden Characterization

Important physical and chemical properties of the Wolf Creek overburden include particle size distribution, saturated paste extract chemistry, acid-base account/sulfur fractionation and X-ray diffraction analysis of the clay (< .002 mm) fraction. Results of these analyses, excluding X-ray diffraction analysis, are presented in Tables 3, 4 and 5, respectively.

X-ray diffraction analysis of the clay fraction of the Wolf Creek overburden indicated that the majority of the clays are comprised of kaolinite (68%) and randomly interstratified mica-vermiculite with traces of smectite (32%). This

suggests, in conjunction with the relatively low clay content, that exchange reactions do not play a major role in affecting leachate chemistry.

Table 3. Particle size distribution in the Wolf Creek overburden.

Particle Size (mm)	Textural Class	Relative % in Sample
2.0 - 0.05	sand	3
0.05 - 0.002	silt	90
< 0.002	clay	7

Table 4. Saturated paste water extract chemistry of Wolf Creek overburden.

pH	EC mmhos/cm	Ca	Fe	P	S	Al
		mg/l				
2.15	15.73	616	21250	926	33680	6129

Table 5. Sulfur fractionation and acid-base account analyses of Wolf Creek overburden.

Total S (%)	1.72
Hot Water Extractable S (%)[1]	0.72
HCl Extractable S (%)[2]	0.18
HNO_3 Extractable S (%)[3,5]	0.71
Residual S (%)[4,5]	0.11
Neutralization Potential (t/1000t)	<1.00
Acid Potential (meq/100g)	59.76
Acid-Base Account (t/1000t)[6]	-29.38

1. water soluble sulfates
2. non-water soluble sulfates
3. pyritic sulfur
4. Total S - sum(1,2,3)
5. sum of 3 and 4 = total pyritic sulfur
6. ABA = NP - [HCl-S(23.44) + FeS_2-S(31.25)]; if NP < 1, let NP = 0.5.

Leachate Chemistry

Results of the five soxhlet leaching cycles are shown in Table 6. Treatment means, percent reduction of analytical parameters versus the control and significance classes are presented. Negative values represent an increase in a given parameter versus the control. An analysis of variance and determination of least significant difference (p=.05) were performed on cumulative data (sum of replicates for cycles 1 through 5) (Figures 1 through 3) as well as on data from each cycle (Figures 4 through 6).

It is also relevant to note at this time that there was considerable variation between replicates for some treatments. This was most likely due to discrepancies in heating and degree of leaching between individual soxhlets and is believed to have had a negligible effect on the cumulative measured response to each treatment. Where appropriate, these variations will be discussed. Data for all leachates produced are shown in Appendix A.

Cumulative Response to Amendments

All treatments resulted in a significant (p=.05) reduction in total sulfur (S) (assumed to be SO_4^{2-}; see MATERIALS AND METHODS-Amendment Materials), iron (Fe) and acidity concentrations compared to the control, with the exception of the Cominco ore at 3% and the Cominco waste at 1%. These two treatments did not significantly reduce sulfur levels (Figures 1 through 3). The Cominco ore also did not significantly reduce Fe levels.

Table 6. Cumulative leachate ion concentrations, % reduction versus control and significance (p=.05) levels.

Treatment (% apatite)	Fe	S	Acidity	Ca	P	EC	pH
	Average ; % Reduction						
	mg/l					mmhos/cm	
Control	1414[1] 0[2]	3695 0	9424 0	713 0 a[6]	10.8 0 a	4.16[3] 0 c	2.41[4] 0 e
Cominco ore (3%)	1299 8	3482 6	8187 13	868 -22[5] b	28.3 -161 bcd	3.75 10 bc	2.38 -8 f
Cominco waste (1%)	1181 16	3681 0	8783 7	918 -29 bc	27.8 -157 bcd	4.03 3 c	2.33 -20 g
Cominco waste (3%)	1029 27	3362 9	8060 14	893 -25 bc	25.5 -136 bc	3.69 11 bc	2.39 -4 ef
Cominco waste (5%)	1015 28	3423 7	7675 19	1004 -41 c	30.7 -183 cd	3.67 12 bc	2.41 0 e
Stauffer sludge (1%)	1041 16	3300 11	7673 19	979 -37 bc	21.0 -94 b	3.65 12 bc	2.51 20 d
Stauffer sludge (3%)	709 50	2960 20	5235 44	1405 -97 d	34.8 -222 c	3.36 19 ab	2.79 58 c
Stauffer sludge (5%)	522 63	2785 25	4460 53	1465 -105 d	29.4 -172 cd	3.82 7 bc	3.07 78 a
Texas Gulf ore (3%)	539 62	2744 26	3086 67	1501 -110 d	62.2 -474 e	2.81 32 a	2.87 65 b

1. table values are means of the 5 cycle (15 replicate) means.
2. % reduction versus control.
3. average values for EC are the means of the sum of the 5 cycle means.
4. average values and % reduction calculated from actual $[H^+]$.
5. note: negative (-) values denote increase relative to control.
6. values marked with same letters are not significantly different at p=.05 level.

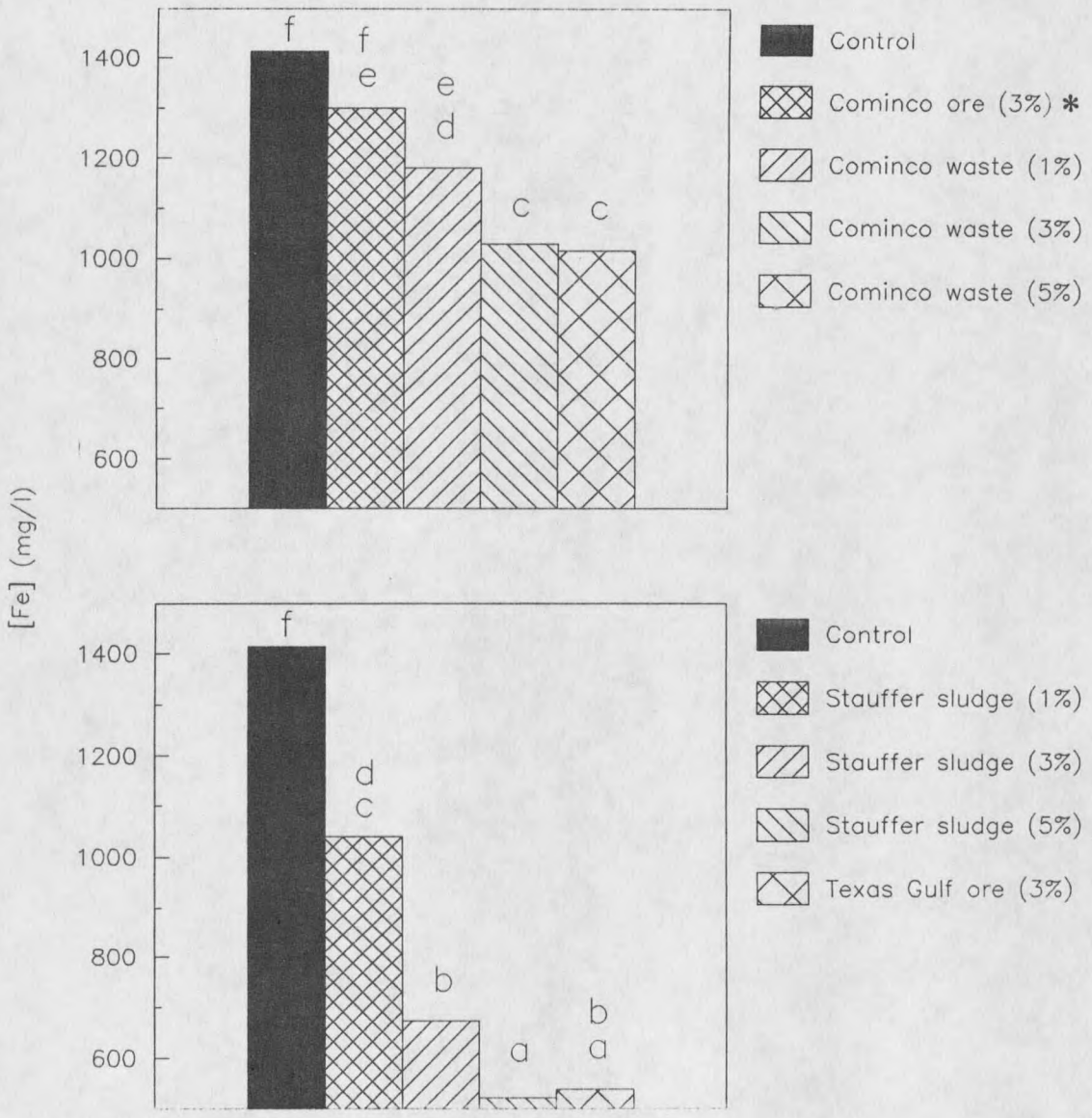

Figure 1. Effect of phosphate treatments on overburden leachate iron levels. Bar values capped with same letter are not significantly different at the p = .05 level. Comparisons of significance can be made between all treatments. * Amendment rates are % apatite.

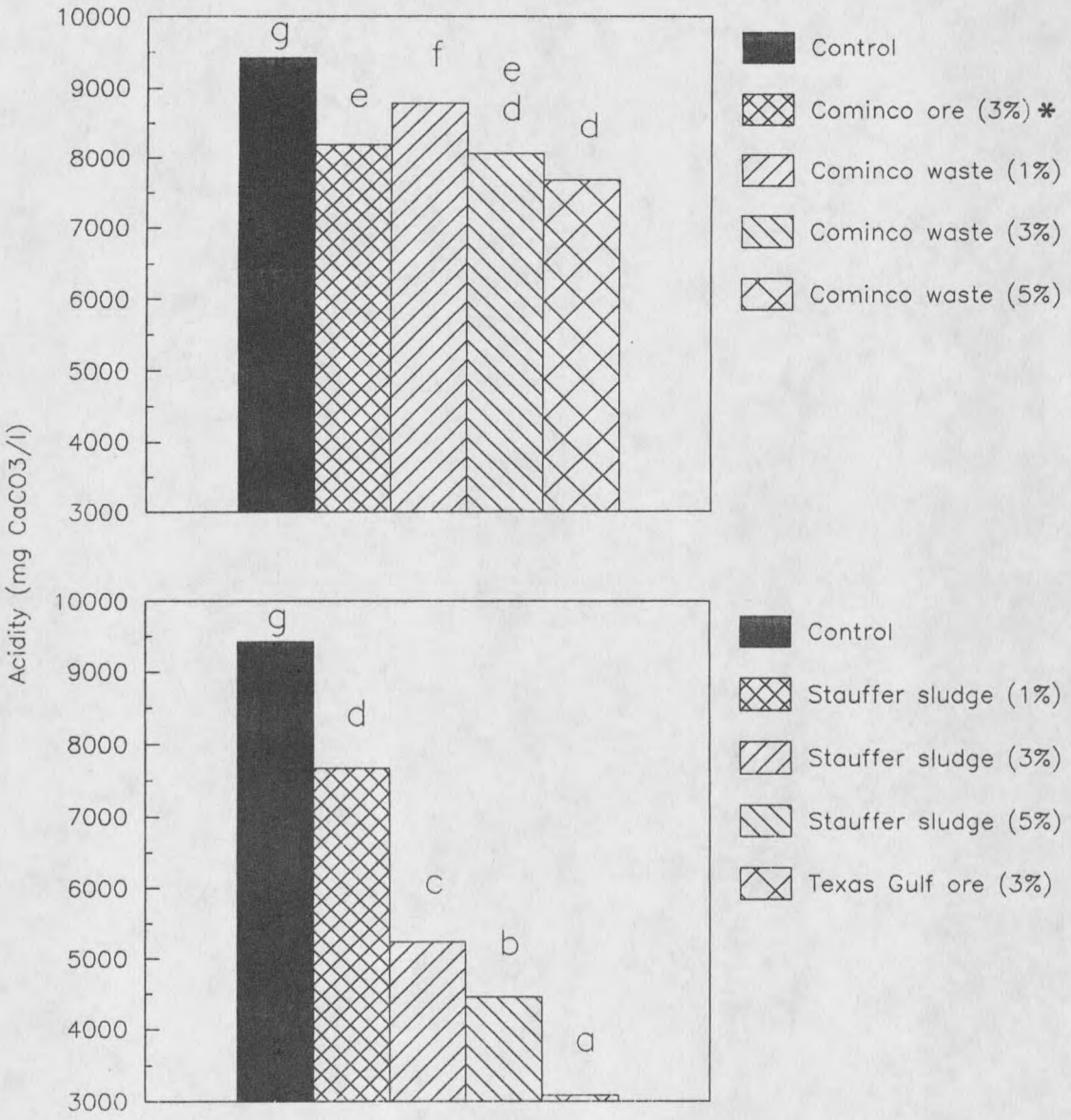

Figure 2. Effect of phosphate treatments on overburden leachate acidity levels. Bar values capped with same letter are not significantly different at the p = .05 level. Comparisons of significance can be made between all treatments. * Amendment rates are % apatite.

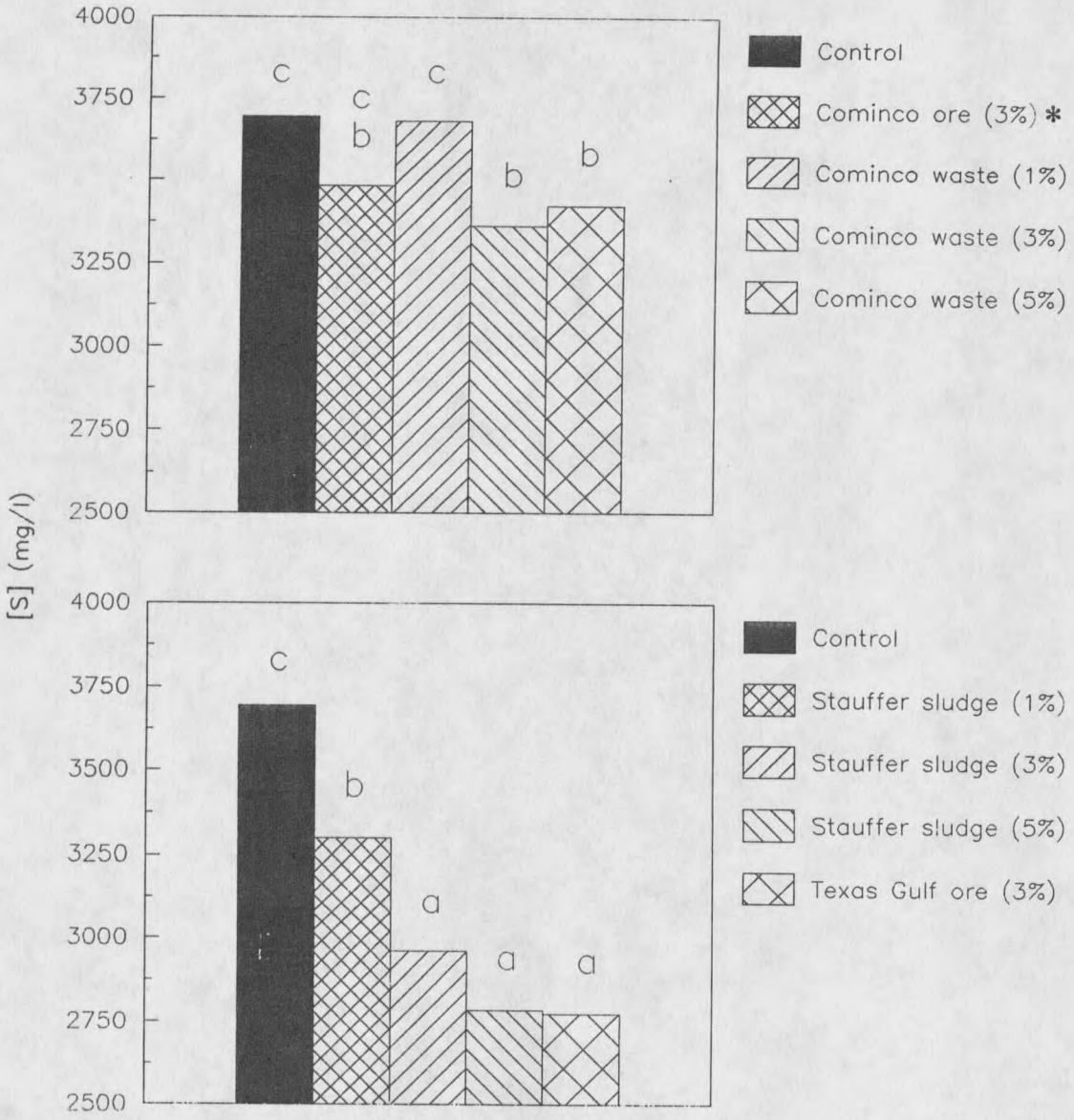

Figure 3. Effect of phosphate treatments on overburden leachate sulfur levels. Bar values capped with same letter are not significantly different at the p = .05 level. Comparisons of significance can be made between all treatments. * Amendment rates are % apatite.

Among the treatments, Stauffer sludge at applications of 5% and 3% and Texas Gulf ore at 3% were significantly more effective than the remaining treatments, resulting in Fe reductions of 63%, 50% and 42% and S reductions of 20%, 25% and 26%, respectively. Texas Gulf ore was significantly more effective than all other treatments at reducing acidity (67%), followed by Stauffer sludge at 5% (53%) and Stauffer sludge at 3% (44%).

Only samples treated with Stauffer sludge at all application rates and Texas Gulf ore significantly increased pH levels, although in all cases the rise in pH was less than 1 log unit compared to the control. Texas Gulf ore and Stauffer sludge at 3% were the only treatments which significantly reduced EC values compared to the control, although all treatments led to a decline in average EC values. The order of amendment performance at reducing EC levels mirrored that observed for S levels.

All treatments resulted in significantly higher concentrations of calcium (Ca) and phosphorous (P) (assumed to be PO_4^{3-}; see MATERIALS AND METHODS - Amendment Materials) relative to the control. Those amendments proving most successful at reducing Fe, S and acidity, namely Stauffer ore at 5% and 3% and Texas Gulf ore at 3%, resulted in the greatest concentrations of Ca in leachate. Samples treated with Texas Gulf ore had much higher P (significant at $p = .05$) concentrations than those treated with any other amendment.

It is also relevant to discuss the affect of amendment application rate on leachate chemistry at this time. Stauffer sludge at an application rate of 5% P was significantly more effective at reducing Fe and acidity than a 3% application rate, and both of these sludge rates caused significant reductions in Fe, acidity and S relative to a 1% rate of application. Applications of Stauffer sludge and Texas Gulf ore also resulted in significantly lower concentrations of Fe, acidity and S than samples treated with Cominco waste and Cominco ore at comparable application rates. The single exception to this trend was observed in leachate Fe concentrations from samples treated with Stauffer sludge at 1%, which were not significantly different than those treated with Cominco waste at this rate. Applications of Cominco waste at 3% produced a greater diminution in Fe levels than Cominco ore at 3%. It is also worthy to note that Stauffer sludge at 1% performed as well as Cominco waste at 3% and 5% application rates at reducing Fe, S and acidity levels.

These results, in which higher application rates of the Stauffer sludge and Cominco waste result in lower levels of Fe and acidity in leachate suggest that it is a mass action process which governs the success of the phosphate amendments and also indicates that the response to the application of phosphate is quite rapid, as is evidenced by the significant initial declines in Fe, S and acidity values in overburden samples treated with Stauffer sludge and Texas Gulf ore. Specific factors and mechanisms affecting amendment performance will be addressed in later sections.

Cyclic Response to Amendments

The results of leachate analysis from each leaching cycle are discussed below. The primary purpose of this discussion is to point out abberations and trends which developed as leaching progressed. Iron, S and acidity concentrations as well as significance ranking for each cycle are shown in Figures 4 through 6. Although not presented graphically or in tabular form, statistical analysis of Ca, P, EC and pH levels were performed and will be discussed for cyclic data. For actual measured levels of these parameters, refer to Appendix A.

Cycle 1

Results from the first leaching cycle exhibit trends very similar to the cumulative response to amendments discussed above. Specifically, Stauffer sludge at 3% and 5% and Texas Gulf ore at 3% were the most significantly effective treatments at reducing Fe, S and acidity. Cominco waste at 1% and Cominco ore at 3% did not significantly reduce Fe compared to the control. Stauffer sludge at all rates of application and Texas Gulf ore produced significantly greater increases in pH levels, with Stauffer sludge at 5% resulting in an increase of 0.58 log units relative to the control.

Stauffer sludge at 3% and 5% and Texas Gulf ore at 3% application rates were also the most significantly effective treatments at lowering EC levels, with Stauffer sludge at 1% the only other treatment to significantly affect EC. As was

the case for the cumulative response to treatments, EC performance by treatment mirrored that observed for S.

All treatments significantly increased Ca concentrations in leachate, but only Stauffer sludge at 3% and 5% and Texas Gulf ore at 3% significantly increased P levels.

It should be noted that Stauffer sludge significantly outperformed Cominco waste and ore at reducing concentrations of Fe, S and acidity at comparable rates of application. In fact, Stauffer sludge at 1% was better than Cominco waste at decreasing Fe levels and resulted in significantly lower concentrations of acidity than Cominco waste at 3%. Stauffer sludge at 1% also significantly reduced Fe, S and acidity concentrations compared to Cominco ore at 3%. Cominco waste at all rates of application was better at reducing Fe than Cominco ore at 3%. It is also important to note that approximately 63% of all solutes were leached during this cycle, having a significant impact on the cumulative results.

Cycle 2

Concentrations in leachate of all analytical parameters were much lower in cycle 2 than in cycle 1 for all treatments, including the control (Figures 4 through 6). This is due to a large release of soluble salts and ions during the initial leaching cycle and is not indicative of any treatment effects.

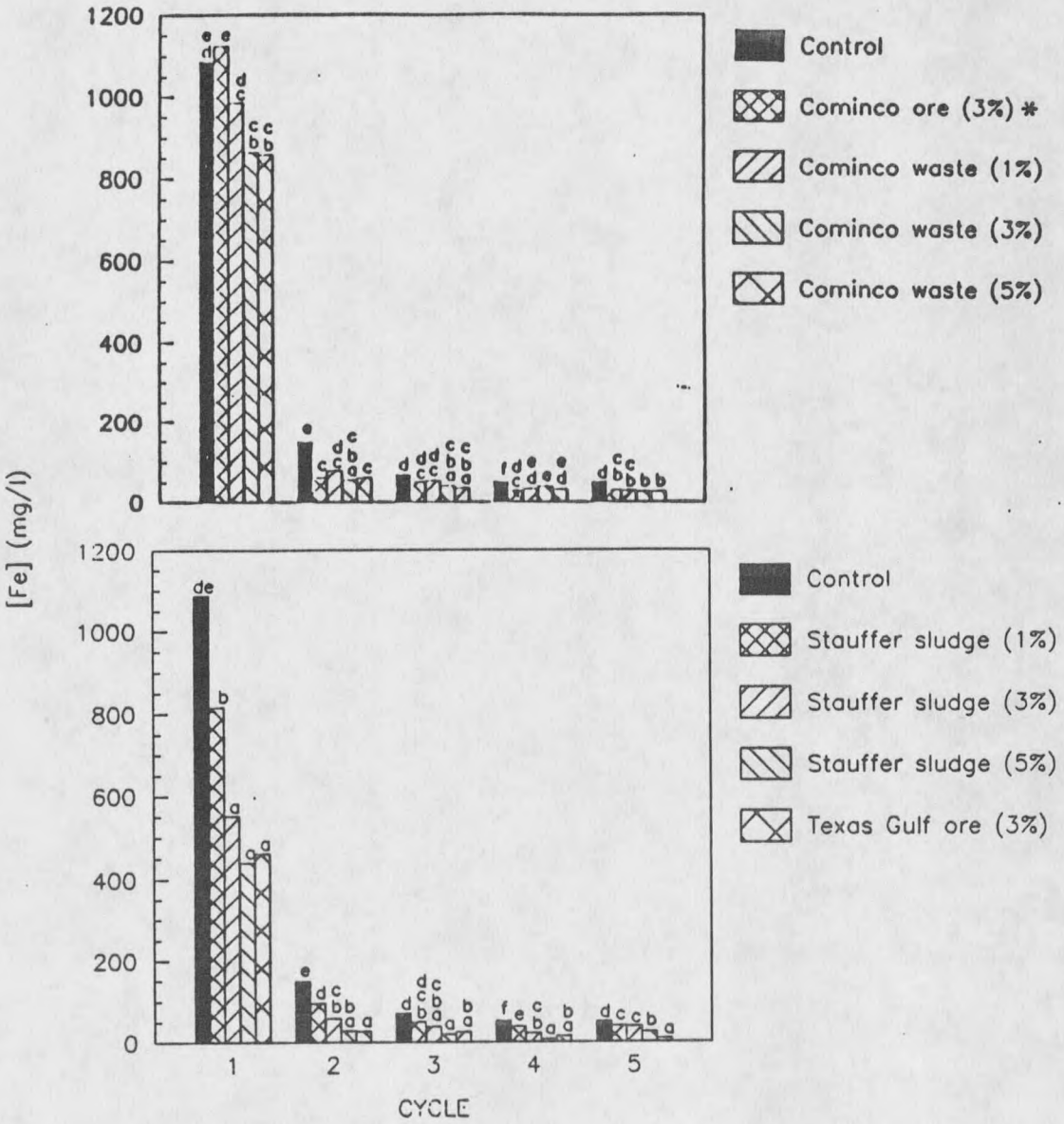

Figure 4. Effect of phosphate treatments on overburden leachate iron concentrations for each leaching cycle. Bar values capped with the same letter are not significantly different at the p = .05 level. Comparisons of significance can be made between all treatments. * Amendment rates are % apatite.

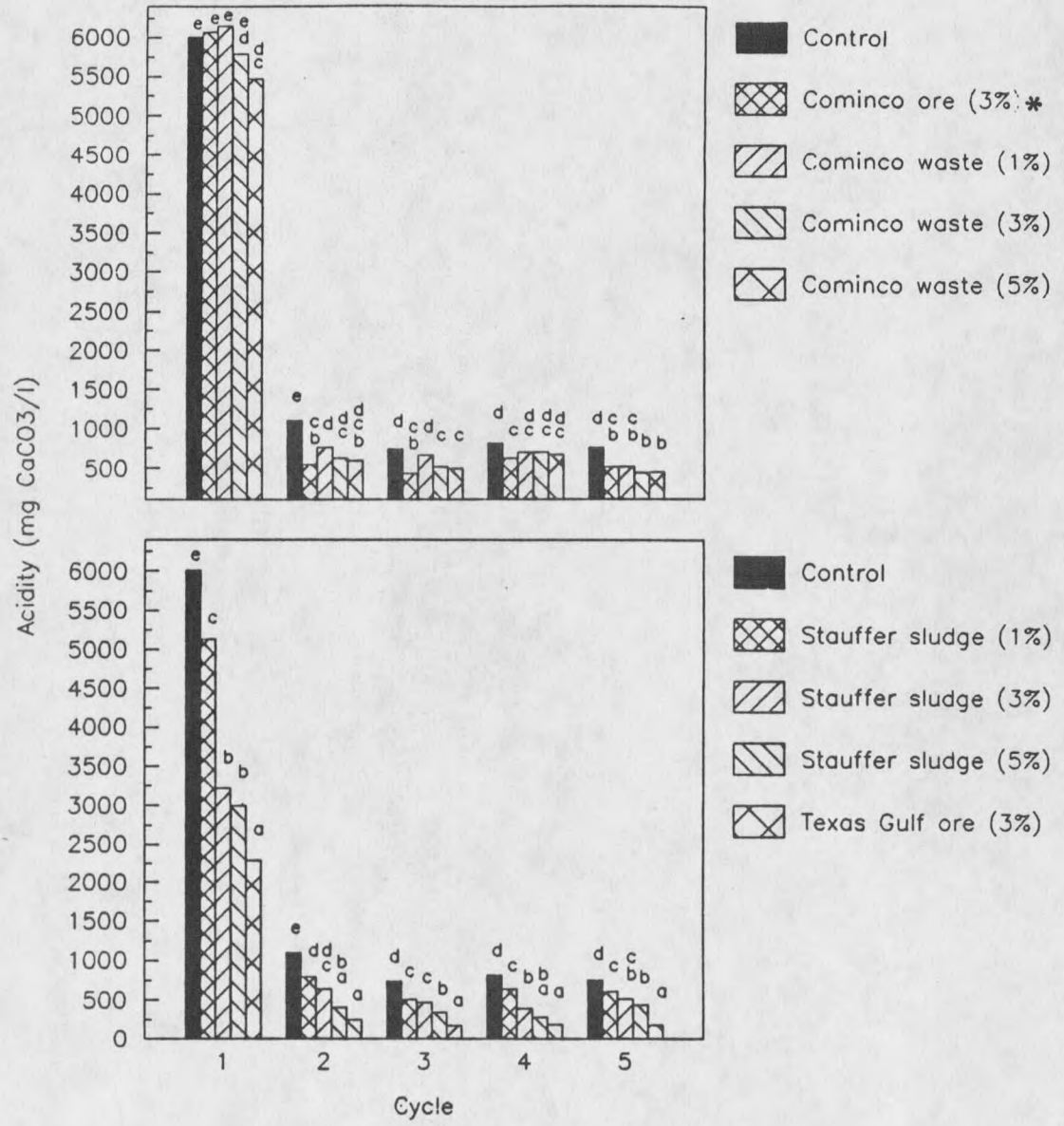

Figure 5. Effect of phosphate treatments on overburden leachate acidity concentrations for each leaching cycle. Bar values capped with the same letter are not significantly different at the p = .05 level. Comparisons of significance can be made between all treatments. * Amendment rates are % apatite.

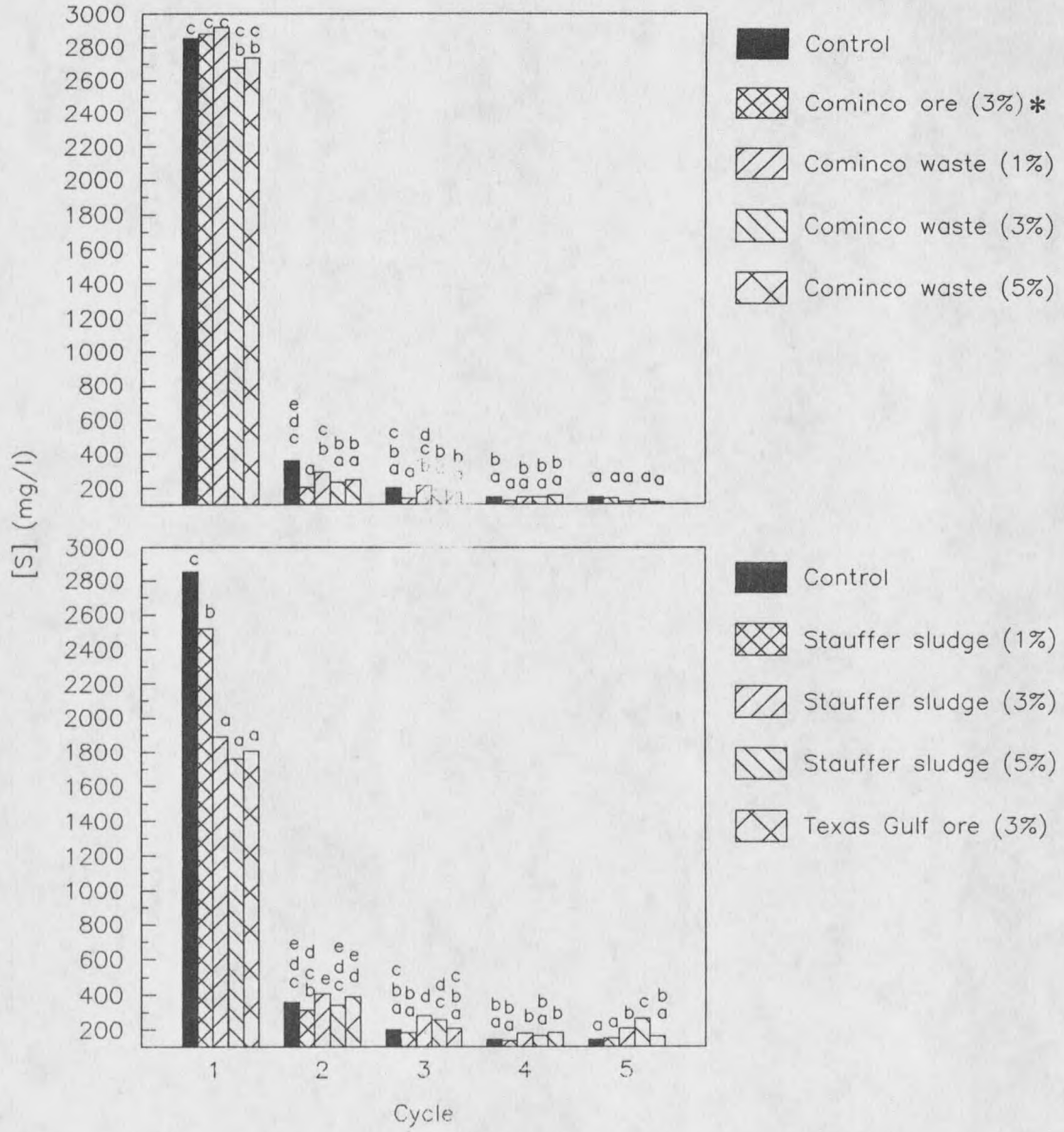

Figure 6. Effect of phosphate treatments on overburden leachate sulfur concentrations for each leaching cycle. Bar values capped with the same letter are not significantly different at the p = .05 level. Comparisons of significance can be made between all treatments. * Amendment rates are % apatite.

Compared to the control, all treatments resulted in significant reductions in Fe, acidity and EC levels and increases in pH values, with the exception of Stauffer sludge at 3%, which did not significantly reduce EC levels. Texas Gulf ore was the most effective treatment at reducing Fe and acidity in leachate. The application of Stauffer sludge at 5% also considerably lowered Fe and acidity concentrations. The Texas Gulf ore treatment at 3% resulted in much greater concentrations of Ca and P in leachate than any of the other treatments.

The most notable distinction between cycles 1 and 2 was observed in the S results (Figure 6). Only Cominco ore at 3% and Cominco waste at 3% and 5% significantly lowered leachate S concentrations versus the control, with Cominco ore producing the most notable S reductions. This is interesting because neither of these amendments produced a significant response in cycle 1. Also, Stauffer sludge at 3% and 5% and Texas Gulf ore at 3%, which were the most effective treatments at reducing S concentrations in cycle 1, did not significantly affect S levels in this cycle, although they maintained their effectiveness at reducing Fe and acidity. This discrepancy was also apparent in later cycles and may be due in part to a contribution of S to the leachates from the amendments themselves. This subject will be discussed in greater detail in a later section.

Cycle 3

Samples treated with Stauffer sludge at 3% and 5%, Cominco waste at 3% and 5% and Texas Gulf ore at 3% resulted in significantly reduced Fe

concentrations (Figure 4). Applications of Stauffer sludge at 5% and Texas Gulf ore at 3% produced the most notable reductions in Fe of 73% and 65%, respectively. All treatments with the exception of Cominco waste at 1% led to significant reductions in acidity and increases in pH. The sample treated with Texas Gulf ore at 3% again far outperformed (77% reduction) the other treatments at reducing acidity and resulted in the greatest increase in pH (0.79 log units) and P (1110%). Only samples amended with Stauffer sludge at 3% and 5% and Texas Gulf ore at 3% significantly increased the levels of Ca versus the control. EC values were lowered with respect to the control only for samples treated with Cominco ore at 3%, Cominco waste at 5%, Texas Gulf ore at 3% and Stauffer sludge at 1%. The reason for the lack of a significant reduction and increase in acidity and pH, respectively, in samples treated with Cominco waste at 1% is probably due to excessive leaching. This is evidenced by concurrent elevated Fe, S and EC levels in cycles 2 and 4 relative to this cycle (3).

No treatments led to significant reductions in S, but as was the case in cycle 2, samples treated with Cominco ore at 3% showed the most notable decline (31%) versus the control. Samples treated with Stauffer sludge at 1% actually significantly increased the amount of S in leachate and samples treated with Stauffer sludge at 5%, Cominco waste at 1% and Texas Gulf ore at 3% had considerably higher S values than the control.

Cycle 4

All treatments resulted in significant reductions in Fe levels. Stauffer sludge at 5% was the most effective treatment, with an 85% reduction versus the control (Figure 4). Samples treated with Texas Gulf ore at 3% and Stauffer sludge at 3% also exhibited considerable (72% and 58%, respectively) diminutions in Fe levels.

All treatments except Cominco waste at 1%, 3% and 5% significantly decreased acidity levels, with the Texas Gulf ore again resulting in the largest (77%) declines. It again produced by far the greatest increase in P (1060%) relative to the control. Leachates from samples treated with Stauffer sludge at 3% and 5% and Texas Gulf ore at 3% again yielded the greatest concentrations of Ca. Values for pH were greater than the control for all treatments except Stauffer sludge at 1%. Electrical conductivity was significantly reduced only in samples treated with Cominco ore and Cominco waste at 3% and actually increased significantly in samples treated with Stauffer sludge at 3% and 5%.

As was the case in cycle 3, none of the treatments significantly reduced S levels compared to the control, but samples treated with Cominco ore at 3% had the most notable decline (14%) in S values while those treated with Stauffer sludge at 3% and Texas Gulf ore at 3% resulted in significant increases in S concentrations in leachate.

Cycle 5

Responses to treatments in the final cycle were similar to those observed in previous cycles, excluding cycle 1 (Figures 4 through 6). All treatments produced a significant reduction in leachate Fe levels relative to the Control, and samples treated with Texas Gulf ore at 3% and Stauffer sludge at 5% resulted in the greatest Fe reductions (83% and 52%, respectively). Iron concentrations increased notably from the previous cycle in samples treated with Stauffer sludge at 3% and 5%. However, this is most likely due to an excessively severe leaching cycle, which is evidenced by notable concurrent increases in EC, Ca, P and S concentrations. All treatments also significantly reduced acidity and increased pH, with Texas Gulf ore at 3% again leading to the greatest decreases (74%) in acidity. Samples treated with Stauffer sludge at 5% and Texas Gulf ore at 3% both led to a 0.65 increase in pH versus the control. There was no significant difference between Stauffer sludge and Cominco waste at comparable application rates at reducing acidity. Samples treated with Stauffer sludge at 3% and 5% application rates and Texas Gulf ore at 3% resulted in the highest levels of Ca and P, although the excessive leaching mentioned above must be taken into consideration.

Once again, none of the treatments produced a significant decline in S concentrations. Samples treated with Cominco ore at 3% and Cominco waste at all application rates resulted in actual declines in S concentrations versus the control.

Cyclic Trends

Several general trends can be ascertained from examination of the results of each cycle. It is clear that samples treated with Stauffer sludge at 3% and 5% and Texas Gulf ore at 3% consistently resulted in the lowest leachate Fe concentrations. In general, these treatments also produced the lowest acidity and highest Ca levels. Samples treated with Texas Gulf ore at 3% had the greatest P concentrations in leachate. Electrical conductivity values in leachate for all treatments closely paralleled S leachate values.

The initial response (cycle 1) of S concentrations in leachate to the treatments showed that Stauffer sludge at 3% and 5% and Texas Gulf ore at 3% were the most effective treatments at reducing S, in addition to reducing Fe and acidity. However, while these treatments continued to achieve notable reductions in Fe and acidity levels in later cycles, they did not significantly reduce S levels relative to the other amendments. This trend manifests itself in an obvious discrepancy between the acidity and S results for cycles 2 through 4. In an attempt to resolve this discrepancy, the solubility of S in each amendment at various pH values was measured, in addition to P, to determine how much S was being contributed to leachate by each amendment in excess of that associated with FeS_2 oxidation. Mass balance calculations based on the stoichiometry of FeS_2 oxidation were also performed on leachate data and compared to the initial and post-leaching sulfur fractionation analyses. Results of theses exercises are presented in later sections.

Amendment Solubility and Surface Area Determination

The solubility of an amendment is an important factor in determining its initial and long term effectiveness and overall success. It is also important in the determination of application rates. A relatively soluble amendment will provide a more immediate response and may or may not experience a temporal decrease in effectiveness if it is too readily leached from soil or overburden. Conversely, relatively low solubility in an amendment may inhibit its initial effectiveness but produce a desirable long-term effect. In the case of very low solubility it may even preclude the use of a material as an amendment.

Surface area is another well documented factor affecting the success of an amendment (Motto and Melstad 1960, Renton et al 1988b). Greater surface area results in higher amendment reactivity and, in conjunction with solubility, determines to a large extent the amount of anions (PO_4^{3-}) available for reaction with Fe and other cations. With the objectives of quantifying these important factors, the solubility experiment and surface area determination were performed. In addition it was believed that these data could be used in conjunction with the results of SEM and EDAX analyses to help explain the performance of each amendment.

Phosphorous Solubility

Linear regressions on the results of the phosphate solubility experiment showed a strong positive correlation between $[H^+]$) and P concentrations for all amendments. Phosphorous concentrations at pH 2.0, 3.0, 4.0, 5.0 and 6.0 were calculated from the regression equation and are presented in Table 7 and shown graphically in Figure 7. Surface area determination results are also shown in Table 7. Although not tested in the soxhlet rate determination experiment, the solubility and surface area of the Stauffer ore was determined so comparisons could be made with the Stauffer sludge and insights could be gained into the possible effectiveness of the use of the ore as an amendment.

Table 7. Solubility of P and surface area of amendments used in soxhlet leaching experiment.

Source	r	pH					surface area (m^2/g)
		2.0	3.0	4.0	5.0	6.0	
		P (mg/l)					
Cominco ore	.996	2171	222	28	8	6	3.518
Cominco waste	.999	1493	152	18	5	3	10.211
Stauffer ore	.999	2049	208	25	6	4	13.052
Stauffer sludge	.970	17550	1780	202	45	29	19.907
Texas Gulf ore	.884	37750	3782	385	45	11	19.390

Because the pH values of the leachate throughout the soxhlet experiment were predominantly between 2.0 and 3.5, the discussion of the results of the amendment solubility experiment will focus on this range.

Figure 7 indicates that the solubility of P decreases linearly to pH 4.0 for all amendments with only the Stauffer sludge and Texas Gulf ore yielding

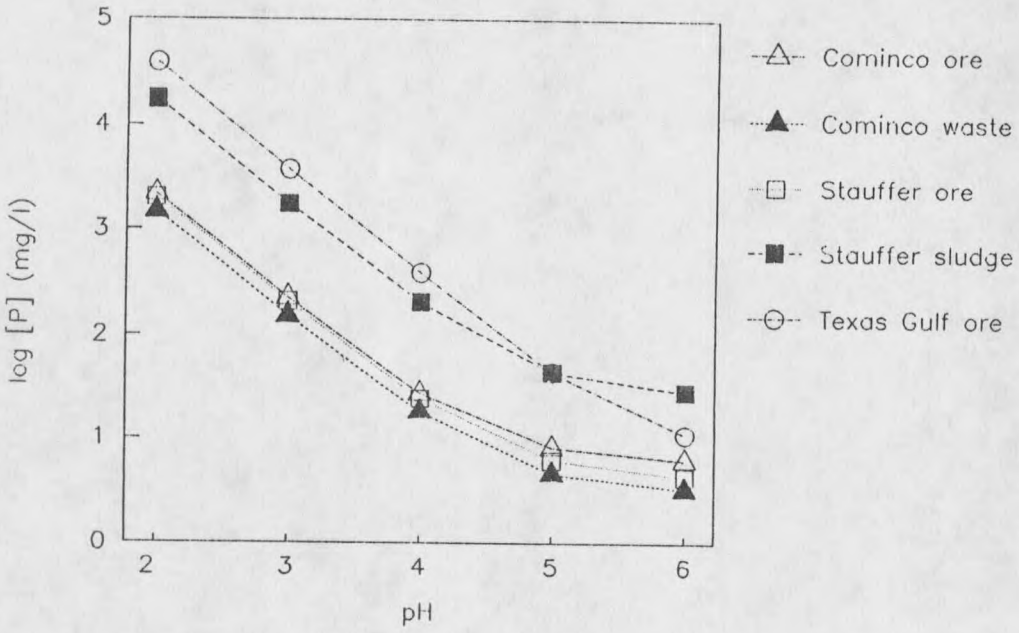

Figure 7. Amendment phosphorous solubility in pH range 2.0 - 6.0.

appreciable amounts of P (202 and 385 mg/l, respectively) into solution. Phosphorous concentrations for all amendments at pH 5.0 are low (5 to 45 ppm). Although these distinctions were not a factor in this experiment due to the lower pH values of the leachates, it is quite possible that they would affect amendment performance if used on materials where the equilibrium pH is 4.0 or greater. Stauffer sludge and Texas Gulf ore have considerably more surface area and are much more soluble at pH 2.0 through 4.0 than the other amendments. These characteristics explain their strong initial (cycle 1) and overall performance at

reducing concentrations of Fe and acidity in leachate and also offer an explanation for the greater concentrations of Ca and P in leachates associated with these amendments. The relatively low (6.9%) P content of the Stauffer sludge may explain its limited effectiveness at an application rate of 1%.

Conversely, lower relative surface area and subsequent lower P solubilities also explains the poorer performance of Cominco waste (1%, 3% and 5%) and Cominco ore at decreasing leachate Fe and acidity levels relative to the Stauffer sludge (3% and 5%) and Texas Gulf ore. Part of the reduction in acidity observed in the amended samples may be due to the liberation of OH^- groups upon the dissolution of hydroxy apatite [6].

$$Ca_5(PO_4)_3OH + 3\ Fe^{3+} + H^+ = 3\ FePO_4 + 5\ Ca^{2+} + H_2O \qquad [6]$$

This claim is supported by the considerable increase in pH of the buffer solutions into which the amendments were placed, particularly the Stauffer sludge and Texas Gulf ore.

Another component in the success of the Texas Gulf ore at reducing acidity relative to the other amendments is most likely due to its inherent neutralizing capacity associated with the presence of basic carbonates ($CaCO_3$ equivalents = .264 gram $CaCO_3$/gram amendment). The presence of calcium magnesium carbonate was verified by powder mount XRD analysis. No carbonates were present in the Cominco or Stauffer phosphate sources as indicated by XRD analysis.

It is also possible that the formation of aluminum phosphates is occurring in the amended samples, thereby reducing acid production associated with the hydrolysis of Al [7].

$$Al^{3+} + H_2O = Al(OH)_3 \qquad [7]$$

This mechanism will be discussed in more detail in a later section.

Sulfur Solubility

Linear regressions run between S solubility and $[H^+]$) for each amendment indicated that the degree of correlation was not strong for any of the amendments with the exception of the Stauffer ore (r = .957). In light of these results, S concentrations are given for actual buffer pH values recorded at the time of solution collection (Table 8).

Table 8. Amendment sulfur solubility (mg/l) at buffer pH value.

Amendment	r	pH	S	pH	S	pH	S	pH	S
Cominco ore	.637	3.01	57	4.13	57	5.06	52	5.93	52
Cominco waste	-.286	2.99	75	4.13	76	5.06	74	5.94	78
Stauffer ore	.957	3.25	7	4.30	4	5.14	4	6.09	4
Stauffer sludge	.794	4.06	108	4.63	106	5.32	95	6.22	87
Texas Gulf ore	-.404	4.77	101	5.09	111	6.10	101	7.60	109

These results suggest that the amendments may be contributing S to leachate in the pH ranges prevalent in the soxhlet leaching experiment. Blatt et al (1972) noted that the average S composition as SO_3 of the Permian Phosphoria Formation,

from which the Cominco and Stauffer amendments originate, is 1.8% by weight. The occurrence of S in apatite is attributed to the substitution of hexavalent S (S^{6+}) as SO_4^{2-} for pentavalent P (P^{5+}) as PO_4^{3-}.

The amount of S contributed by the amendments would constitute a considerable amount of the total S in leachate for cycles 2 through 5, even at the concentrations present in the higher pH environment of the buffers. This assumes that the amendments would be able to continue contributing S throughout all leaching cycles. At the lower pH values, which increase amendment solubilities, and strongly oxidizing conditions prevalent in the leachates, it is likely that S would be present as SO_4^{2-} and be at least as concentrated as in the buffers. This is especially true for the more soluble amendments and is supported by the results of the leachate analysis.

Thus, it is probable that the discrepancy between S and acidity levels in leachate in cycles 2 through 5 is the result of the neutralization capacity of the amendments associated with the release of OH^- during dissolution and, to a lesser extent, the contribution of S from the amendments.

SEM - EDAX Analyses of Amendments

Scanning electron microscope (SEM) photographs of each amendment and the Stauffer ore are presented at 450X and 4700X magnification to illustrate the differences in particle size and morphology of each amendment (Figures 8 and 9).

Low magnification (< 250X) energy dispersive analysis of X-rays (EDAX) showing the general amendment composition (Figure 10) and chemical composition of specific calcium phosphate particles (Figure 11) are presented on the pages following the photographs.

Examination of the photographs on the left hand side (450X) of the following pages indicate that all amendments are similar in particle size range and general morphology. The exception to this observation is the Cominco ore sample, which has a larger, more massive crystalline form. It is also apparent from viewing the photographs in the right hand column (4700X) that the Stauffer phosphate sources, particularly the Stauffer sludge, and the Texas Gulf ore have a loosely agglomerated, almost frambiodal appearance exhibiting many voids and surfaces. The Stauffer ore sample appears similar but seems to have less void space. The Cominco waste sample is very similar to the Stauffer ore in appearance but has a smaller percentage of small particles (Figures 8 and 9, left hand column). It is clearly distinct from the Cominco ore.

These observations complement the results of the amendment solubility and surface area experiment, (Table 7) which shows that the Stauffer sludge and Texas Gulf ore have the greatest surface area, followed by the Stauffer ore, Cominco waste and Cominco ore. In addition, it is important to note that there is a predominance, relative to the other phosphate sources, of the purest calcium

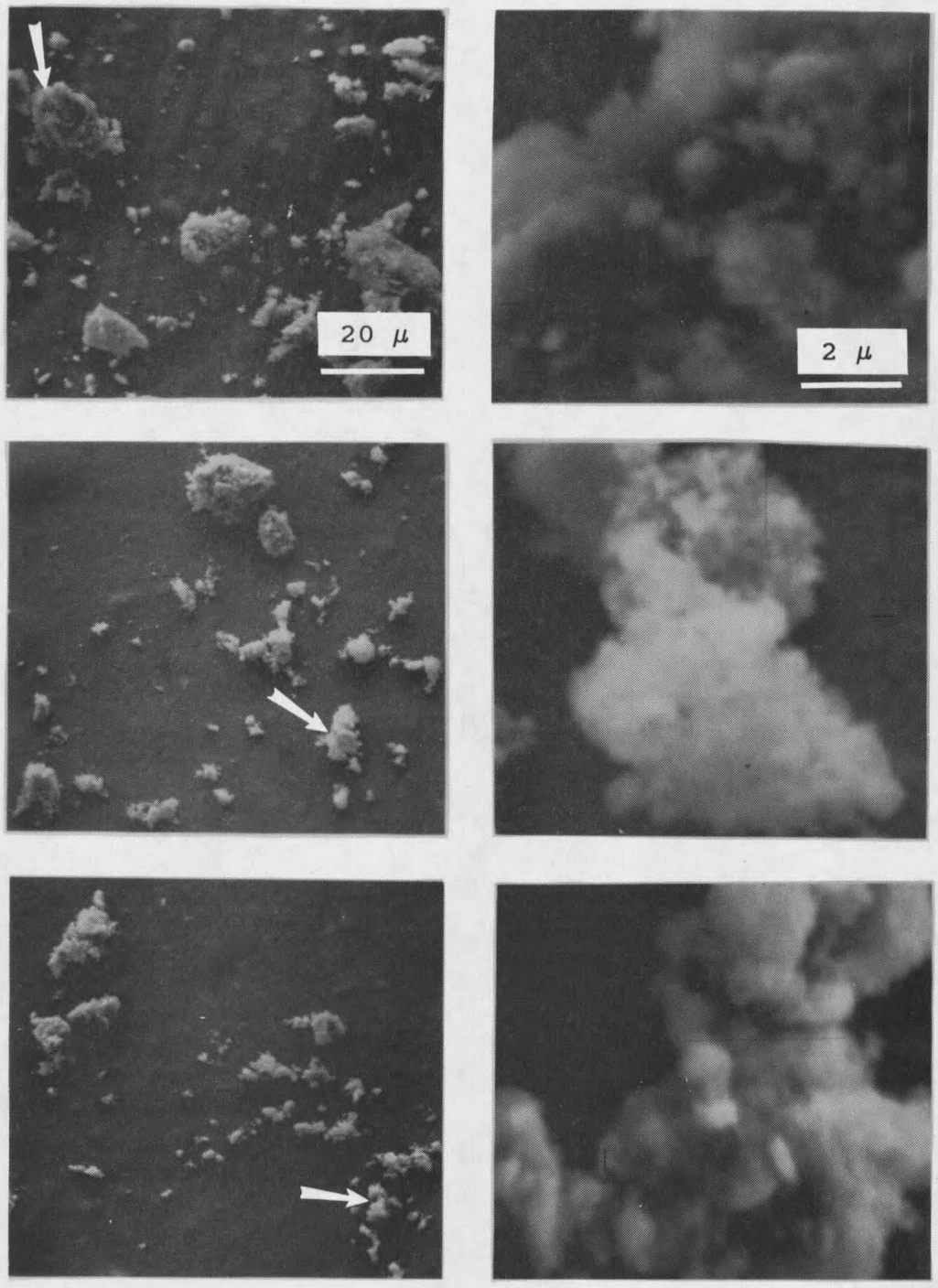

Figure 8. Scanning electron microscope photographs showing particle size range and morphological characteristics of phosphate amendments at 450X (left) and 4700X (right) magnification. Top: Stauffer ore; middle: Stauffer sludge; bottom: Texas Gulf ore. Photographs on right are closeups of particles shown by arrow on left.

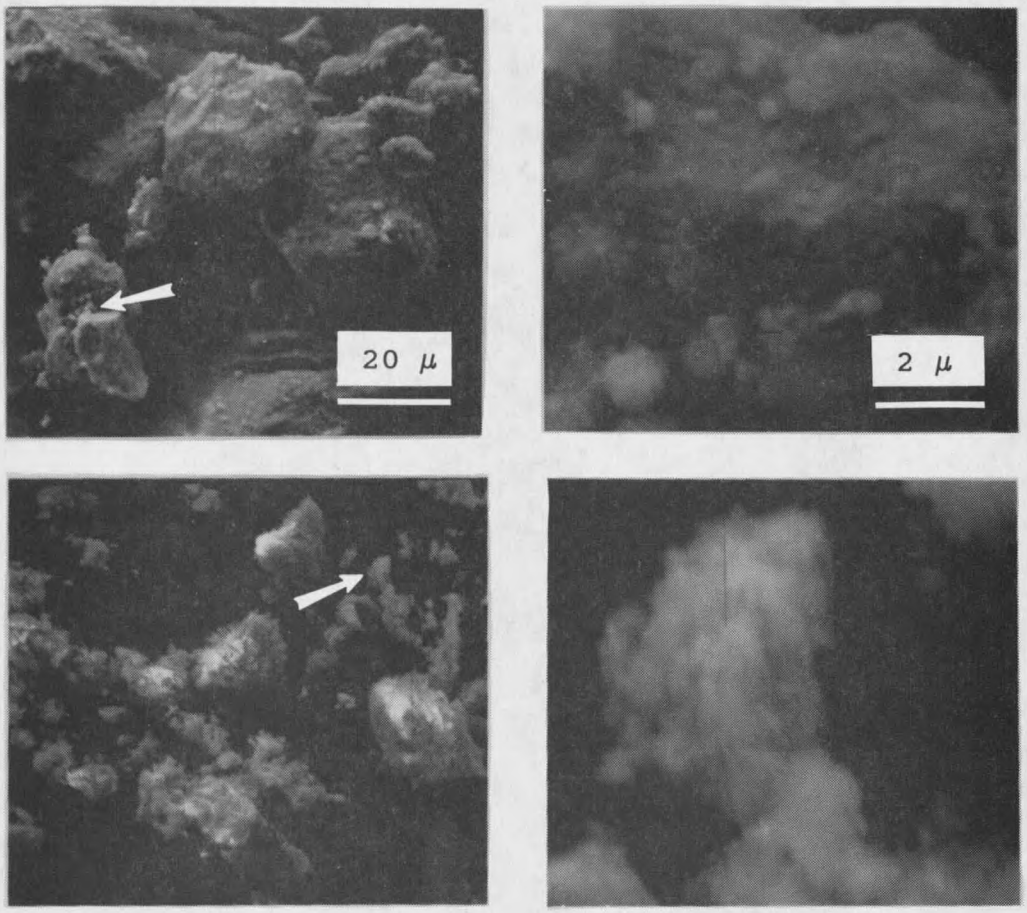

Figure 9. Scanning electron microscope photographs showing particle size range and morphological characteristics of phosphate amendments at 450X (left) and 4700X (right) magnification. Top: Cominco ore; bottom: Cominco waste. Photographs on right are closeups of particles shown by arrow on left.

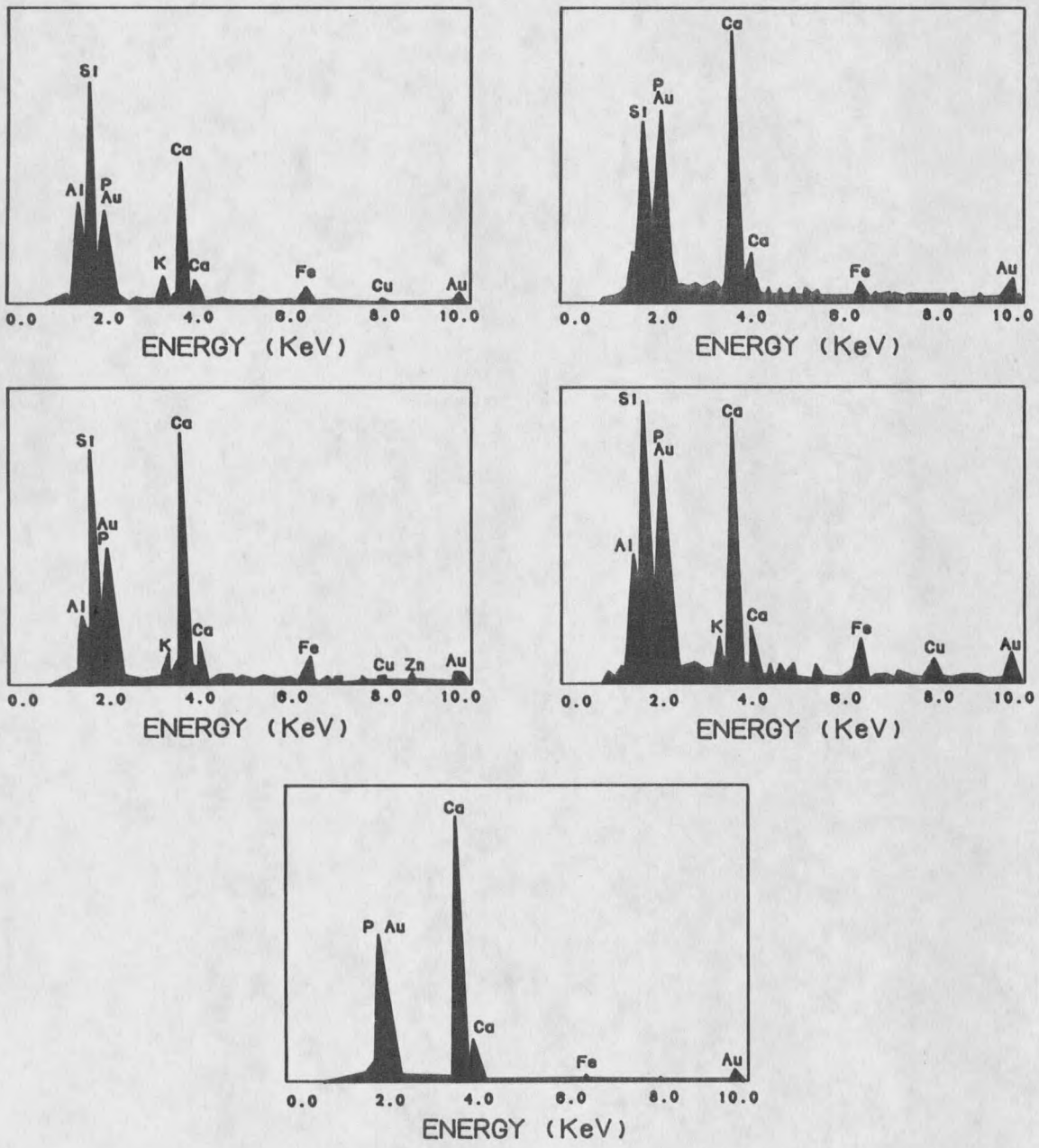

Figure 10. Area EDAX spectra of phosphate amendments. Top left: Stauffer ore; top right: Cominco ore; middle left: Stauffer sludge; middle right: Cominco waste; bottom: Texas Gulf ore.

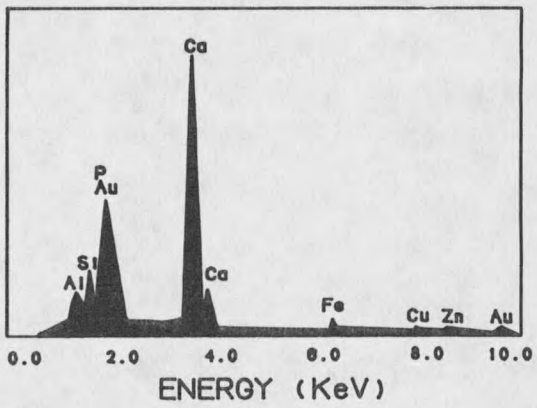

Figure 11. Typical EDAX spectra of calcium phosphate particles in the Cominco ore, Cominco waste, Stauffer ore and Stauffer sludge amendments (spectra from Stauffer sludge).

phosphate particles (Figure 11) present in sizes smaller than 2 micrometers or less in the Stauffer sludge and Texas Gulf ore samples.

EDAX analysis indicates that there is a significant amount of aluminum (Al) and silica (Si) present in the Cominco waste and ore and Stauffer sludge and ore samples. This is not true for Texas Gulf ore (Figure 10). EDAX and SEM analyses of individual particles in these amendments indicate the presence of aluminosilicate minerals and relatively pure silicate minerals in a wide range of sizes (<1 to >100 micrometers) in association with the calcium phosphate particles. Conversely, EDAX analysis of individual particles in the Texas Gulf ore yielded almost identical results as an area EDAX scan (Figure 10), suggesting a relatively homogeneous calcium phosphate source.

These findings in conjunction with phosphate solubility and surface area data provide an explanation for the performance of the respective amendments. The small particle size, "porous" morphology, large surface area and consequently high solubility of the Stauffer sludge and Texas Gulf ore amendments result in a very effective initial response in reducing acid production and Fe levels. However, because of the lower phosphorous content of the Stauffer sludge (6.9%) relative to the Texas Gulf ore (13.6), higher rates of application are necessary to achieve similar results.

Post-Leaching Sulfur Fractionation

The results of the post-soxhlet leaching sulfur fractionation analysis of the amended overburden samples generally corroborates the findings of the leachate analysis. That is, the overall production of acid from the oxidation of FeS_2 was lower for samples treated with a phosphate amendment compared to the control (Table 9).

This fact is illustrated by the greater percentage of S remaining as FeS_2 in the treated samples compared to the control. However, it should again be noted that this analysis was performed on a single homogenized bulk sample derived from the mixing of treatment replicates. In addition, although all treated samples contain more S as FeS_2 than the control, the difference is relatively small and may be within the boundaries of laboratory error.

Table 9. Post-leaching sulfur fractionation and acid-base account analyses of the amended Wolf Creek overburden.

	Treatment								
	Control	Cominco ore	Cominco waste			Stauffer sludge			Texas Gulf ore
		3%	1%	3%	5%	1%	3%	5%	3%
Total S (%)	0.72	0.75	0.76	0.74	0.77	0.80	0.84	0.90	0.89
Hot Water Extractable S(%)[1]	0.11	0.09	0.11	0.03	0.08	0.08	0.11	0.22	0.09
HCl Extractable S (%)[2]	0.03	0.03	0.05	0.09	0.02	0.13	0.07	0.03	0.16
HNO_3 Extractable S (%)[3,5]	0.14	0.19	0.17	0.18	0.19	0.12	0.11	0.09	0.13
Residual S (%)[4,5]	0.44	0.44	0.43	0.44	0.48	0.47	0.55	0.56	0.51
Neutralization Potential (t/1000t)	<1	5	<1	4	5	<1	4	7	2
Acid Potential (meq/100g)	38	41	41	44	43	45	46	42	50
Acid-Base Account (t/1000t)[6]	-18.33	-15.40	-19.43	-17.50	-16.41	-19.83	-19.23	-18.52	-20.13
Difference Pre-leaching FeS_2-S and Post-Leaching FeS_2-S	-0.24	-0.19	-0.22	-0.20	-0.15	-0.23	-0.16	-0.17	-0.18

1. water soluble sulfates
2. non-water soluble sulfates
3. pyritic sulfur
4. Total S - sum(1,2,3)
5. sum of 3 and 4 = total pyritic sulfur
6. ABA = NP - [HCl-S(23.44) + FeS_2-S(31.25)]; if NP < 1, let NP = 0.5.

Nonetheless, this analysis provides useful information when compared to the pre-leaching sulfur fractionation data from the Wolf Creek overburden and will be addressed in a later section.

It is also noteworthy that residual S comprises the majority of FeS_2-S in the leached samples but is a minor component of FeS_2-S compared to HNO_3 extractable S in the original sample. It is not clear why this is the case, but it may be due to laboratory analytical error.

Stoichiometric Balance of FeS_2 Oxidation

Cumulative iron, sulfate and acidity balances were calculated and compared to the theoretical concentrations based on the stoichiometry of FeS_2 oxidation [1], [2], [3] and [4]. These calculations were performed 1) to determine if the cumulative concentrations of analytical parameters in leachate were representative of the theoretical reaction consistency and stoichiometry associated with the oxidation of FeS_2, 2) to gain insight into the chemical mechanisms involved in FeS_2 oxidation during soxhlet leaching, and 3) to corroborate the findings of the leaching and solubility experiments. To achieve these results, the following equation was used:

$$\text{moles } FeS_2/\text{g sample} = (\text{mg ion/l leachate})\ (\text{l leachate/g sample})\ (\text{moles ion/mg ion})\ (\text{moles } FeS_2/\text{moles ion}) \quad \{1\}$$

Ion represents Fe, SO_4^{2-} and acidity as $CaCO_3$, and the term moles FeS_2/moles ion represents the moles of a given ion produced per 1 mole of FeS_2 oxidized. In this way, the molar concentrations of Fe, SO_4^{2-} and acidity were converted to moles of FeS_2 oxidized.

The actual amount of FeS_2 oxidized during the soxhlet leaching experiment could also be determined from results of the sulfur fractionation analysis of the amended samples following the last leach cycle (Table 9). By comparing the amount of FeS_2 sulfur in the initial overburden sample (Table 5) with that

remaining after the final leach cycle, the amount of oxidized pyrite can be determined through use of the following equations. First, the moles FeS_2/g sample are calculated:

$$g\ FeS_2 = (\%\ FeS_2\text{-}S/g\ overburden)\ (g\ FeS_2/g\ S)\ (100\ g\ overburden) \quad \{2\}$$

$$moles\ FeS_2 = (1\ mole\ FeS_2/119.97\ g\ FeS_2)\ (g\ FeS_2) \quad \{3\}$$

The amount of S as FeS_2 in the leached sample is then subtracted from the amount of S as FeS_2 in the original sample to yield the molar amount of FeS_2 oxidized during the soxhlet leaching experiment:

$$moles\ FeS_2\ oxidized = moles\ FeS_2\ original\ overburden - moles\ FeS_2\ leached\ overburden \quad \{4\}$$

These values can then be compared to the cumulative moles of FeS_2 oxidized as determined from Fe, acidity and S concentrations to determine reaction consistency and which mechanisms may be affecting ion concentrations (Table 10). This comparison will also provide insight into which parameter may be most indicative of the actual amount of FeS_2 oxidized.

The consistency of the values of the unitless ratios of moles FeS_2 oxidized as determined from cumulative leachate data to FeS_2 oxidized as determined from sulfur fractionation data (moles FeS_2-ion:FeS_2 oxidized) indicates that the relationship between the actual amount of FeS_2 oxidized and the molar concentrations of Fe, SO_4^{2-} and acidity in leachate are consistent for all treatments.

Table 10. Moles of FeS_2 oxidized as determined from sulfur fractionation data[1] and cumulative ion leachate levels.

Treatment (% apatite)	FeS_2 oxidized[1] moles FeS_2	calculated moles FeS_2 oxidized					
		Fe[2]		SO_4^{2-} (3)		acidity[4]	acidity[5]
		moles FeS_2 , FeS_2-ion:FeS_2 oxidized					
Control	0.0037	0.0061[6]	1.65[7]	0.0046	1,24	0.0114 3.08	0.0076 2.05
Cominco ore (3%)	0.0030	0.0056	1.87	0.0044	1.47	0.0100 3.33	0.0067 2.23
Cominco waste (1%)	0.0034	0.0051	1.50	0.0046	1.35	0.0106 3.12	0.0065 2.09
Cominco waste (3%)	0.0031	0.0045	1.45	0.0043	1.39	0.0098 3.16	0.0063 2.10
Cominco waste (5%)	0.0023	0.0045	1.96	0.0044	1.91	0.0095 4.13	0.0067 2.74
Stauffer sludge (1%)	0.0036	0.0045	1.25	0.0041	1.14	0.0092 2.56	0.0061 1.69
Stauffer sludge (3%)	0.0025	0.0030	1.20	0.0037	1.48	0.0063 2.52	0.0042 1.68
Stauffer sludge (5%)	0.0027	0.0022	0.81	0.0035	1.30	0.0053 1.96	0.0035 1.30
Texas Gulf ore (3%)	0.0028	0.0023	0.82	0.0034	1.21	0.0037 1.32	0.0025 0.89

1. moles FeS_2 original overburden - moles FeS_2 overburden after leaching (by S fractionation)
2. (moles Fe) (1 mole FeS_2/1 mole Fe)
3. (moles SO_4^{2-}) (1 mole FeS_2/2 moles SO_4^{2-})
4. (moles H^+) (1 moles FeS_2/2 moles H^+)
5. (moles H^+) (1 moles FeS_2/3 moles H^+)
6. moles FeS_2 oxidized as determined from cumulative Fe concentrations.
7. ratio of moles FeS_2 oxidized determined from pre-leaching and post-leaching sulfur fractionation data to moles FeS_2 oxidized determined from cumulative Fe concentrations.

This suggests a reaction consistency across all treatments and lends corroborative evidence to the results of the solubility experiment, which indicated that the discrepancy between S and acidity values is due in part to the contribution of S from the amendments in conjunction with the neutralization potential of the amendments related to the dissolution of hydroxy apatite.

Iron

The molar balance values for Fe using cumulative Fe concentrations in leachate indicate there is more Fe in leachate than would be expected from FeS_2 oxidation by reactions [1], [2] and [3] or by reaction [5] (Fe^{3+} oxidation of FeS_2) for all treatments except Stauffer sludge at 5% and Texas Gulf ore at 3%. The

elevated Fe values are probably due to a large flux of soluble Fe associated with initial (cycle 1) leaching (Appendix A). Some Fe is most likely forming $Fe(OH)_3$. The formation of $Fe(OH)_3$ via hydrolysis may also help explain the higher acidity levels in the control compared to the treated samples.

The lower Fe molar leachate concentrations from the treated overburden samples suggests that Fe is being removed in excess of that which would be expected if only $Fe(OH)_3$ were forming. These lower Fe levels can most likely be attributed to the formation of $FePO_4$ [6], although some $Fe(OH)_3$ can still be expected to form.

$$Fe^{3+} + H_2PO_4^- = 2H^+ + FePO_4 \qquad [8]$$

The above reaction assumes phosphate is present as $H_2PO_4^-$ in the pH range of the leachates. This reaction produces 2 moles of acidity (H^+) compared to 3 moles of H^+ associated with the formation of $Fe(OH)_3$ [3]. Therefore, the acidity levels in the samples in which this reaction is occurring (treated samples) should be lower than the control. Also, this reaction should be predominant in those samples with the highest application rate of a given amendment and result in correspondingly lower acidity levels. Leachate data indicates that in general this is the case.

Sulfate

Molar balance calculations for SO_4^{2-} indicate there is SO_4^{2-} present in leachate in excess of what would be expected from the oxidation of FeS_2. This is true for all treatments, including the control. Although it is possible that part of this discrepancy may be due to the presence of other forms of S detected by ICP analysis and/ or laboratory error associated with S fractionation analyses, the discrepancy is large enough to suggest another cause.

The elevated cumulative levels of S, as indicated by FeS_2-ion:FeS_2 oxidized ratios greater than unity) are most likely due to a large contribution of soluble, non-FeS_2 forms of S associated with the initial leaching cycle (Table 6). In later cycles (2 through 5), S derived from the amendments themselves may have contributed to S leachate levels, as is suggested by the results of the solubility experiment and may explain the lack of significant reductions in S concentrations for all treatments in cycles 2 through 5.

Acidity

Molar acidity balances were calculated for two separate scenarios. Assuming that all Fe is in the Fe^{3+} oxidation state and is precipitated as $FePO_4$, the total amount of acidity produced would be 3 moles of H^+ for every mole of FeS_2 by reactions [1], [2] and [6].

If one assumes that all Fe is in the form of Fe^{3+} and is precipitated as $Fe(OH)_3$, then 4 moles of acidity (H^+) will be produced for every mole of FeS_2

oxidized by reactions [1], [2] and [3]. If all Fe was not in the Fe^{3+} oxidation state, then less than 3 moles of H^+ would be produced from the oxidation of 1 mole of FeS_2.

The larger acidity values (as FeS_2-acidity) calculated from leachate data compared to the amount of acid production from actual FeS_2 oxidation as calculated from sulfur fractionation data indicate that more acidity is present than can be explained by FeS_2 oxidation. This is true for both assumptions.

Although all treatments significantly reduced cumulative acidity levels relative to the control, excess acidity, relative to theoretical acid production, is present in all leachates except those treated with Texas Gulf ore at 3%. This treatment resulted in acidity levels comparable to and lower than the theoretical maximum assuming 2 moles or 3 moles of acidity per mole of FeS_2, respectively. These lower acidity values relative to the other treatments underscore the role of the inherent neutralization capacity associated with Texas Gulf ore. Part of the relative decline in acidity may also be attributed to the absence of aluminosilicates in the amendment, although this would be expected to be only a minor component of the overall acidity.

It is possible that hydrolysis of aluminum [7], which was present in considerable concentrations in the overburden saturated paste extract (Table 4), released from the sample and/or amendments during leaching was contributing to the production of acid. It may also be possible that other metals in addition to iron

and aluminum are undergoing hydrolysis reactions and may or may not be forming compounds with phosphate ions in solution. Finally, the lower values for moles of FeS_2 as determined from acidity values in all treated samples relative to the control corroborates the findings of the solubility experiment and suggests that the dissolution of hydroxyapatite is contributing OH^- during dissolution of hydroxyapatite [6]. It may also be that PO_4^{3-} is precipitating aluminum as $AlPO_4$, thereby reducing acid production associated with aluminum hydrolysis.

Operative Mechanisms of FeS_2 Oxidation

Recall that, based upon the stoichiometry of FeS_2 oxidation, S (assumed to be SO_4^{2-}) was measured as a direct indication of acid production. Therefore, if phosphate was effectively reducing the production of acid associated with FeS_2 oxidation, samples treated with phosphate should theoretically produce lower S concentrations in leachates than an untreated control sample. This was quite clearly the case in the initial leaching cycle for samples treated with Texas Gulf ore and Stauffer sludge at all rates of application. However, in leachate cycles 2 through 5, none of the amendments at any rate of application consistently resulted in significant reductions in S concentrations in leachate relative to the control. They did, however, continue to produce consistent reductions in Fe and acidity.

Reductions in acidity and Fe levels in the treated samples can be attributed to the activity of several mechanisms. Results of the solubility experiments suggest

that there is considerable neutralization potential derived from the liberation of OH^- groups upon dissolution of the amendments. Also, the more soluble amendments (Stauffer sludge and Texas Gulf ore) contribute notable amounts of PO_4^{3-} ions to solution and lead to the formation of iron phosphates, reducing the amount of Fe in solution and considerably diminishing the production of acid associated with the hydrolysis of Fe^{3+}. Phosphate ions may also complex Al and other metals and diminish the production of acid via their hydrolysis.

Theoretically, when the ratio of Fe^{2+}:Fe^{3+} is reduced below approximately $1:10^{-6}$ (at pH <3.5), oxidation of FeS_2 by Fe^{3+} is halted and the autocatalytic nature of FeS_2 oxidation cycle is severely inhibited. Although not measured directly in this experiment, results of the initial and post-leaching overburden sulfur fractionation analyses and cycle 1 leachate ion concentration data suggest that, at least initially, this mechanism of FeS_2 oxidation was occurring in the samples and that applications of the phosphate amendments were successful at reducing the amount of FeS_2 which was oxidized.

Although all of these mechanisms explain the decreases in acidity and Fe levels observed in the leachate data, they do not fully explain the lack of any significant declines in S in the treated samples compared to the control in cycles 2 through 5.

Several explanations may be offered for the trends noted in S leachate data in cycles 2 through 5. It may be possible that the application of phosphate at the

appropriate rates was successful at halting the oxidation of FeS_2 by Fe^{3+}. This may explain the success of the Stauffer sludge and Texas Gulf ore (the most soluble amendments) at significantly reducing S levels in the initial cycle. Assuming this mechanism of FeS_2 oxidation was stopped, oxidation of FeS_2 would be limited to that achieved by O_2 during the leaching and drying phases of the experiment. Because the application of phosphate does nothing to stop the oxidation of FeS_2 by O_2 and the subsequent production of SO_4^{2-} [1], there should theoretically be no difference in the S leachate concentrations between samples treated with phosphate and the control.

Leachate data for cycles 2 through 5 show that overburden treated with Cominco waste and Cominco ore did not achieve the initial (cycle 1) reductions in S observed for samples treated with Stauffer sludge and Texas Gulf ore and did not significantly reduce S relative to the control. However, in cycles 2 through 5, Cominco waste and Cominco ore-treated samples yielded S levels similar to the control and samples treated with Stauffer sludge and Texas Gulf ore. This suggests that the operative mechanism for the production of acid during these cycles was the same for all samples, including the control. The fact that S levels were the same for the treated samples as the control also suggests that the Fe^{3+} oxidation of FeS_2 was no longer taking place or was occurring at a very limited rate. It is possible that leaching of the majority of Fe in the initial cycle reduced the Fe^{3+}:Fe^{2+} ratio and Fe levels to a point where this mode of FeS_2 oxidation was no longer prevalent.

What little reductions in S levels in the treated samples occurred in cycles 2 through 5 may have been masked by contributions of S from the amendments.

It is also possible that the lower S, as well as Fe and acidity levels observed in cycles 2 through 5, are the result of a decreased rate of FeS_2 oxidation associated with the coating of FeS_2 crystals. Baker (1983) noted that iron phosphates were observed to form on the surface of FeS_2 crystals. Therefore, it is possible that iron phosphates formed on FeS_2 crystals during cycle 1 led to a decrease in the surface reactivity of the FeS_2 and a consequent decrease in FeS_2 oxidation and associated Fe, S and acidity levels.

Economic Considerations

The Stauffer sludge appears to be the most effective of the regional phosphate sources tested. Although it is possible that the characteristics of the Stauffer sludge which render it effective at higher application rates (high surface area and solubility) in conjunction with its relatively low phosphorous content (6.9%) may also contribute to a temporal decrease in effectiveness at lower rates of application relative to the other amendments tested in this study. However, Stauffer sludge is an unwanted byproduct of the phosphate industry and is readily available regionally in a form which needs no additional grinding. These characteristics should render it an economically feasible amendment for controlling AMD and offset the possible requirement of higher application rates. Although generally not

as effective as the Stauffer sludge, these characteristics of Cominco waste warrant its consideration as an amendment, particularly in view of its performance relative to the more expensive Cominco ore.

Although not tested in the soxhlet leaching experiment, results of the amendment solubility experiment and SEM/EDAX analyses suggest that the Stauffer ore may be an effective source of phosphate for controlling AMD. It is also possible that despite the low surface area of the Cominco ore, it may provide an effective long term source of phosphate ions. However, in lieu of its performance relative to the Cominco waste and Stauffer sludge in this study, its greater expense does not justify its use over these amendments.

The performance of the Texas Gulf ore at a 3% application rate was not markedly better than the Stauffer sludge at a 5% rate of application. Although it achieved the most significant reductions in acidity, Stauffer sludge at 5% was just as effective at reducing Fe levels and both initial (cycle 1) and cumulative S concentrations. Since it was not the objective of this study to evaluate the feasibility of the use of the Texas Gulf ore as an amendment in the western United States, this issue will not be addressed. However, the performance of the Stauffer sludge relative to this phosphate source is encouraging, especially in light of the results of previous research (Renton et al 1988b), which had determined the Texas Gulf ore to be a very effective source of phosphate at controlling acid production relative to other sources tested.

SUMMARY AND CONCLUSIONS

Cumulative leachate data indicate that application of all phosphate sources to acid-producing coal overburden reduced iron, acidity and sulfate levels compared to a control. All reductions were significant at the 95% confidence level with the exception of those achieved for iron by samples treated with Cominco ore at a 3% by weight apatite application rate.

Cominco waste at application rates of 3% and 5% apatite were more effective at decreasing iron, sulfate and acidity concentrations (27% and 28%, 9% and 7% and 14% and 19%, respectively) than a 1% rate of application (16%, <1% and 7%, respectively). However, there was no significant difference between application rates of 3% and 5% for these parameters. Overburden treated with a 3% apatite application of Cominco waste resulted in significantly lower iron levels than those treated with Cominco ore (8%) at the same rate.

Application of Stauffer sludge to overburden at 3% apatite led to significant reductions in iron, sulfate and acidity (50%, 20% and 44%) compared to applications of only 1% apatite (16%, 11% and 19%) and 5% application rates produced a significant diminution in levels of iron and acidity (63% and 53%) relative to a 3% application rate. These results suggest that a mass action process governs the success of phosphate as an amendment for AMD and corroborates the findings of other researchers.

Overall, Stauffer sludge and Texas Gulf ore were the most effective amendments, leading to greater reductions in iron, acidity and sulfate levels and a larger increase in pH than samples treated with Cominco waste at comparable rates of application. These findings can be attributed to the greater solubility, preponderance of small calcium phosphate particles and greater surface area of the Stauffer sludge and Texas Gulf ore, which resulted in increased concentrations of phosphate and hydroxyl groups in solution. Basic carbonates present in the Texas Gulf ore also contributed to its neutralizing potential. Stauffer sludge achieved these results despite the fact that it had the lowest phosphorous content of any amendment tested. These factors also explain the strong initial response wrought by the application of Stauffer sludge and Texas Gulf ore and their effectiveness relative to the Cominco ore.

Finally, the strong performance of the phosphate byproducts, especially the Stauffer sludge, in conjunction with their regional availability render them a promising, economically feasible amendment for the control of acid mine drainage.

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APPENDICES

APPENDIX A

OVERBURDEN LEACHATE DATA

Table 11. Values of leachate analytical parameters for all cycles.

Amendment	Rate % apatite	Rep[1]	Cycle	Fe	S	Acidity ($CaCO_3$)	Ca	P	EC mmhos /cm	pH
				mg/l						
C[2]	0	1	1	1206	3265	355	377	7.1	14.16	1.97
C	0	2	1	1173	2832	351	312	6.0	12.93	2.00
C	0	3	1	1048	2882	375	322	6.5	13.54	1.97
CO	3	1	1	1206	3265	359	448	7.1	13.75	1.80
CO	3	2	1	1414	2987	372	451	7.1	13.70	1.81
CO	3	3	1	922	2822	361	430	6.6	13.37	1.80
CW	1	1	1	996	2907	358	421	6.5	13.32	1.78
CW	1	2	1	1097	3314	390	473	8.4	14.59	1.77
CW	1	3	1	1005	2975	358	439	6.2	13.38	1.81
CW	3	1	1	898	2650	335	360	5.3	12.28	1.84
CW	3	2	1	928	2982	356	527	6.4	13.63	1.80
CW	3	3	1	897	2800	350	403	6.4	13.19	1.81
CW	5	1	1	981	3051	315	492	7.1	12.71	1.86
CW	5	2	1	866	2800	338	581	6.4	13.13	1.85
CW	5	3	1	859	2768	331	507	6.4	12.99	1.85
SS	1	1	1	889	2731	315	485	6.3	12.69	2.03
SS	1	2	1	838	2632	300	521	6.2	12.18	2.05
SS	1	3	1	847	2570	308	387	6.4	12.04	2.04
SS	3	1	1	592	2017	202	489	5.6	8.89	2.25
SS	3	2	1	619	2082	202	497	5.2	8.66	2.36
SS	3	3	1	525	1858	175	539	4.9	7.33	2.50
SS	5	1	1	483	1912	195	494	5.7	8.43	2.45
SS	5	2	1	471	1877	170	483	4.7	7.49	2.62
SS	5	3	1	436	1759	173	543	5.1	7.20	2.67
TG	3	1	1	525	1981	131	466	5.4	7.83	2.32
TG	3	2	1	452	1780	131	498	4.4	7.78	2.32
TG	3	3	1	483	1925	150	493	5.8	8.19	2.27
C	0	1	2	115	257	31	140	1.4	1.94	2.59
C	0	2	2	192	471	54	195	2.1	2.81	2.52
C	0	3	2	163	400	46	188	1.3	2.63	2.59
CO	3	1	2	55	203	22	161	3.8	1.43	2.96
CO	3	2	2	58	252	22	174	7.4	1.69	2.87
CO	3	3	2	82	190	20	125	2.3	1.33	2.97
CW	1	1	2	91	302	29	201	4.5	1.95	2.78
CW	1	2	2	63	276	25	180	4.7	1.82	2.83

Table 11--Continued

CW	1	3	2	96	344	36	186	7.0	2.22	2.71
CW	3	1	2	65	227	28	158	1.9	1.51	2.96
CW	3	2	2	51	255	21	187	7.0	1.58	2.94
CW	3	3	2	61	244	24	158	2.7	1.53	2.97
CW	5	1	2	69	255	22	188	6.2	1.58	2.98
CW	5	2	2	58	249	22	184	9.0	1.58	2.98
CW	5	3	2	65	275	26	196	5.8	1.66	2.98
SS	1	1	2	119	364	32	262	4.1	2.06	2.81
SS	1	2	2	108	355	30	229	6.4	1.86	2.82
SS	1	3	2	71	261	32	176	1.6	2.16	2.78
SS	3	1	2	58	385	23	293	4.7	1.93	3.13
SS	3	2	2	67	493	29	382	6.9	2.36	3.02
SS	3	3	2	61	399	23	323	5.2	2.04	3.06
SS	5	1	2	35	360	16	320	5.9	1.77	3.49
SS	5	2	2	26	356	14	307	4.1	1.68	3.58
SS	5	3	2	28	358	17	316	4.0	1.81	3.32
TG	3	1	2	34	421	10	457	20.3	2.05	3.15
TG	3	2	2	25	368	8	388	18.0	1.78	3.32
TG	3	3	2	25	440	11	470	24.3	2.02	3.30
C	0	1	3	82	218	31	88	1.6	1.90	2.65
C	0	2	3	76	218	29	105	1.2	1.82	2.70
C	0	3	3	66	190	27	100	0.9	1.68	2.71
CO	3	1	3	30	151	16	110	4.8	1.25	2.76
CO	3	2	3	88	163	19	121	7.6	1.37	2.72
CO	3	3	3	45	122	16	87	1.6	1.01	2.78
CW	1	1	3	61	222	25	141	4.7	1.93	2.62
CW	1	2	3	53	211	23	138	5.0	1.79	2.69
CW	1	3	3	58	231	30	144	8.8	1.99	2.62
CW	3	1	3	46	182	21	114	3.8	1.51	2.80
CW	3	2	3	36	174	17	135	10.6	1.47	2.91
CW	3	3	3	49	226	22	160	6.2	1.76	2.85
CW	5	1	3	35	178	19	128	6.2	1.33	2.81
CW	5	2	3	31	152	17	110	6.0	1.22	2.83
CW	5	3	3	43	209	22	147	7.8	1.51	2.77
SS	1	1	3	79	241	22	159	4.6	1.64	2.88
SS	1	2	3	54	241	21	138	6.1	1.45	2.92
SS	1	3	3	24	87	17	71	0.8	0.99	2.96
SS	3	1	3	49	321	20	245	8.6	1.97	3.01
SS	3	2	3	36	267	17	223	6.0	1.80	2.95

Table 11--Continued

SS	3	3	3	39	293	17	252	6.1	1.94	3.02
SS	5	1	3	12	232	11	216	4.7	1.48	3.45
SS	5	2	3	17	248	13	230	5.0	1.58	3.43
SS	5	3	3	32	329	16	308	6.7	1.90	3.40
TG	3	1	3	41	214	6	236	13.8	1.31	3.50
TG	3	2	3	27	246	8	270	18.4	1.60	3.44
TG	3	3	3	10	190	6	217	13.7	1.29	3.57
C	0	1	4	3	141	27	53	1.1	1.44	2.56
C	0	2	4	2	152	35	74	1.2	1.52	2.66
C	0	3	4	3	164	35	74	1.0	1.55	2.70
CO	3	1	4	31	113	25	81	3.3	1.02	2.97
CO	3	2	4	32	132	25	101	6.0	1.27	2.84
CO	3	3	4	31	144	22	105	3.5	1.22	2.96
CW	1	1	4	39	159	24	102	4.9	1.38	2.74
CW	1	2	4	34	140	28	93	4.5	1.26	2.81
CW	1	3	4	36	149	30	101	6.7	1.26	2.79
CW	3	1	4	50	149	31	95	3.8	1.22	2.79
CW	3	2	4	35	129	22	99	5.4	1.04	2.94
CW	3	3	4	40	170	31	113	5.6	1.30	2.84
CW	5	1	4	33	146	28	97	4.6	1.18	2.84
CW	5	2	4	29	147	27	109	7.5	1.20	2.86
CW	5	3	4	42	194	24	134	8.9	1.54	2.77
SS	1	1	4	44	167	28	124	4.9	1.38	2.56
SS	1	2	4	37	149	23	104	6.2	1.37	2.60
SS	1	3	4	42	115	24	70	1.8	1.07	2.78
SS	3	1	4	21	184	16	178	5.2	3.13	3.13
SS	3	2	4	24	192	16	177	7.6	3.01	3.01
SS	3	3	4	25	181	14	176	6.9	3.10	3.10
SS	5	1	4	7	153	11	149	3.4	3.45	3.45
SS	5	2	4	13	240	15	234	6.2	3.34	3.34
SS	5	3	4	5	120	7	120	2.4	3.50	3.50
TG	3	1	4	9	176	7	185	9.5	1.77	3.36
TG	3	2	4	17	196	8	205	12.8	1.76	3.30
TG	3	3	4	22	203	8	226	14.4	1.46	3.26
C	0	1	5	52	139	30	62	0.8	1.31	2.81
C	0	2	5	53	151	31	79	0.9	1.52	2.75
C	0	3	5	60	156	28	80	1.0	1.66	2.70
CO	3	1	5	35	145	22	111	7.9	1.25	3.03

Table 11--Continued

CO	3	2	5	25	124	17	100	7.5	1.18	2.92
CO	3	3	5	38	155	21	127	12.8	1.36	3.04
CW	1	1	5	33	130	21	95	3.7	1.18	2.88
CW	1	2	5	25	103	18	81	3.2	1.02	2.96
CW	1	3	5	36	132	22	99	8.7	1.34	2.81
CW	3	1	5	26	122	15	88	3.1	1.05	2.95
CW	3	2	5	27	134	16	102	5.8	1.07	3.00
CW	3	3	5	32	145	20	114	6.5	1.25	2.92
CW	5	1	5	28	113	16	88	4.1	1.04	2.90
CW	5	2	5	29	124	18	105	6.5	1.24	2.90
CW	5	3	5	28	119	18	97	4.1	1.11	2.86
SS	1	1	5	36	132	23	104	3.3	1.16	2.93
SS	1	2	5	28	118	21	93	3.9	1.05	2.96
SS	1	3	5	63	229	28	161	3.7	1.71	2.80
SS	3	1	5	42	215	20	215	10.2	1.38	3.02
SS	3	2	5	42	229	23	225	16.8	1.53	3.02
SS	3	3	5	37	206	18	212	9.7	1.33	3.16
SS	5	1	5	23	237	15	256	11.3	1.39	3.41
SS	5	2	5	20	235	13	257	8.4	1.34	3.48
SS	5	3	5	37	357	23	383	15.0	1.83	3.34
TG	3	1	5	9	161	7	198	13.5	1.06	3.41
TG	3	2	5	9	182	7	220	12.6	1.17	3.41
TG	3	3	5	8	163	7	196	9.3	1.04	3.42

1. Rep = Replicate
2. C = Control, CO = Cominco ore, CW = Cominco waste, SS = Stauffer sludge, TG=Texas Gulf ore

APPENDIX B

ANALYSIS OF VARIANCE FOR LEACHATE DATA

Table 12. Analysis of variance and least significant difference for cumulative leachate analytical parameters

	EC[1]	Acidity	Ca	Fe	P	S	pH
NO. REPS USED	3	3	3	3	3	3	3
NO. TRTS USED	9	9	9	9	9	9	9
REPLICATE MS	3.741	.4147E+05	8182	.256E+05	60.38	.3279E+05	.1831E-07
TREATMENT MS	11.62	.1401E+08	.2580E+06	.3132E+06	576.1	.3879E+06	.5990E-05
ERROR MS	2.653	.8082E+05	5387	7490	21.79	.2032E+05	.1388E-07
ERROR DF	16	16	16	16	16	16	16
F-RATIO TRTS	4.379	173.4	47.88	41.82	26.43	19.09	431.6
P-VALUE TRTS	.0050	.0000	.0000	.0000	.0000	.0000	.0000
STD DEV (S)	1.629	284.3	73.40	86.54	4.668	142.6	.1178E-03
LSD(0.05 by t)	2.819	492.1	127.0	149.8	8.081	246.8	.2039E-03
COUNT PER MEAN	3	3	3	3	3	3	3

TREATMENT MEAN:

TREATMENT	Reps[2]	EC	Acidity	Ca	Fe	P	S	pH
C	3	20.80 C[3]	9424 G	713.3 A	1414 F	10.8 A	3695 C	.387E-02 E
SS1	3	18.27 BC	7673 D	979.3 BC	1041 CD	21.0 B	3300 B	.311E-02 D
SS3	3	16.80 AB	5235 C	1405.0 D	673 B	34.8 C	2960 A	.161E-02 C
SS5	3	19.12 BC	4460 B	1465.0 D	522 A	29.4 BCD	2785 A	.847E-03 A
CW1	3	20.14 C	8783 F	917.7 BC	1181 DE	27.8 BCD	3681 C	.465E-02 G
CW3	3	18.46 BC	8060 DE	893.0 BC	1029 C	25.5 BC	3362 B	.404E-02 EF
CW5	3	18.34 BC	7675 D	1004.0 C	1015 C	30.7 CD	3423 B	.388E-02 E
CO3	3	18.73 BC	8187 E	867.7 B	1299 EF	28.3 BCD	3482 BC	.417E-02 F
TG3	3	14.04 A	3086 A	1501.0 D	539 AB	62.2 E	2744 A	.135E-02 B

1 - mean values in mmhos/cm; means of other analytical parameters in mg/l.
2 - Reps = number of replicate samples.
3 - multiple comparisons are 0.05 LSD.

Table 13. Analysis of variance and least significant difference for cycle 1 leachate analytical parameters.

	EC	ACIDITY	Ca	Fe	P	S	pH
NO. REPS USED	3	3	3	3	3	3	3
NO. TRTS USED	9	9	9	9	9	9	9
REPLICATE MS	.2998	.1597E+05	2908	.2151E+05	.7445E-01	.5250E+05	.2844E-06
TREATMENT MS	21.07	.6936E+07	8895	.2002E+06	1.558	.7152E+06	.8508E-04
ERROR MS	.3055	.4724E+05	1741	6528.	.3644	.2094E+05	.3915E-06
ERROR DF	16	16	16	16	16	16	16
F-RATIO TRTS	68.98	146.8	5.107	30.66	4.274	34.15	217.3
P-VALUE TRTS	.0000	.0000	.0023	.0000	.0057	.0000	.0000
STD DEV (S)	.5527	217.3	41.73	80.80	.6037	144.7	.6257E-03
LSD(0.05 by t)	.9567	376.2	72.23	139.9	1.045	250.5	.1083E-02
COUNT PER MEAN	3	3	3	3	3	3	3

Table 13--Continued

TREATMENT MEANS:

TREATMENT	REPS	EC	ACIDITY	Ca	Fe	P	S	pH
C	3	13.54 C	6009 E	321.0 A	1088 ED	6.233 C	2851 C	.1047E-01 D
SS1	3	12.30 B	5130 C	442.3 CBD	417.3 B	6.000 BC	2519 B	.9133E-02 C
SS3	3	8.293 A	3218 B	484.0 CD	551.3 A	5.000 AB	1891 A	.4400E-02 B
SS5	3	7.707 A	2991 B	482.3 CD	441.3 A	4.933 A	1761 A	.2667E-02 A
CW1	3	13.76 C	6148 E	423.0 CB	983.7 CD	6.700 C	2919 C	.1637E-01 G
CW3	3	13.03 CB	5786 DE	409.7 B	864.3 CB	5.733 ABC	2677 CB	.1527E-01 G
CW5	3	12.94 CB	5469 CD	501.7 D	859.0 CB	6.333 C	2736 CB	.1400E-01 E
CO3	3	13.61 C	6070 E	422.3 CB	1125 E	6.633 C	2881 C	.1570E-01 EF
TG3	3	7.933 A	2290 A	462.7 CBD	463.3 A	4.933 A	1805 A	.5000E-02 B

Multiple comparisons are 0.05 LSD.

Table 14. Analysis of variance and least significant difference for cycle 2 leachate analytical parameters.

	EC	ACIDITY	Ca	Fe	P	S	pH
NO. REPS USED	3	3	3	3	3	3	3
NO. TRTS USED	9	9	9	9	9	9	9
REPLICATE MS	.3575E-01	9104	191.8	3.593	5.038	2278	.9259E-08
TREATMENT MS	.2925	.1767E+06	.2590E+05	4140	85.70	.1519E+05	.1498E-05
ERROR MS	.4269E-01	.1495E+05	874.5	316.6	3.688	2285.	.2051E-07
ERROR DF	16	16	16	16	16	16	16
F-RATIO TRTS	6.852	11.82	29.61	13.08	23.24	6.647	73.05
P-VALUE TRTS	.0005	.0000	.0000	.0000	.0000	.0006	.0000
STD DEV (S)	.2066	122.3	29.57	17.79	1.920	47.80	.1432E-03
LSD(0.05 by t)	.3576	211.6	51.19	30.80	3.324	82.74	.2479E-03
COUNT PER MEAN	3	3	3	3	3	3	3

TREATMENT MEANS:

TREATMENT	REPS	EC	ACIDITY	Ca	Fe	P	S	pH
C	3	2.460 D	1102 E	166.0 AB	149.3 E	1.500 A	358.3 DCE	.2733E-02 E
SS1	3	1.973 C	793.3 D	212.0 B	94.67 D	3.833 AB	311.3 DBC	.1567E-02 D
SS3	3	2.110 DC	638.3 DC	317.0 C	59.00 BC	5.367 B	405.7 E	.8667E-03 B
SS5	3	1.753 ABC	403.3 AB	299.3 C	28.33 AB	4.433 AB	341.0 DC	.3667E-03 A
CW1	3	1.997 C	761.7 D	179.7 AB	79.33 DC	5.167 B	293.0 BC	.1700E-02 D
CW3	3	1.540 A	625.8 DC	159.3 A	56.33 ABC	3.700 AB	230.3 AB	.1067E-02 CB
CW5	3	1.607 AB	595.0 DBC	180.3 AB	61.00 C	6.667 B	247.3 AB	.1000E-02 CB
CO3	3	1.483 A	545.8 BC	146.0 A	61.67 C	4.267 AB	204.7 A	.1167E-02 C
TG3	3	1.950 BC	249.2 A	417.7 D	26.67 A	19.83 C	390.0 DE	.5667E-03 A

Multiple comparisons are 0.05 LSD.

Table 15. Analysis of variance and least significant difference for cycle 3 leachate analytical parameters.

	EC	ACIDITY	Ca	Fe	P	S	pH
NO. REPS USED	3	3	3	3	3	3	3
NO. TRTS USED	9	9	9	9	9	9	9
REPLICATE MS	.2070E-02	2338.	60.59	126.3	5.788	177.9	.1444E-07
TREATMENT MS	.1993	.8181E+05	.1066E+05	758.5	39.52	5568	.1345E-05
ERROR MS	.3735E-01	3793.	748.1	234.3	4.399	1627.	.1819E-07
ERROR DF	16	16	16	16	16	16	16
F-RATIO TRTS	5.338	21.57	14.25	3.237	8.984	3.423	73.93
P-VALUE TRTS	.0018	.0000	.0000	.0196	.0001	.0155	.0000
STD DEV (S)	.1932	61.58	27.35	15.31	2.097	40.33	.1349E-03
LSD(0.05 by t)	.3345	106.6	47.34	26.49	3.630	69.81	.2335E-03
COUNT PER MEAN	3	3	3	3	3	3	3

TREATMENT MEANS:

TREATMENT	REPS	EC	ACIDITY	Ca	Fe	P	S	pH
C	3	1.800 C	740.0 D	93.00 A	71.00 D	1.167 A	199.0 ABC	.2033E-02 F
SS1	3	1.360 AB	504.2 C	116.7 A	49.67 BCD	3.667 AB	181.0 AB	.1200E-02 CB
SS3	3	1.903 C	466.7 C	228.3 B	39.33 ABC	6.567 B	279.7 D	.1033E-02 B
SS5	3	1.653 BC	348.3 B	239.3 B	19.00 A	5.233 B	256.7 CD	.4000E-03 A
CW1	3	1.903 C	661.7 D	134.0 A	54.33 CD	5.900 B	210.7 BCD	.2267E-02 F
CW3	3	1.580 BC	512.5 C	130.0 A	41.67 ABC	6.533 B	184.7 AB	.1400E-02 CD
CW5	3	1.353 AB	495.0 C	122.3 A	34.67 ABC	6.333 B	171.3 AB	.1567E-02 ED
CO3	3	1.210 A	434.2 CB	101.0 A	52.00 CD	4.433 AB	138.3 A	.1767E-02 E
TG3	3	1.400 AB	170.0 A	229.7 B	25.00 AB	14.53 C	206.3 ABC	.3333E-03 A

Multiple comparisons are 0.05 LSD.

Table 16. Analysis of variance and least significant difference for cycle 4 leachate analytical parameters.

	EC	ACIDITY	Ca	Fe	P	S	pH
NO. REPS USED	3	3	3	3	3	3	3
NO. TRTS USED	9	9	9	9	9	9	9
REPLICATE MS	.1737E-02	711.3	451.4	30.33	7.114	206.8	.1004E-06
TREATMENT MS	2.226	.1370E+06	5877.	563.2	25.06	1105.	.1503E-05
ERROR MS	.1939E-01	7591.	565.9	21.67	2.085	703.1	.7245E-07
ERROR DF	16	16	16	16	16	16	16
F-RATIO TRTS	114.8	18.04	10.38	25.99	12.02	1.572	20.75
P-VALUE TRTS	.0000	.0000	.0000	.0000	.0000	.2060	.0000
STD DEV (S)	.1393	87.13	23.79	4.655	1.444	26.52	.2692E-03
LSD(0.05 by t)	.2410	150.8	41.18	8.057	2.499	45.90	.4659E-03
COUNT PER MEAN	3	3	3	3	3	3	3

Table 16--Continued

TREATMENT MEANS:

TREATMENT	REPS	EC	ACIDITY	Ca	Fe	P	S	pH
C	3	1.503 BC	815.8 D	63.33 A	53.33 F	1.033 A	145.0 AB	.2333E-02 D
SS1	3	1.273 AB	635.8 C	94.67 AB	39.00 E	4.100 B	137.0 AB	.2333E-02 D
SS3	3	3.080 D	394.2 B	169.0 C	22.33 BC	6.267 CB	176.7 B	.8333E-03 AB
SS5	3	3.430 E	283.3 AB	159.7 C	8.000 A	3.800 B	163.0 AB	.4000E-03 A
CW1	3	1.300 AB	695.8 CD	94.00 AB	34.33 DE	5.133 CB	142.0 AB	.1633E-02 C
CW3	3	1.187 A	700.0 CD	97.33 AB	39.67 E	4.667 CB	142.3 AB	.1367E-02 C
CW5	3	1.307 AB	671.7 CD	108.0 B	33.00 DE	6.667 C	154.7 AB	.1500E-02 C
CO3	3	1.170 A	622.5 C	91.00 AB	30.00 DC	4.033 B	123.7 A	.1200E-02 BC
TG3	3	1.663 C	191.7 A	195.3 C	15.33 AB	11.63 D	182.7 B	.4667E-03 A

Multiple comparisons are 0.05 LSD.

Table 17. Analysis of variance and least significant difference for cycle 5 leachate analytical parameters.

	EC	ACIDITY	Ca	Fe	P	S	pH
NO. REPS USED	3	3	3	3	3	3	3
NO. TRTS USED	9	9	9	9	9	9	9
REPLICATE MS	.1046	8297.	1809.	163.0	4.243	2362.	.4111E-07
TREATMENT MS	.8117E-01	.7088E+05	.1580E+05	434.3	46.33	7128.	.5967E-06
ERROR MS	.2453E-01	4379.	622.3	38.67	5.724	788.4	.2694E-07
ERROR DF	16	16	16	16	16	16	16
F-RATIO TRTS	3.310	16.19	25.38	11.23	8.094	9.041	22.14
P-VALUE TRTS	.0179	.0000	.0000	.0000	.0002	.0001	.0000
STD DEV (S)	.1566	66.17	24.95	6.218	2.392	28.08	.1641E-03
LSD(0.05 by t)	.2711	114.5	43.18	10.76	4.141	48.60	.2841E-03
COUNT PER MEAN	3	3	3	3	3	3	3

TREATMENT MEANS:

TREATMENT	REPS	EC	ACIDITY	Ca	Fe	P	S	pH
C	3	1.497 C	757.5 D	70.00 A	52.33 D	.9000 A	141.7 A	.1767E-02 D
SS1	3	1.307 ABC	609.2 C	113.7 B	40.33 C	3.433 A	152.0 A	.1300E-02 C
SS3	3	1.413 BC	517.5 CB	207.0 C	38.33 C	11.63 C	206.3 B	.9000E-03 B
SS5	3	1.520 C	434.2 B	284.7 D	25.33 B	11.03 C	263.3 C	.4000E-03 A
CW1	3	1.180 AB	515.8 CB	87.00 AB	29.67 CB	4.933 AB	116.0 A	.1300E-02 C
CW3	3	1.123 A	435.8 B	96.67 AB	27.00 B	4.900 AB	127.3 A	.1100E-02 BC
CW5	3	1.130 A	443.3 B	92.00 AB	27.33 B	4.667 A	113.0 A	.1333E-02 C
CO3	3	1.263 ABC	514.2 CB	107.3 AB	31.00 CB	8.933 BC	134.7 A	.1000E-02 B
TG3	3	1.090 A	185.0 A	195.3 C	8.667 A	11.27 C	160.3 AB	.4000E-03 A

Multiple comparisons are 0.05 LSD.