PHOSPHATE CYCLING IN COPPER MINE TAILINGS

by

Margaret B. Wilson

A Thesis Submitted to the Faculty of the

DEPARTMENT OF SOILS, WATER AND ENGINEERING

In Partial Fulfillment of the Requirements
For the Degree of

MASTER OF SCIENCE
WITH A MAJOR IN SOIL AND WATER SCIENCE

In the Graduate College

THE UNIVERSITY OF ARIZONA

1 9 8 1

STATEMENT BY AUTHOR

This thesis has been submitted in partial fulfillment of requirements for an advanced degree at The University of Arizona and is deposited in the University Library to be made available to borrowers under rules of the Library.

Brief quotations from this thesis are allowable without special permission, provided that accurate acknowledgment of source is made. Requests for permission for extended quotation from or reproduction of this manuscript in whole or in part may be granted by the head of the major department or the Dean of the Graduate College when in his judgment the proposed use of the material is in the interests of scholarship. In all other instances, however, permission must be obtained from the author.

SIGNED: Margaret B. Wilson

APPROVAL BY THESIS DIRECTOR

This thesis has been approved on the date shown below:

Jack L. Stroehlein

JACK L. STROEHLEIN
Associate Professor of Soils,
Water and Engineering

16 March 1981

Date

ACKNOWLEDGMENTS

The author wishes to express her gratitude to Dr. Jack L. Stroehlein, her major professor and to the other members of her committee: Dr. Donald F. Post and Dr. Arthur W. Warrick.

Sincere gratitude is also expressed to Dr. Ted Chester for his help and advice on the statistical analysis of the data used in this paper.

Appreciation is extended to Dr. David M. Hendricks for the X-ray diffraction data.

Special gratitude is expressed to the Duval Corporation, especially Erika Smith, for the assistance received.

TABLE OF CONTENTS

TABLE OF CONTENTS--Continued

LIST OF TABLES

LIST OF ILLUSTRATIONS

ABSTRACT

The vegetation reclamation of copper mine wastes depends on the plants ability to obtain a dependable nutrient source within the tailings. Phosphorus is often the most limiting nutrient. To plan for the most effective management practices, the reactions of phosphorus with tailings and with other minerals within the tailing solution must be understood.

The phosphorus in the tailings at the Duval Sierrita Mine was determined to be insufficient for plant growth. In addition, the availability of phosphorus was affected by two important factors: a positive particle charge, and a pH decrease as the tailings aged.

Initial tests indicate that tailings at a pH of 7 have a net positive charge which results in a greater ability to fix anions than cations. This reduces the available phosphate, the form of phosphorus most easily absorbed by plants. A high anion exchange capacity is rarely found in soils, so it must be considered for planning management practices.

The tailings initial pH of 7.7 dropped to 6.2, when water was added. As the pH decreases, the minerals to which phosphate is attracted will change, temporarily releasing the phosphate for the plants use.

The consideration of these factors in planning reclamation will help to establish a self-sufficient plant community within a shorter period of time.

INTRODUCTION

Surface mining has become increasingly important in the past fifty years when it became economically feasible to extract copper from low grade ore. It will continue to increase in importance in the future because of the safer working conditions, better recovery rate and lower costs.

However, as the method of recovery from low grade ore has improved, the amount of waste material has also increased. In 1938, 27 pounds of copper could be produced from one ton of ore. But by 1975, as the higher grade ore deposits were depleted and extraction methods improved, only 9½ pounds of copper was produced from one ton of ore (Eddy, 1979). As the need for copper increased, the production also increased. In Arizona alone copper production increased from 813,211 tons of copper in 1975 to 1,027, 871 tons in 1979.

Meanwhile the population is also growing. In 1960 the population of Arizona was 1,302,161, by 1970 the population was 1,772,482, and the estimated figure for 1980 is 2,200,000 (Tucson Metropolitan Chamber of Commerce, 1980).

The mines, caught between the greater demands by greater numbers of people for reclamation and an increased amount of waste materials, have accelerated their efforts in reclamation. Vegetation stabilization has always been an important part of this activity, but there is still much to learn about the interaction between mine wastes, or tailings, and the plants.

A variety of nutrients are needed by plants to survive and reproduce. Nitrogen and phosphorus are two important elements which are often found deficient in tailings. While nitrogen can be derived from the atmosphere with the help of microorganisms the plants must obtain phosphorus from the parent material or from fertilizers. Thus phosphorus is often the most limiting nutrient in tailings and was chosen for study.

The objectives of this research are: 1) to determine if there is a sufficient quantity of phosphorus in the tailings; 2) to determine what are the most important factors affecting the plants utilization of phosphorus; and 3) the best methods of managing tailings to provide a sufficient phosphorus supply.

LITERATURE REVIEW

Reasons for Revegetating Mined Lands

The goals for vegetation reclamation of mined lands have been listed in many ways.

Haase (1980) classified the reasons for land reclamation as being the reduction of wind and water erosion and the improvement of the aesthetics by establishing a self-perpetuating plant community.

The Soil Conservation Service (1977) stressed the same reasons, but added the restoration of land to productive use.

These reasons can be summarized into four categories. They are to reduce health and safety hazards from wind and dust, to limit property hazards by stabilizing the tailings and preventing of erosion, to improve public relations by beautifying the area, and to make the land useful again (Ludeke, 1972).

Problems in Vegetation Stabilization

All plants have basically the same requirements from the soil. The major needs are air and water storage, mechanical support, and a supply of nutrients (Brady, 1974).

Disturbed soils, as a result of the method of their formation, often have more problems than are found in natural soils. These problems include high salinity, acid conditions, toxic concentrations of heavy metals, and low fertility (Haase, 1980). In addition steepness of slope (Hanlon, 1977), soil instability caused by erosion, abrasion

to plants from wind carried particles, lack of soil structure and lack of organic matter also create problems (Soil Conservation Service, 1977).

In establishing plants on mined sites other conditions can be important. Climatic conditions such as temperature, wind, humidity, daylength, and the amount and season of rainfall must be considered. The use to which the land will be put and the aspect of slopes are also vital in the selection of plant species and the method of planting (Vallentine, 1971).

Methods of Reclamation of Mined Wastes

As a result of these problems establishing vegetative cover on land disturbed by mining requires special planting techniques, especially in the hot, arid climate of the southwest (Soil Conservation Service, 1977).

Reclamation can be done more economically if it is planned as part of the mining operation. Machinery can be set up to reduce costs, and planning for toxic materials, drainage, and irrigation can be done more economically (Strip and Surface Mine Study Policy Committee, 1967).

Hanlon (1977) described three methods of reclamation practiced by the mines between Tucson and Nogales; Arizona. The first method involves capping the tailing berms with 18 to 30 cm of overburden, or topsoil when available. This is then seeded with range grasses and irrigated by a sprinkler system.

The second method is to build the tailings into a better growing medium as rapidly as possible. The tailing berms are scarified to provide a stable growth site. It is then planted with barley,

fertilized, mulched and irrigated for several years with the detritus being worked back into the tailings. The permanent plantings are then made (Day and Ludeke, 1978).

The third method used involves the planting of nursery grown shrub species. Fertilizer is added at the time of the initial planting and added later through the drip irrigation system for the first growing season. This is the method used on the Duval Mine tailings (Hanlon, 1977).

Formation of Tailings

The development of all soils are the result of five factors. Jenny (1941) listed these factors as climate, biotic effect, topography, parent material, and time.

When soil materials are formed by mining these factors change. The particle size is changed by grinding, the natural parent material is changed by the removal of copper, molybdenum and other minerals, the soil solution is changed by the addition of processing chemicals. Then the tailings material which had previously been buried deep in the ground, is left exposed to the factors of soil formation. Eventually, if undisturbed they will become soils, but the mining companies are striving to make them a favorable site for plant growth as quickly as possible.

Parent Material

Much of the copper ore mined south of Tucson is from porphyry deposits. Some of the common minerals found in this type of deposit and their theoretical composition are listed in Table 1.

Table 1. Partial list of minerals commonly found in porphyry copper deposits.

Mineral	Theoretical Composition
Gossan	
Alunite	$KAl_3(SO_4)_2(OH)_6$
Azurite	$Cu_3(CO_3)_2(OH)_2$
Chrysocolla	$Cu_2H_2Si_2O_5(OH)_4$
Cuprite	Cu_2O
Goethite	$FeO(OH)$
Hematite	Fe_2O_3
Jarosite	$KFe_3(SO_4)_2(OH)_6$
Malachite	$Cu_2CO_3(OH)_2$
Porphyritic Intrusion and Host Rock	
Albite	$NaAlSi_3O_8$
Amphiboles	$(Ca,Na)_2(mg,Fe,Al)_5Si_8O_{22}(OH)_2$
Bornite	Cu_5FeS_4
Calcite	$CaCO_3$
Chalcocide	Cu_2S
Chalcopyrite	$CuFeS_2$
Chlorite	$(Mg,Fe,Mn)\ (Al,Si)_3O_{10}(OH)_8$
Clinozoisite	$Ca_2Al_2Si_3O_{12}(OH)$
Covellite	CuS
Diopside	$CaMgSi_2O_6$
Galena	PbS
Garnet	$(Ca,Mg,Fe,Mn)_3(Al,Fe,Ti,Cr)_2(SiO4)_3$
Hedenbergite	$CaFeSi_2O_6$
Kaolinite	$Al_2Si_2O_5(OH)_4$
Magnetite	Fe_3O_4
Molydenite	MoS_2
Montmorillonite	$(Na,Ca).33(Al,Mg)_2Si_4O_{10}(OH)_2n(H_2O)$
Muscovite	$KAl_2(Al,Si_3)O_{10}(OH)_2$
Orthoclase	$KAlSi_3O_8$
Plagioclase	$CaAlSi_3O_8$
Pyrite	FeS_2
Pyroxenes	$(Ca,Fe,Mg,Al)SiO_3$
Sphalerite	ZnS
Tremolite	$Ca_2Mg_5Si_8O_{22}(OH)_2$

From Anthony, Williams, Bideaux, 1977; Flint and Skinner, 1974; Sinkankas, 1964.

These deposits are usually found covering large areas ranging from ten to hundreds of square miles, but not all of the deposits have a sufficient concentration of copper to make mining practical. The minimum concentrations which are economically feasible for exploitation usually contain about 0.4 to 0.6 percent copper.

The ore mineral is usually associated with an intrusive calc-alkalic porphyritic rock. The host material may be limestones, shales, sandstones, volcanics, schists and gneisses (Anthony, Williams and Bideaux, 1977).

The copper deposits are formed when hot rock heated by volcanic action flows into any fractures within the rock and cools beneath the earth's surface (Flint and Skinner, 1974). Then as the porphyry cools it fractures again leaving smaller openings which are filled with hot, aqueous fluids which changes the mineralogy as well as the particle structure (Anthony, Williams and Bideaux, 1977).

The resulting formation includes a mixture of coarse mineral grains scattered through a mixture of fine mineral particles. The size of the grains depends on the rate of cooling and the pressure the magma is under as it cools (Flint and Skinner, 1974).

With the cessation of primary sulfide mineralization, the surrounding rock is weathered away exposing sulfides which percolate downward replacing pre-existing minerals especially chalcopyrite. Chalcocide is the most common secondary copper sulfide, although covellite, bornite, and even chalcopyrite can be formed in this manner.

The gossan or residual minerals left on the surface after oxidation and leaching are generally silicate rocks with secondary iron

oxides and sulfates. These materials can often produce large quantities of copper ore (Anthony, Williams and Bideaux, 1977).

The mineralogy at any location or depth will vary in ratio and there may be many other minerals in addition to those listed on Table 1.

Mining, Milling and Concentrating Processes

The second major factor in tailing formation is the treatment by which the copper is extracted. The total operation needed to turn ore into copper are mining, milling, concentrating, smelting, converting, anode casting, electro refining, melting, and casting (Smith, 1970). However, only the first three stages: mining, milling, and concentrating result in the production of tailings as a waste product, so only they will be discussed.

The mining is the blasting of the ore minerals from the ground and transporting them to the milling site.

In the milling step, two methods are used to break up the rock. Crushing has been found to be more economical for the initial stage, which starts with pieces as large as 150 cm in diameter. By crushing, dry ore is broken into pieces less than 2 cm in diameter.

The second stage of milling is the grinding of particles in an aqueous solution using steel rods and balls, or the ore itself until the particles are between 10 and 100 μm in size. The reagents needed for flotation are added throughout the second part of the milling process.

The final particle size depends on the initial size of the copper grains, and if the tailings are not ground fine enough the copper particles will be too large for the collecting and frothing reagents to

separate from the gangue. On the other hand, if the particles are too small they will form a slime which coats the minerals and lowers the flotation efficiency.

The mineralogy of the ore is determined before the method of concentration can be selected. If the material is an oxide it is generally concentrated by leaching and rarely by froth flotation; but low grade sulfides are almost always concentrated by flotation. Ninety percent of the ore produced today is the result of froth flotation. This method often begins with ore containing as little as 0.4% copper and concentrates it to 20 or 30% copper ore.

Concentrating by froth flotation is done in three processes: rougher cells, cleaner cells and scavenger cells. The roughers separates the copper and similar minerals from the gangue. The cleaner cells remove some of the non-copper minerals, and the scavenger cells are used to increase the recovery rate of copper (Biswas and Davenport, 1980).

During flotation the selected minerals are attached to the polar end of the collector reagent, while the nonpolar end attaches to the air bubbles being fed into the bottom of the flotation cell. The mineral particles then become part of the froth collecting on the surface and are allowed to overflow into the collecting bins (Crozier and Ottley, 1978). The gangue remains in the water solution and is pumped out through an underflow system and onto the tailing ponds where the aqueous solution may be decanted for reuse. The residue includes the tailings, and any reagents that are still with the tailings (Biswas and Davenport, 1980).

The selected minerals can be separated by varying the reagents, the pH of the solution, the rate of air flow, and the ratio of water to ore (Crozier and Ottley, 1978).

The reagents used include the collectors, the frothers, and regulating reagents, such as the hydroxyl ion for pH control, the cyanide ion for mineral selection, and the sulfide ion for oxide mineral flotation.

The collectors are reagents which attach the ore mineral to the air bubbles. Xanthate ($CH_3(CH_2)_4$-O-C(=S)-S-$CH_2CH{=}CH_2$) is the most commonly used collector. Other common collectors are xanthate dithiophosphate, thionocarbamates and fuel oil (Crozier and Ottley, 1978). The amount of collectors normally used is 0.035 to 0.040 kg per ton (Biswas and Davenport, 1980). In 1975, the Esperanze Mine used xanthate and xanthic esters at the rate of 0.01 kg per ton. The Sierrita Mine used xanthate, xanthic esters and fuel oil at the amount of 0.06 kg per ton (Crozier and Ottley, 1978).

The frothers are a group of chemical reagents that aid in the formation and stabilization of a suitable froth. They include pine oil, cresylic acid, methyl isobutyl carbinol, polyglycol esters and triethoxybutane. The amounts commonly used are 0.04 kg to treat one ton of ore (Biswas and Davenport, 1980). In 1975, the Esperanza Mine used polyglycol esters and the Sierrita Mine used methyl isobutyl carbinol (Crozier and Ottley, 1978).

The regulating reagents used are the hydroxyl ion, the cyanide ion, and the sulfide ion. The hydroxyl ion is used to control the pH.

A basic solution is needed for xanthate to remain stable, and different minerals will float as the pH changes. The pH of the rougher cell is usually between 8.5 and 12.5 (Biswas and Davenport, 1980). In 1975, the Esparanza Mine kept the pH in the rougher cell at 11.5 and the Sierrita Mine used a pH of 11.0 (Crozier and Ottley, 1978).

Cyanide is another ion used to prevent the collectors from attaching to the undesirable minerals, such as galena or pyrite. As it attaches to the undesired mineral, preventing the collector from attaching to it, it will remain with the tailings. If too much is used it will also prevent the collectors from attaching to copper minerals as well. Between 0.2 and 0.4 kg may be used per ton of ore.

Oxidized copper minerals do not respond to most collectors, so they must be pretreated with sulfide ions to provide a reactive surface. The amounts of sodium sulfide used is from 0.5 to 5.0 kg per ton of oxide ore. As this procedure does not always work, the copper in oxide is often separated by leaching instead of froth flotation (Biswas and Davenport, 1980).

The mining process dictates the particle size of the tailings, what part of the parent material is removed, and which chemicals remain in the soil solution. This will affect any efforts to reclaim the tailings.

Nutrient Cycling

In normal soils, nutrients are supplied by weathering of parent materials, adsorption from the air, decomposition of organic matter,

release by chemical reactions, fertilizer, and by moving in with air and water from other areas.

The nutrients can be lost by leaching, erosion, plant uptake, chemical change to a form plants cannot use, fixation by soils, and microbial use (Thompson and Troeh, 1973).

The nutrients required for manufacture of proteins are carbon, hydrogen, oxygen, nitrogen, phosphorus, and sulfur. Carbon, hydrogen, and oxygen are supplied by the air and water, while nitrogen, phosphorus and sulfur are supplied through the soil (Tisdale and Nelson, 1975).

The nitrogen requirements by plants are high, ranging from 0.5 to 5.0% of the dry weight of the plant. The plants uptake varies with the type of plant, the stage of plant growth, the source and the availability of nitrogen. It is normally supplied to plants by the oxidation of organic matter (Jones, 1979). In desert soils organic matter is relatively low, as a result nitrogen is often supplied naturally by free living bacteria and algae converting atmospheric sources to a form which the plants can use. Also many desert plants are legumes, which can fix nitrogen with the aid of a symbiotic bacteria Rhizobium (Fuller, 1975).

Phosphorus can be provided naturally to growing plants by the decomposition of organic matter, but a more important source is inorganic minerals such as apatite (Sauchelli, 1965). It becomes unavailable to plants through the fixation by soils, by plant uptake and by leaching, with fixation the most important factor and very little lost by leaching (Thompson and Troeh, 1973).

Sulfur is sometimes classified as a macronutrient, but in many mined soils the concentration becomes too high for plant tolerance.

In soils most of a plant's requirements for sulfur are supplied by the weathering of parent materials, with a little resulting from the decomposition of organic matter. Most of the losses are due to leaching. The average soil parent material contains approximately 0.06% sulfur (Thompson and Troeh, 1973).

From six samples tested by Duval Sierrita Corporation in October 1975, the average phosphorus content was less than 0.01 ppm, and the average sulfur content was 0.065% or 650 ppm in soil solution extracted with water. The same samples when extracted by acid had 1.51% sulfur and 89.5 ppm phosphorus. Nitrogen was not determined in these tests, but had been found to be insufficient for normal plant growth by Ludeke (1972) on the nearby Pima Mine.

Conditions Affecting the Availability of Phosphorus

Phosphorus fertilizer is second only to nitrogen in the amounts applied, however, plants require less phosphorus than they do nitrogen, potassium or calcium (ASA, 1968). Even though a soil generally has more total phosphorus than nitrogen, there is considerably less phosphorus available for plant use, the reason being that soils will fix phosphorus so strongly that it is unavailable for plant use.

The factors affecting phosphorus fixation are the soil mineralogy, the soil pH, the amount and state of organic matter decomposition, the activities of microorganisms, the time required for phosphorus

fixation, the temperature (Brady, 1974), the total amount of phosphorus and the size and charge of the soil particles (Grim, 1968). Even the vigor of shaking of a sample in the laboratory can affect the phosphate fixation by soils (Barrow and Shaw, 1979).

Mineralogy

Most of the factors affecting phosphorus fixation do not react independently, e.g., mineralogy, pH, particle size and charge. Brady (1974) estimated the interaction of mineralogy and pH as shown in Illustration 1. The reaction with iron, aluminum and manganese ions in solution is also shown.

As most desert soils are high in calcium and have a basic pH, it is generally assumed that phosphate is made unavailable by calcium in this area (Fuller, 1975).

The tests run by Duval (1975) on tailing solutions would tend to corroborate this assumption. The average pH of the six samples was 7.2 and the soil solution had 2,400 ppm calcium, while containing only 0.22 ppm iron, less than 0.01 ppm of aluminum and 0.11 ppm of manganese in solution.

When the same samples were extracted using acid, the amounts present were calcium, 14,800 ppm; iron, 37,700 ppm; aluminum 15,500 ppm; and manganese, 440 ppm, indicating if the pH were to change, the solubility would change.

pH

The mineralogy and particle size can have an effect on the pH. Palmer (1973), in studying coal mine spoils, found that the pH of the

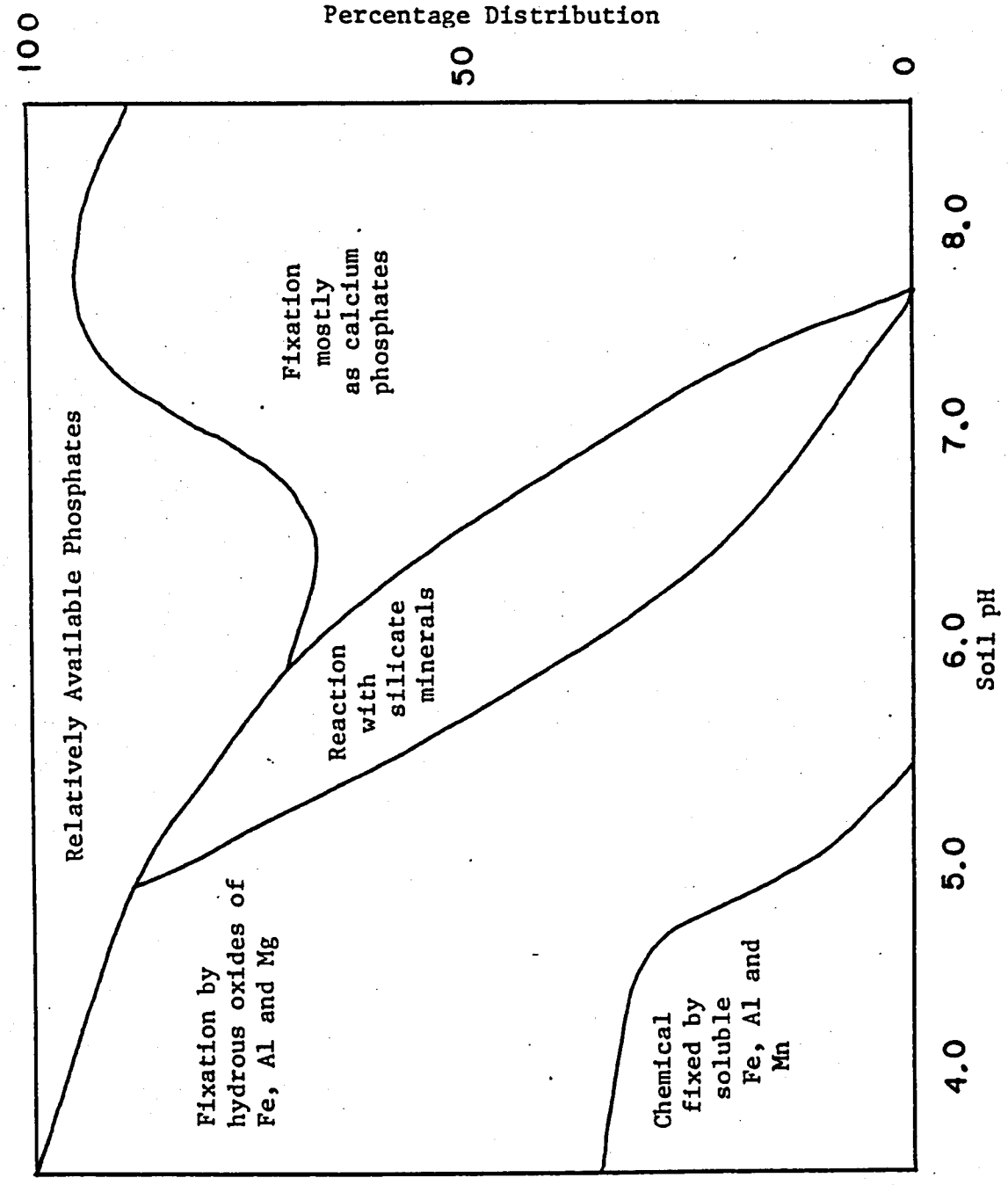

Illustration 1. "Inorganic fixation of added phosphates at various soil pH values. Average conditions are postulated and it is not to be inferred that any particular soil would have exactly the same distribution. The actual proportion remaining in an available form will depend upon contact with the soil, time of reaction, and other factors. It should be kept in mind that some of the added phosphorous may be changed to an organic form in which it would be temporarily unavailable." (Brady, 1974)

mine waste was affected by the amount of pyrite, the particle size or reactive surface, and the buffering capacity of the mine wastes when exposed to air.

The oxidation of pyrite can result in development of extreme acid conditions. However, the pH change will be limited by the soils buffering capacity.

Others (Michelutti, 1974; van Breeman, 1975; Arora, Dixon and Hossner, 1977) found the exposure of pyrite or any soil material with a high content of sulfur can have the same effect.

Particle Size

It has been proven that the smaller the particle, or the larger its surface in relation to its density, the more cation exchange capacity (CEC) it will be likely to have (Baver, Gardner and Gardner, 1972). Dean and Rubins (1947) showed the capacity of clay minerals to adsorb anions in Sassafrass soil is proportional to the surface area.

Particle Charge

Most natural soils have a negative charge. Those few that can have a positive charge, or anion exchange capacity (AEC), such as kaolinite (Grim, 1968) or allophane (Rajan, 1979), are generally pH dependent, with the positive charge decreasing as the pH increases.

Grim (1968) listed 3 possible mechanisms for AEC. They are 1) the replacement of the OH ion in clay minerals; 2) the fixation on the broken edge of anions of similar size and shape to the silica tetrahedron. This mechanism would work for anions such as phosphate, arsenate, and borate, but not for sulfate, chloride or nitrite. 3) The third possible

cause is the same type of isomorphic substitution that is responsible for CEC. In this last example, however the AEC and the CEC would tend to cancel each other out if they are close together.

Other factors such as the development of the crystal structure, specific anion sorption, and the formation of insoluble salts also make the study of AEC difficult.

When the molecules form a poor crystal structure, more OH ions are exposed and can easily be replaced (Millar, Turk and Foth, 1965). Phosphate is often fixed in this way (Marshall, 1977).

The loss of phosphate due to its interaction with various ions such as calcium, iron, and aluminum has already been covered.

Though the availability of phosphate in soils has been extensively studied, little is known about its behavior in tailings. Before effective management practices can be planned, a better understanding must be achieved.

METHODS AND MATERIALS

Various procedures were used to determine if the tailings contained sufficient quantities of phosphorus, to indicate what factors affected the plants abilities to remove phosphorus from the tailings and to decide on the best methods of managing tailings for phosphorus.

Initially the tailings were tested for mineralogy, for easily extracted nutrients, for particle size and charge.

The effects of tailings on nitrates, sulfate, and phosphate was made using two sets of columns, one of which was planted with barley (Hordeum vulgare) and the other left unplanted. These were tested approximately every 10 days during the early stages of growth.

The possibilities of pH changes was sampled over a 25 day period, using various moisture contents.

Field samples were collected from the tailing berms planted during the last five years. These samples were tested for nutrients and pH.

Sampling

Tailings can vary not only from mine to mine, but also within the tailing ponds. If the ore being processed changes, the layers in the pond will also change. Then as the ponds dry, the more mobile ions will move with the water.

The particle size will vary depending on its distance from the edge of the pond. The tailing slurry is discharged on the outer edge

of the pond. The tailing slurry is discharged on the outer edge of the pond, where the larger, heavier particles fall from the solution while the smaller, lighter particles move towards the center. After each pond is filled the next berm will be constructed using tailings from close to the edge of the previous pond. The lower pond berm will then be planted.

The tailings used for this research were taken from the top surface of the Duval Sierrita pond which is indicated in the extreme south of Illustration 2, and is enlarged in Illustration 3.

As the laboratory and greenhouse experiments were a comparison of chemical properties within a homogeneous tailing sample, only two samples were collected. These samples were taken from the top 45 cm of the pond at the points indicated by the letters A (collected October 8, 1979) and B (collected December 26, 1979) on Illustration 3. Each sample was mixed as it was collected and both samples were mixed together before packing the columns or being used in the laboratory.

The location of the field samples collected on March 21, 1980 from the berms are designated by the numbers 1 to 13 on Illustration 3. The berms are separated by concentric lines, with Sites 1 and 2 located on the first berm constructed, and Sites 12 and 13 on the last berm constructed.

Tailing Composition

There is no way to determine exactly what the original parent material composition was, but an indication of the present composition was obtained by X-ray diffraction.

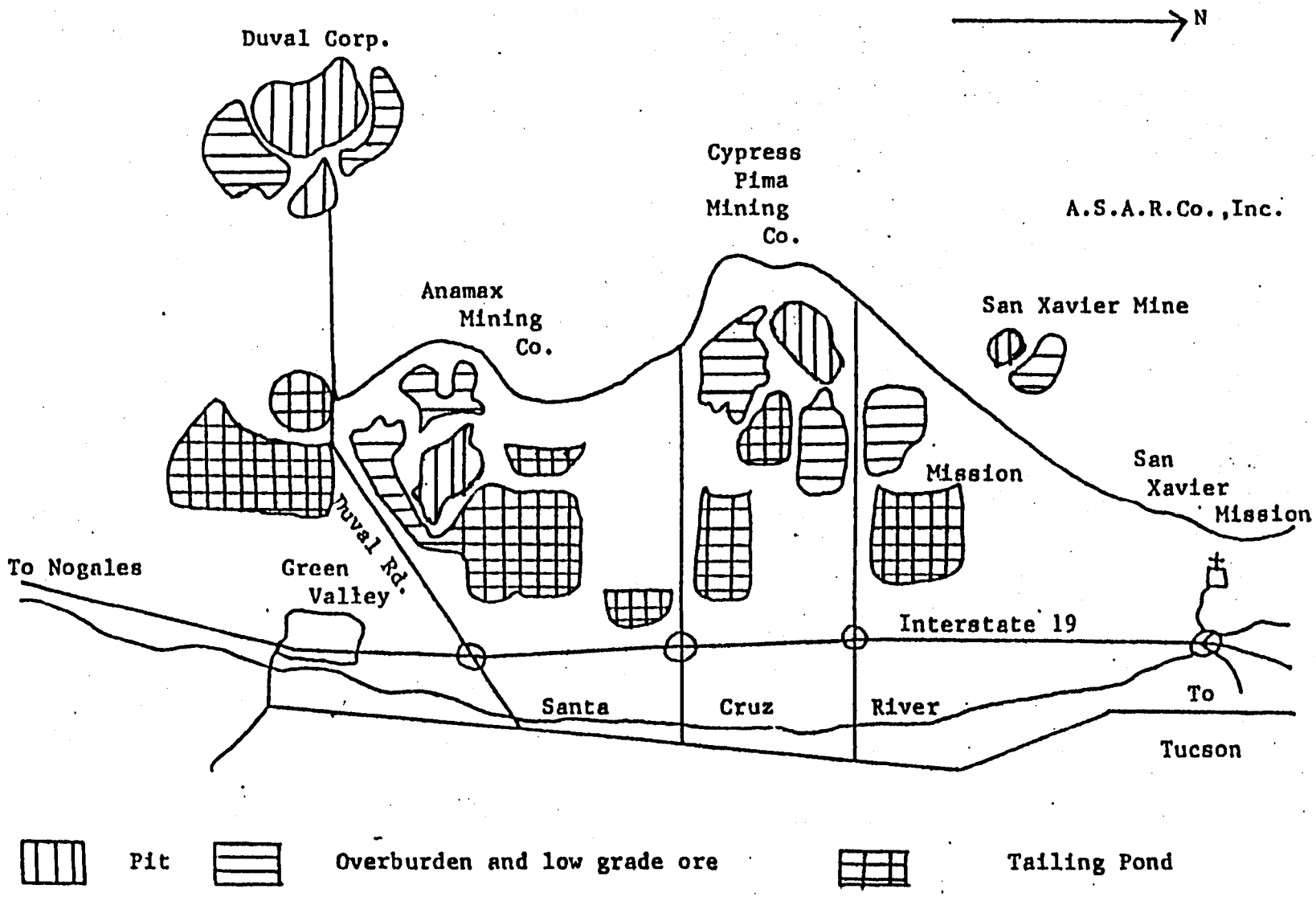

Illustration 2. The mines, ore dumps and waste materials located south of Tucson, Arizona. (Matter, 1974)

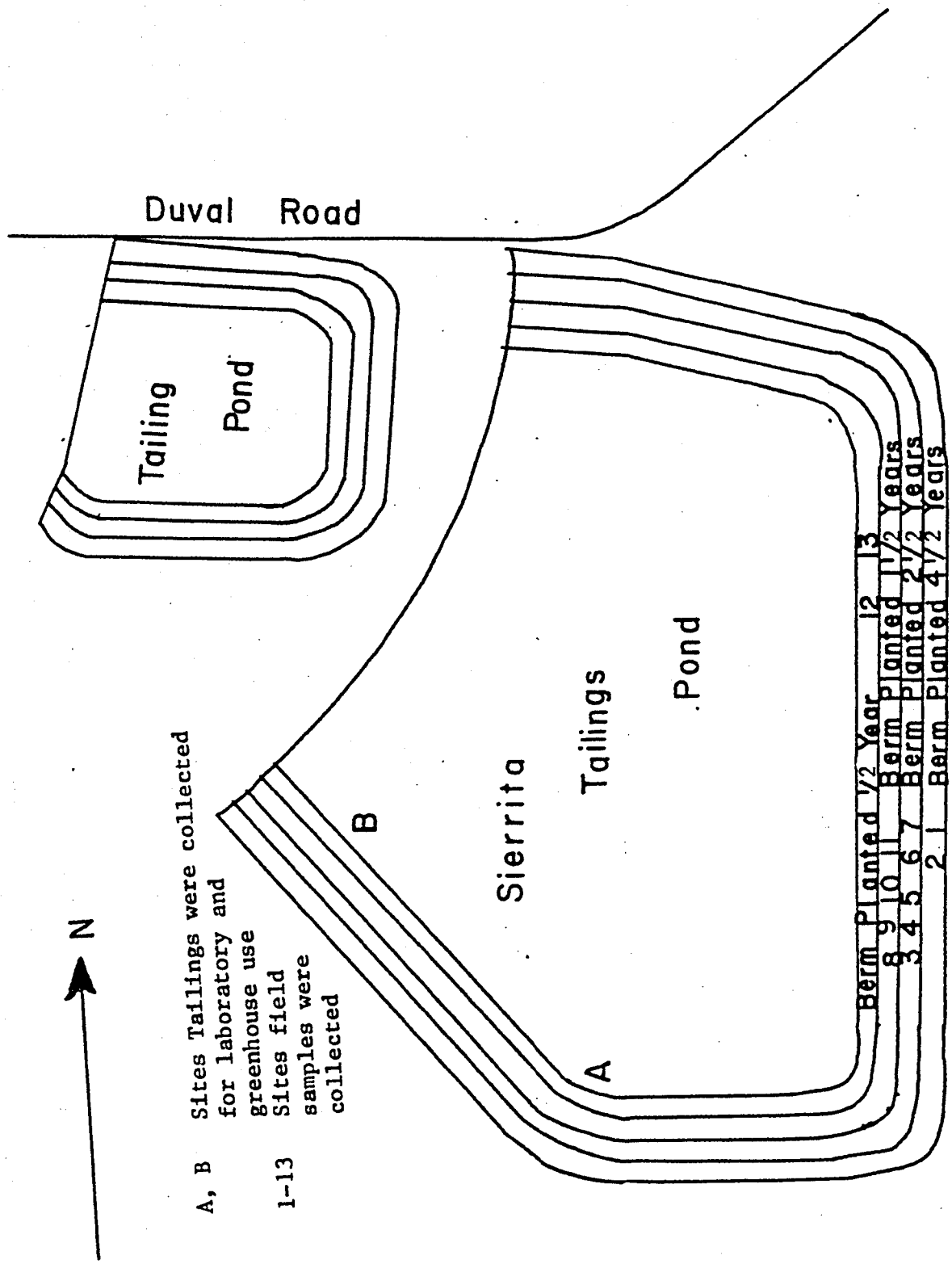

Illustration 3. Enlarged diagram of the Duval tailings pond.

A sample of mixed tailings was washed with distilled water three times to remove the salts. It was then subjected to X-ray diffraction.

As the iron minerals were not in significant quantities to be recorded by X-ray diffraction, a mixed sample of tailings was checked for iron content. A 100 g sample of air dried tailings was separated by magnet. The iron extract and the remaining tailings were then weighed.

By use of a microscope some of the iron was visually identified as pyrite. The remainder was probably magnitite. Percentage could not be calculated visually or by the X-ray diffraction method.

Soil Solution

The extractable metals of fresh tailings were also determined. The metal ions of copper, iron, manganese, and zinc extracted with DTPA (diethlenetriaminepentaacitic acid) with a 1:2 ratio (Black et al., 1965).

A saturated paste was made for a pH measurement with a glass electrode. The paste was vacuum extracted for determination of soluble salts. The EC was determined by a Solubridge.

Particle Size

Particle size was determined by testing two mixed samples of tailings using the hydrometer method according to Black et al. (1965). The readings were adjusted for temperature change. The dispersing agent used was sodium hexametaphosphate.

Ion Exchange Capacity

The cation exchange capacity (CEC) was tested using the method from Agriculture Handbook No. 60 (1954). Sodium acetate, ethanol and ammonium acetate were used to test two samples of 4 g each of tailings.

The anion exchange capacity (AEC) was tested using the method suggested by Dean and Rubins (1947). As some anions are fixed more rapidly and held much stronger than others, three anions; nitrate, sulfate, and phosphate were used. The tailings were first washed with a solution of 0.5 M sodium acetate at pH 7 to remove any exchangeable cations which might affect the results. The nitrate ions were exchanged with sodium sulfate, the sulfate ions were exchanged with sodium phosphate, and the phosphate ions were exchanged with sodium fluoride. The solutions were all 0.5 M concentrations at pH 7. Two samples of 6 g for each ion were tested.

Columns

The form of phosphorus most readily taken up by plants is phosphate. Generally phosphates are immobile and strongly fixed by soils. To study its movement and availability, it was compared with two other anions. They were nitrate, a mobile anion that is seldom fixed by soils, and sulfate, an intermediate anion that is moderately fixed by soils.

Twelve planted columns and 12 unplanted columns were set up on December 28, 1979. Each column consisted of PVC plastic and was 15 cm in diameter and a little more than 60 cm in height. A plastic cap was sealed on the bottom of the column which was tapped for drainage.

The columns were packed with tailings to which monocalcium phosphate ($Ca(H_2PO_4)_2 \cdot H_2O$) had been added in the amount of 8.74 g per column.

The columns were filled by weight using 14,600 g of the tailing mixture, resulting in a bulk density of 1.68 g/cm^3. They were packed by shaking, then 15 seeds of barley (Hordeum vulgare) were added to 12 of the columns. As columns, planted and unplanted, were dusted with a fungicide and an additional 266 g of tailings were added to each column. Next 1900 ml of tap water was added to each column and the tailings were placed in the greenhouse.

Tap water was added at a rate of 600 ml per column 10, 21, 31, 42, and 52 days after planting. On days 10 and 31, 1.5 g of ammonium nitrate were added in the water. Two hours after irrigation samples were collected for analysis. One of each of the planted and unplanted columns was selected for the first samples, and two of each of the planted and unplanted columns were sampled there after. As the unplanted column was too wet to sample on the 52nd day, it was taken two days later.

An Oakfield probe was used to take samples at the depths of 0 to 5, 5 to 10, 10 to 15, 15 to 20, 20 to 35, and 35 to 50 cm. The samples were then made into a saturated paste and the soil solution extracted. As the concentrations with depth did not prove to be significantly different, they were averaged together to determine the available nitrate, sulfate, and phosphate. The number of seedlings to germinate was counted.

The results were analyzed statistically using the analysis of variance method.

pH Effects

To determine if the pH in the columns was affected by differences in moisture content, a series of containers was maintained at various moisture levels.

Changes in pH can result from microorganism effects or natural chemical changes. To determine if microorganisms caused the change, a sample of the tailings was heated 4 times in an autoclave for 4 hours at 123° C. A comparable sample of air dried tailings was used to determine the total pH change.

The initial pH was determined by testing 100 g sample of both treated and untreated tailings in a paste made with 35 ml of distilled water. The soil solution was then extracted and tested for available nitrate, sulfate and phosphate.

For both the treated and untreated tests, 25 styrofoam cups were filled approximately ¼ full with 100 g of tailings. To five cups of each type of tailings distilled water in the amounts of 5, 10, 15 and 25 ml were added. Five cups were left dry. The cups was then covered and stored at room temperature.

After five days enough water was added to bring all cups back to their original moisture content. One cup of each type and for each moisture level was selected at random for testing. The moisture content was increased to 35% by weight. The pH was determined by pH meter first

and then the soil solution extracted by suction. The soil solution was tested for available nitrate, sulfate, and phosphate.

The same procedure was repeated after 10 and 15 days. On day 20 and 25 the same procedure was used except water was not added to maintain the initial water level. The samples were tested at 35% moisture by weight.

The data were analyzed for significance using the analysis of variance method.

Field Samples

To determine how the results obtained in the greenhouse and laboratory compare with the actual field conditions a few samples were taken from the planted tailing berms.

Duval plants nursery-grown shrub species from five gallon containers. Granular fertilizer is placed below the plants at the time of planting. Planting is done during the months of June, July and August. The plants are watered by drip irrigation, and additional nitrogen fertilizer is occasionally added. At the time the samples were taken all berms were still being irrigated.

Thirteen sites were selected using various soil materials, plant species, depth of sampling, and age of planting. The location of the sites are shown on Illustration 3. The samples were tested for pH, moisture content, sulfate, and phosphate.

The bottom berm was constructed using over burden material and was planted in 1975. Of the two plant species selected for testing only the Chilean mesquite (Prosopis chilensis) was growing on this site.

Soil samples were taken from the surface to 15 cm, from 30 to 45 cm, from 60 to 75 cm, and from 90 to 105 cm depths. The samples were taken at the edge of the drip line of the foliage.

All other berms were constructed using tailings. Each berm was planted during the summer following its formation in the years of 1977, 1978 and 1979. Planting and irrigation practices were the same for all berms. The second plant species tested was Australian saltbush (Atriplex semibaccata).

The sites were selected at random and were all on the east facing slope. The soil material was put in plastic bags as they were collected. They were tested for moisture content the next day. Enough distilled water was added to make a paste of 35% moisture which was tested for pH, sulfate and phosphate using the same methods described earlier.

Multiple regression was used to compare the effects of the various conditions on pH. The effects of pH on phosphate availability was determined using simple regression.

RESULTS AND DISCUSSION

Of the many things that can affect phosphate availability, the tailings composition, the particle size, the particle charge, the weathering, and the pH, were selected for consideration.

X-Ray Diffraction

The exact content of the ore from which the tailings result cannot be determined at this time. To identify what minerals are likely to remain in the tailings, X-ray diffraction was used. The list of rock fragments found is shown on Table 2, together with their theoretical composition. This method of identification does not give the quantities of any of the minerals, but an estimated ratio is shown.

As iron is not identifiable when being tested by X-ray diffraction, it was separated by magnet. The contents removed by magnet were determined to be approximately 2% of the sample. With the use of a microscope some of the particles were visually identified as pyrite (FeS_2).

No phosphorus bearing minerals were identified from this examination. There is always a possibility of some phosphorus minerals being found in other samples, but the content is probably so low amendments will be needed to meet the plants needs.

From these samples the only identified minerals which contained sulfur was pyrite. As any minerals extracted by flotation would have to contain sulfur, the high sulfate content of tailings could result from

Table 2. Mineral composition of copper mine tailings as determined by X-ray diffraction.

Mineral	Theoretical Composition	Estimated Percentage
Quartz	SiO_2	48
Kaolinite	$Al_2SiO_5(OH)_4$	11
Mica	$K_x((Al_4)(Si_{4-n}Al_n)O_{10}(OH)_2)$	15
Calcite	$CaCO_3$	7
Halite	NaCl	4
Feldspar	$(Na,K,Ca)AlSi_3O_8$	15

the residue of the minerals extracted, from the flotation chemicals, or possibly from undetected minerals.

The source of minerals identified by X-ray diffraction is likely to be from the host rock, rather than resulting from later volcanic action.

Soil Solution

The ions in the soil solution affect what is readily available to plants, the weathering of the soil particles, the fixation of phosphates, and the soil pH. A list of the ions found in the soil solution of the tailings is shown on Table 3.

While all of the cations in solution were not identified, as shown by comparing the expected meq/100 g of tailings with those listed, these figures do give some information.

The concentration of heavy metals in this sample is not enough to cause any problems to the plants.

When considering the nutrients needed for healthy plants, there is an insufficient amount of nitrate and phosphate for plant growth. Other minerals seem to be in sufficient quantities, with sulfate approaching dangerous concentration level. The sulfate needed is generally considered in its ratio to nitrogen, with 1 part sulfate to 10 parts nitrogen being the highest concentration needed for most plants.

The high concentration of sulfate may be a result of the reagents added during the mining process or a release of the sulfur in the original ore. The grinding has reduced the particle size so that many ions

Table 3. Analysis of minerals found in the soil solution as extracted from a saturated paste of copper mine tailings.

Cations	meq/100 g	Anions	meq/100 g
Calcium	11.4	Chlorine	17.0
Magnesium	2.6	Sulfate	49.5
Potassium	2.9	Nitrate	0.1
Sodium	18.0	Phosphate	Trace
Copper	0.2		
Iron	3.2		
Manganese	0.2		
Zinc	0.1		
Total	38.6		66.6
Expected meq/100 g	65.0		65.0
EC	6.5		
pH	7.7 (Initial)		

in the tailings can be exchanged. Anions such as sulfate can be replaced by hydroxyl ions, thus increasing the concentration.

The soil material was classified as saline, with a pH of 7.7, EC_e of 6.5 and ESP of 7.5. The high salt content can affect the selection of plants and their germination on the berms.

At the initial pH of 7.7 most of the phosphate in the soil would be expected to be fixed by calcium. As the pH drops the fixation of phosphate would change to silicate, then to iron, magnesium and aluminium. After the phosphate has been released by one mineral and before fixation by the next, it would be available for plant absorption.

Particle Size

The particle size affects the amount of reactive surface per unit of tailings, the surface available for weathering, the charge capacity, and probably the pH.

The average fractions for the tailings were:

Sand	60%
Silt	39%
Clay	1%

The corresponding texture is a sandy loam, but due to the effects of grinding these particles would not always react as soil particles would, especially the silt and clay fractions. Probably the greatest effect would result from the exposure of pyrite. Palmer (1973) showed that the exposure of pyrite lowered the pH. The amount of decrease depended on the amount of pyrite present and the buffering capacity of the mine wastes. This decrease could be of a short duration if the buffering capacity of the wastes is high.

Ion Exchange Capacity

The particle size is known to affect the particle charge. The smaller the particle, the greater will be the surface area per gram and the greater will be the reactive surface.

The CEC of the tailings was 5.7 meq per 100 g. This is a reasonable value for soils which have large amounts of sand size particles.

However, the AEC was considerably higher than would be found in most soils. The AEC for phosphate was 36 meq per 100 g tailings and for sulfate it was 93 meq per 100 g of tailings. Nitrate is seldom retained by soils and the tests of nitrate exchange capacity for tailings showed that in this aspect tailings behave like soils.

As the phosphate ion is normally retained more readily than the sulfate ion, the AEC was probably distorted by the high content of sulfate and the low content of phosphate in the tailings itself. Therefore, the AEC as shown by sulfate was considered valid at 36 meq per 100 g.

As most of the positive charges found in soils are the results of broken edges, the unusually high AEC in tailings could be the consequence of the recent grinding.

The removal of copper particles must also be considered. One of the sulfur molecules in the xanthate attaches to a sulfur molecule in the crushed ore, thus removing at least some of the negative charges.

pH also affects AEC. As the pH decreases the AEC increases, with point of zero charge (PZC) for soils with a high positive charge

being between pH 5 and pH 8.5. If the AEC increases in tailings as the pH decreases, the PZC is likely to be high.

The mineralogy affects the AEC, especially the fixation of phosphate. Though the pH changes in tailings were slight, less than 1.5 units, this range could cover several different mineral fixation ranges.

When comparing the exchange ratio of cations to anions, there is a considerable difference from that which occurs in natural soils, as is shown below:

Cation Exchange/Anion Exchange Ratio

Tailings SO_4	0.06
Tailings PO_4	0.15
Kaolinite	0.52
Illite	2.3
Bentonite	4.1

This would indicate that anions would be expected to react differently in tailings than they do in soils.

Columns

The behavior of the three anions being studied and the effect of plants on their availability was tested in columns. The two replicas were averaged and the available nitrate, sulfate and phosphate in the columns are summarized in Table 4 and in the Appendix. The data are graphed on Illustration 3, 4, and 5.

Though provisions were made for drainage, the only leachate collected was from the 52nd day in the unplanted columns. This leachate was not sufficient for testing. The field capacity of this sample was approximately 28%. The 26% moisture content shown on Table 4 was determined during testing, 2 days after irrigation.

Table 4. Average NO_3,SO_4, and PO_4 available in columns of copper mine tailings.

Days	10	21	31	42	52
NO_3-N, ppm					
Unplanted	52.0	78.2	68.7	160.5	158.8
Planted	52.0	51.0	103.0	73.5	108.7
SO_4, ppm					
Unplanted	55.2	1,756	1,932	1,078	921
Planted	55.2	1,846	2,102	1,444	1,745
PO_4-P, ppm					
Unplanted	.50	6.75	7.06	3.70	2.25
Planted	.50	7.76	6.40	1.42	3.71

Significance Test

	NO_3-N	SO_4	PO_4-P
Days	.01	.01	.01
Treatment	.05	.05	NS
Days X Treatment	.05	NS	NS

Days		42	52
pH -	Unplanted	6.5	6.4
	Planted	7.1	6.9
Moisture Content-	Unplanted		14%
	Planted		26%

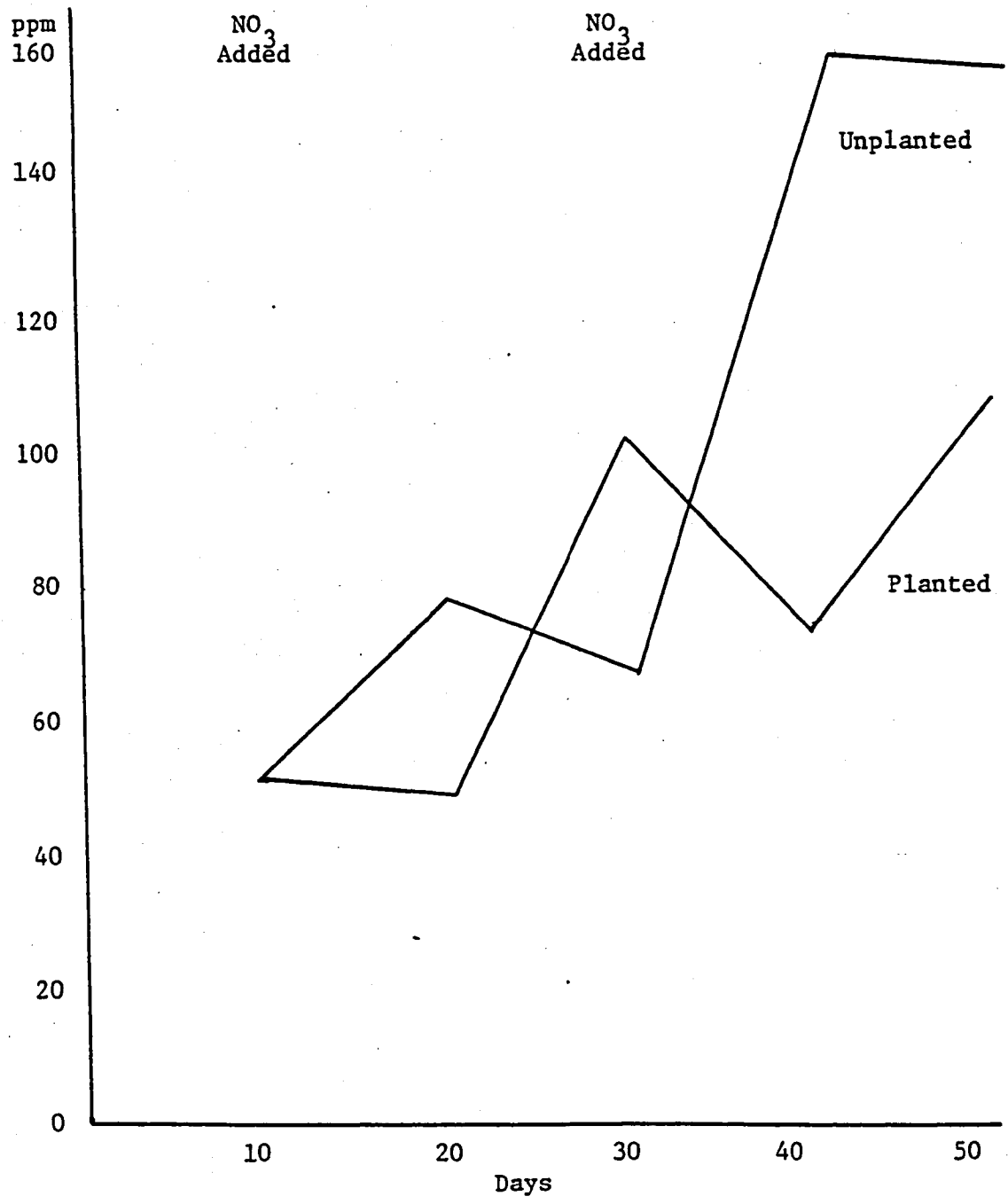

Illustration 4. Available NO_3 in columns.

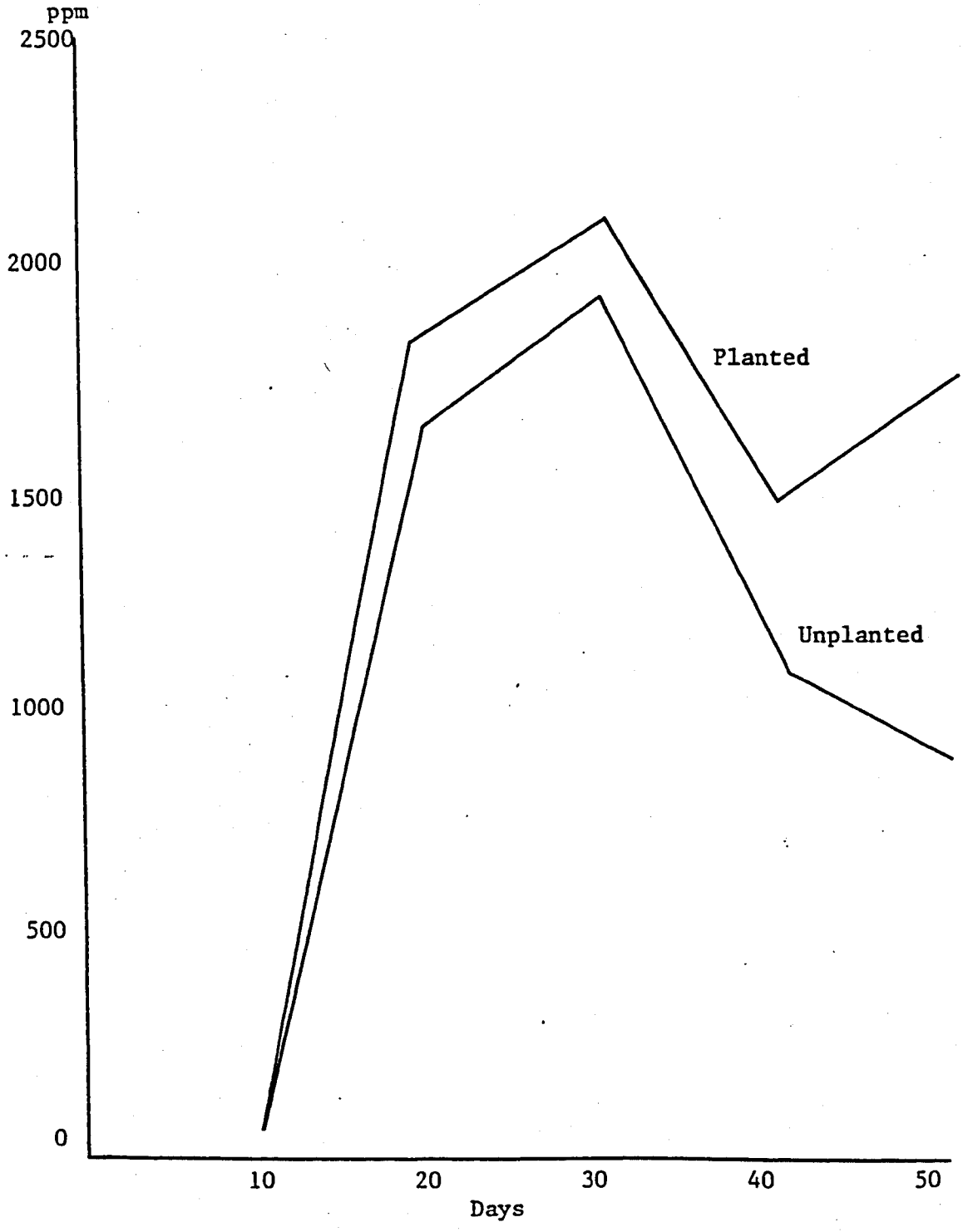

Illustration 5. Available SO_4 in columns.

Even though the results of the nitrate available showed a significance of at least 0.05 in all phases it did not have any effect on the availability of sulfate or phosphate ions.

The information resulting from available sulfur tests was of special interest, because of the obvious changes. By air drying the tailings, sulfate was either fixed or became insoluble so that, it maintained a much lower level than normally found in tailings until after the 10th day. The effect on the available sulfate due to the treatment appears to be the result of the moisture content rather than plant uptake. The surface of the tailings within the columns was approximately 10 cm below the edge of the columns, so much of the water loss was due to transpiration rather than evaporation. The difference between the moisture level in planted and unplanted columns is shown on Table 4.

As a result of the sulfate change, the pH also changed. This was not proven statistically because the pH was not measured until the 42nd and 52nd days. Though the pH changed from 7.7 to 6.9 and 6.4 is not a large change, it is an important change. A second possible reason for phosphate increase could be the result of being replaced by sulfate ions.

The rapid increase of phosphate from less than 1 ppm to about 7 ppm could be an important influence on plant growth. Phosphate is mobile in plants and can be absorbed and stored for later use.

As the amount of available phosphate decreased in both the planted and unplanted columns after day 32, this change would be the result of soil fixation rather than plant uptake.

There were two problems with plant growth. The germination rate for barley was poor, with only 40% of the seeds showing some growth on day 10. Then after day 20 many of the tips of the barley leaves began to show symptoms of salt or sulfate burn.

Chapman (1966) found that barley will grow in sand cultures with up to 205 meq/l, but with less than 50% normal growth.

pH Effects

To determine if a difference in moisture would effect the change in pH, various amounts of distilled water were added to tailings and any pH change was noted. Two series of tests were done simultaneously. One series was autoclaved to eliminate any microorganism effect. The other series used air dried tailings. The results are listed on Table 5 and graphed on Illustrations 7 and 8.

Water was added only until the 15th day, so the statistical effect of moisture was calculated only during that time. The pH for days 20 and 25 are given only to indicate the effect of drying.

The results show a significant effect in all areas except the combination of moisture and treatment. The change in pH of the untreated tailings shows a more rapid decrease in pH as the moisture level increases. The pH change in the autoclaved tailings is more difficult to explain. The lack of reaction for the first five days could be the result of delayed microbial activity due to autoclaving or the result of some destruction of molecular structure when the sample was heated to 123^{o}C. The pH change was considered to be the result of chemical change rather than microbial activity.

Table 5. The effects of moisture content on pH of tailings in a saturated paste.

Moisture Content		Days					
		0	5	10	15	20	25
%				pH			
0	Untreated	7.8	7.7	7.8	7.8	7.6	7.7
0	Autoclaved	7.5	7.6	7.6	7.6	7.6	7.7
5	Untreated	7.8	7.7	7.1	6.9	7.3	7.6
5	Autoclaved	7.5	7.6	7.4	7.4	7.3	7.7
10	Untreated	7.8	7.7	7.0	6.8	7.1	7.4
10	Autoclaved	7.5	7.6	6.8	7.2	7.2	7.6
15	Untreated	7.8	7.5	6.9	6.7	7.0	7.3
15	Autoclaved	7.5	7.6	6.6	6.4	7.2	7.6
25	Untreated	7.8	7.6	6.8	6.2	6.7	7.1
25	Autoclaved	7.5	7.5	6.5	6.3	6.7	7.6

	Significance
Days	.01
Treatment	.05
Moisture	.01
Days X Treatment	.05
Days X Moisture	.01
Treatment X Moisture	NS

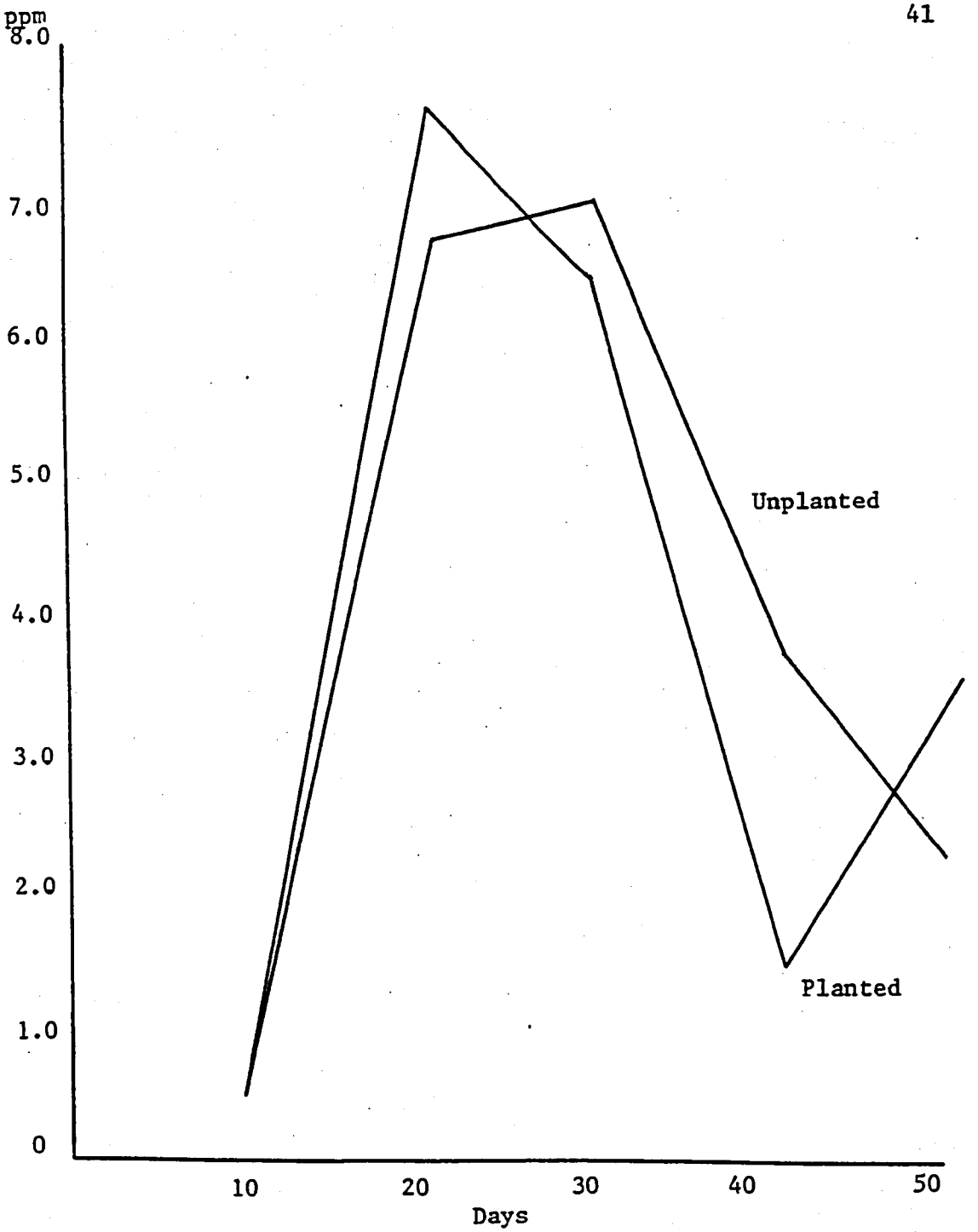

Illustration 6. Available PO_4 in columns.

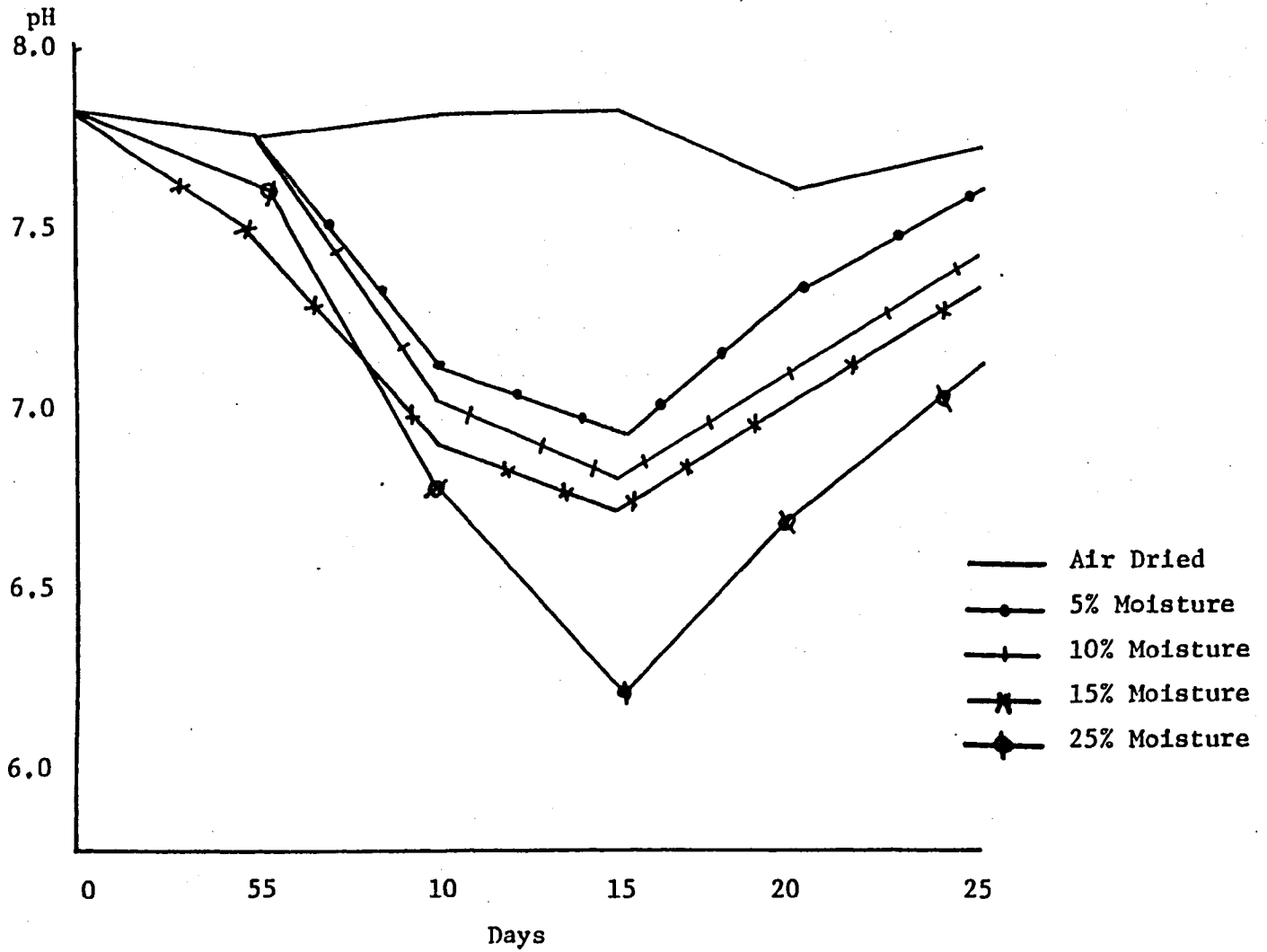

Illustration 7. The effect of moisture content on pH - untreated.

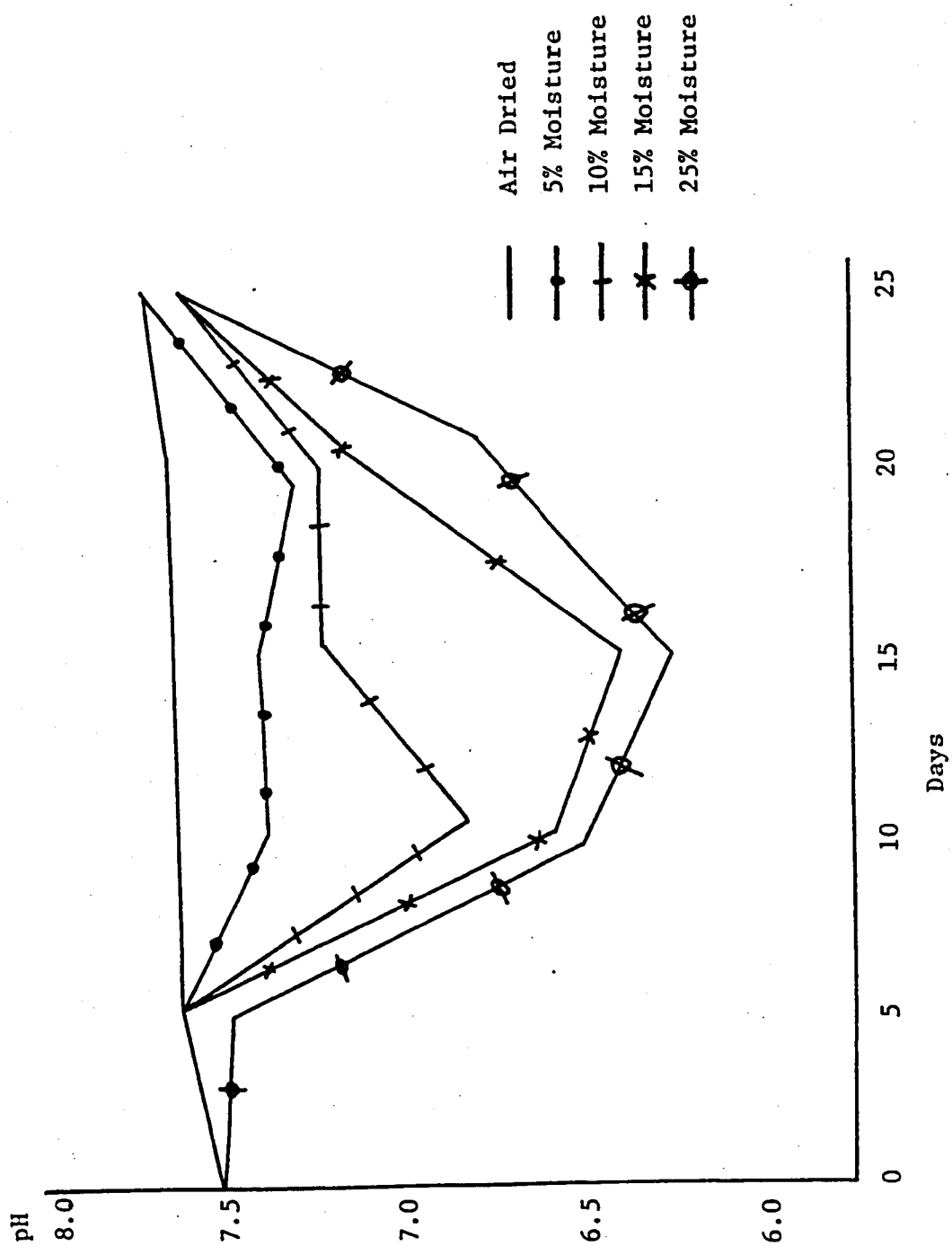

Illustration 8. The effect of moisture content on pH - autoclaved.

The rapid increase in pH as the tailings began to dry seems to indicate a high buffering capacity in the tailings.

Field Samples

All of the research in the laboratory or greenhouse is of little value unless it can be compared to the conditions that exist in the field.

The results of the field sampling are shown on Table 6. When comparing the data on parent material, plant species, age, depth, moisture content and sulfate by multiple regression, with the effect of site removed, the only significant factor affecting pH was the amount of sulfate.

When comparing the effect of the pH on the availability of phosphate by simple regression there was no significance. As all indications are that the tailings contain little phosphorus and what little is present is poorly distributed, these results are reasonable. The samples taken were at a sufficient distance from the initial fertilization, so that any phosphorus added at that time would not have an effect.

The desirable pH range for the best utilization of phosphorus is between 6.0 and 7.0. As most of the pH values in the tailings was within that range any phosphate added should be at close to maximum availability.

Though not listed as significant the pH does tend to be lower on the surface than at deeper levels. This would be due to more oxidation of sulfides close to the surface.

Table 6. Data collected from tailing berms.

Site	Parent Material	Plant Species	Age	Depth	Moisture Content	SO_4	pH	PO_4-P
			(Yrs)	(cm)	(%)	(ppm)		(ppm)
1	Overburden	Mesquite	4½	0-15	5.9	147	7.3	0.25
				30-45	7.4	65	8.1	0.05
				60-75	6.5	75	7.9	0.02
				90-105	9.0	92	9.0	0.02
2	Overburden	Mesquite	4½	0-15	3.4	93	6.7	0.00
				30-45	5.8	78	7.3	0.00
				60-75	8.2	62	7.8	0.00
				90-105	9.6	51	8.1	0.00
3	Tailings	Mesquite	2½	0-15	3.6	1008	6.8	0.00
				30-45	7.0	2352	6.8	0.02
				60-75	7.7	2784	6.9	0.08
				90-105	5.7	1248	7.0	0.02
4	Tailings	Mesquite	2½	0-15	1.5	1200	6.5	0.00
				30-45	7.9	7872	3.0	0.00
				60-75	5.0	2880	3.8	0.00
				90-105	6.6	4320	6.3	0.00
5	Tailings	Saltbush	2½	0-15	7.7	1920	6.1	0.00
				30-45	6.5	1416	6.5	0.00
				60-75	7.2	1824	6.6	0.00
				90-105	6.2	3168	6.7	1.10
6	Tailings	Saltbush	2½	0-15	2.0	1872	6.8	0.03
				30-45	6.2	1776	6.7	0.00
				60-75	7.9	1584	6.7	0.17
				90-105	9.0	1512	9.0	0.12

Table 6--Continued.

Site	Parent Material	Plant Species	Age	Depth	Moisture Content	SO_4	pH	PO_4-P
			(Yrs)	(cm)	(%)	(ppm)		(ppm)
7	Tailings	None	2½	0-15	3.2	1200	6.6	0.10
				30-45	11.3	3024	6.9	0.43
				60-75	7.1	1872	7.0	0.13
				90-105	6.4	1056	7.1	0.17
8	Tailings	Mesquite	1½	0-15	4.3	1248	6.1	0.15
				30-45	5.7	1248	6.5	0.17
				60-75	5.8	1272	6.6	0.17
				90-105	6.1	1224	6.6	0.05
9	Tailings	Mesquite	1½	0-15	7.0	1344	6.2	0.03
				30-45	7.0	912	6.6	0.13
				60-75	8.7	672	6.8	0.10
				90-105	2.8	816	6.6	0.17
10	Tailings	Saltbush	1½	0-15	6.7	1248	6.8	0.00
				30-45	7.3	1008	6.7	0.05
				60-75	7.3	1200	6.6	0.05
				90-105	7.5	1296	7.5	0.05
11	Tailings	Saltbush	1½	0-15	2.9	1200	6.5	0.00
				30-45	4.3	792	6.6	0.03
				60-75	6.6	912	6.4	0.12
				90-105	8.6	1056	8.6	0.12
12	Tailings	Saltbush	½	0-15	15.7	1272	6.5	0.10
				30-45	10.5	912	6.6	0.05
				60-75	18.0	1056	6.7	0.00
				90-105	18.2	1104	6.7	0.03

Table 6--Continued.

Site	Parent Material	Plant Species	Age	Depth	Moisture Content	SO_4	pH	PO_4-P
			(Yrs)	(cm)	(%)	(ppm)		(ppm)
13	Tailings	Mesquite	½	0-15	11.0	960	7.1	0.03
				30-45	12.3	1200	7.2	0.09
				60-75	11.4	1008	6.7	0.40
				90-105	8.8	1200	6.7	0.14
Significance								
Effect on pH	NS	NS	NS	NS	NS	.000	.	.
Effect of pH	.	.	.	.	.	.	.	NS

The plants do not appear to have a significant effect on the pH. However, both sulfate and phosphorus ions could have an effect on plants. Saltbush is known to be sulfate tolerant and the mesquite plants on this mine site do not appear to be affected.

The age and moisture content do not have a significant effect. The parent material does not show a significant effect by the multiple variable regression. However parent material does have an effect on the available sulfate.

High salt and sulfate concentrations have an effect on plant growth so when selecting plants for use in tailings these factors must be considered, as well as such problems as drought tolerance and nutrient availability.

CONCLUSION

The information gained from these experiments provided two unexpected results, the positive charge of the tailings and the pH change. A positive charge can be the result of grinding and the removal of some of the particles by flotation.

The pH change may be due to the large sulfate concentration from both the original parent material and the flotation process.

Both of these factors affect the availability of phosphorus, but the most important effect is the small amount of phosphorus found naturally in tailings. Neither the porphyry ore nor the minerals identified by X-ray diffraction have much phosphorus. The tests on the Duval Mine tailings indicate very little phosphate in the soil solution. The first requirement in phosphorus cycling would therefore be to add sufficient phosphorus to establish permanent plant colonies on the berms. The easiest time to do this would be during the planting as is done by the mines now.

In addition, if the mining companies hope to create a more natural appearance by having other plants establish themselves on the berms, additional phosphorus fertilizer must be added between the planting sites. As phosphorus seldom moves far from its original site, it must be placed at the depth and location where it is most readily available to plants. In the desert many plants have shallow root systems, so phosphorus should be near the surface and located at intervals frequent

enough to allow the roots of any plant to reach the nutrient during the early stages of growth.

In order to take advantage of the pH change, phosphorus added with calcium would allow for more fixation changes due to the tailing's mineral content. The time of phosphate release should coincide with the plants needs as well.

The tailings may eventually fix much of the phosphorus added, so sufficient amounts must be added at the time of planting for permanent growth as well as to establish the plants.

There is still much to learn about tailings. In many ways they do not react as soils, but in studying their development as they begin the long change towards becoming soils, we will also learn much about soils.

APPENDIX A

AVAILABLE NO_3, SO_4 AND PO_4 COLUMNS BY DEPTH (PPM)

Available NO_3 in columns by depth (ppm)

Days	10	21	31	42	52
Depth (cm)		Unplanted Column - Replica 1			
0-5	243.2	288.0	44.8	78.4	73.6
5-10	169.6	40.0	29.6	345.6	84.0
10-15	11.2	40.0	18.4	224.0	291.2
15-20	24.0	9.6	16.8	100.8	262.4
20-35	17.6	5.4	86.4	141.6	153.6
35-50	4.8	8.8	67.2	131.2	147.6
		Unplanted Column - Replica 2			
0-5	11.2	82.4	168.0	275.2	22.8
5-10	116.8	51.2	88.0	176.0	113.6
10-15	64.0	31.2	108.8	136.8	192.0
15-20	64.0	45.6	64.0	155.2	224.0
20-35	68.8	42.4	68.8	136.0	185.6
35-50	20.8	268.8	56.0	164.0	150.4
		Planted Column - Replica 1			
0-5	243.2	256.0	230.4	27.2	243.2
5-10	169.6	72.0	192.0	252.8	358.4
10-15	11.2	13.6	230.4	192.0	153.6
15-20	24.0	36.8	122.4	155.2	224.0
20-35	17.6	40.0	17.6	13.6	107.2
35-50	4.8	24.0	24.0	65.6	33.6
		Planted Column - Replica 2			
0-5	11.2	114.4	230.4	86.4	27.2
5-10	116.8	44.8	204.8	58.4	164.8
10-15	64.0	32.0	116.8	168.0	249.6
15-20	64.0	30.4	120.0	51.2	142.4
20-35	68.8	34.4	100.8	50.4	40.0
35-50	20.8	41.6	61.6	29.6	22.4

Available SO_4 in columns by depth (ppm)

Days	10	21	31	42	52
Depth (cm)		Unplanted Column - Replica 1			
0-5	24	912	3168	720	936
5-10	16	1704	240	528	960
10-15	28	1056	168	720	792
15-20	16	1272	312	744	672
20-35	62	2592	1728	960	720
35-50	82	3360	2688	1368	1152
		Unplanted Column - Replica 2			
0-5	24	672	768	1032	888
5-10	32	768	1248	1272	816
10-15	30	912	1392	1248	744
15-20	30	1248	1392	1536	1008
20-35	75	2304	2304	1008	912
35-50	82	600	3264	1248	1080
		Planted Column - Replica 1			
0-5	24	1056	1488	912	792
5-10	16	1200	1008	720	816
10-15	28	1392	984	720	1240
15-20	16	1776	1296	1056	1296
20-35	62	2446	2280	1824	1920
35-50	82	2304	2408	1704	2208
		Planted Column - Replica 2			
0-5	24	1008	1536	672	1104
5-10	32	1152	1296	528	1056
10-15	30	1296	960	672	1248
15-20	30	1416	1416	1844	1920
20-35	75	1632	2160	1920	1968
35-50	82	2496	2688	1968	2376

Available PO_4 in columns by depth (ppm)

Days	10	21	31	42	52
Depth (cm)			Unplanted Column - Replica 1		
0-5	1.20	1.63	0.93	0.35	0.32
5-10	0.60	10.10	4.95	4.80	0.30
10-15	0.60	10.35	3.80	2.70	0.50
	0.40	3.40	2.85	2.80	3.25
20-35	0.48	9.50	3.05	3.95	2.55
50-50	0.36	7.00	16.32	2.30	2.25
			Unplanted Column - Replica 2		
0-5	0.28	1.20	5.10	0.70	5.15
5-10	0.24	7.07	6.63	2.95	5.00
10-15	1.80	0.47	6.60	2.35	7.70
15-20	0.36	4.70	7.30	6.50	1.70
20-35	0.32	6.02	10.92	6.60	0.90
35-50	0.32	9.48	4.02	4.05	1.30
			Planted Column - Replica 1		
0-5	1.20	0.85	1.27	0.05	0.85
5-10	0.60	7.50	1.87	2.25	2.90
10-15	0.60	16.20	4.26	0.33	2.55
15-20	0.40	11.20	5.40	0.27	1.37
20-35	0.48	7.47	9.18	2.10	1.85
35-50	0.36	14.28	4.12	2.30	2.10
			Planted Column - Replica 2		
0-5	0.28	1.12	1.00	1.00	1.75
5-10	0.24	3.06	4.30	0.20	0.73
10-15	1.80	3.60	1.60	1.45	5.90
15-20	0.36	5.30	1.45	0.35	8.40
20-35	0.32	6.35	9.68	2.60	9.40
35-50	0.32	7.38	12.60	0.45	3.25

LITERATURE CITED

Anthony, J. W., S. A. Williams and R. A. Bideaux. 1977. Mineralogy of Arizona. Univ. of Arizona Press, Tucson.

ASA. 1965. Methods of soil analysis, Parts 1 and 2. C. A. Black, D. D. Evans, J. L. White, L. E. Ensminger, and F. E. Clark (eds.). Amer. Soc. Agron., Inc., Madison.

Arora, H. S., J. B. Dixon, and L. R. Hossner. 1977. Pyrite morphology in Lignitic coal and Associated Strata of East Texas. Soil Sci. 125: 151-159.

Barrow, N. J. and T. C. Shaw. 1979. Effects of solution: Soil ratio and vigour of shaking on the rate of phosphate adsorption by soil. J. Soil Sci. 30: 67-76.

Baver, L. D., W. H. Gardner and W. R. Gardner. 1972. Soil physics, 4th ed. John Wiley and Sons, Inc., New York.

Biswas, A. K. and W. G. Davenport. 1980. Extracting metallurgy of copper, 2nd ed. Pergamon Press, New York.

Black, C. A. 1968. Soil-plant relationships, 2nd ed. John Wiley & Sons, Inc., New York.

Brady, Nyle C. 1974. The nature and properties of soils, 8th ed. MacMillan Publishing Co., Inc., New York.

Chapman, H. D. 1966. Diagnostic criteria for plants and soils. Univ. of California, Div. of Agric. Sci.

Crozier, R. D. and D. Ottley. 1978. Processing of copper sulphide ores: froth flotation reagents - A review. Mining Mag. 332-339.

Day, A. D. and K. L. Ludeke. 1979. Disturbed land reclamation in an arid environment. p. 437-460. In G. O. Argall, Jr. (ed.). Proceedings of the International Tailing Symposium, Vol. 2, Tailing Disposal Today. Miller Freeman Publications, Inc., San Francisco.

Dean, L. A. and E. J. Rubins. 1947. Anion exchange in soils: I. exchangeable phosphorus and the anion exchange capacity. Soil Sci. 63: 377-387.

Duval Sierrita Corporation. 1975. Unpublished data.

Eddy, C. H. 1979. Federal minerals policy and mine waste. p. 507-513. In G. O. Argall, Jr. (ed.), Proceedings of the International Tailing Symposium, Vol. 2, Tailing Disposal Today. Miller Freeman Publications, Inc., San Francisco.

Flint, R. F. and B. J. Skinner. 1974. Physical geology. John Wiley and Sons, Inc., New York.

Fuller, W. H. 1975. Soils of the desert Southwest. Univ. of Arizona Press, Tucson.

Grim, Ralph E. 1968. Clay mineralogy. McGraw-Hill Book Co., New York.

Haase, Edward F. 1980. Ecological consideration for reclamation in the Southwest. Speech given at the Vegetation Reclamation of Mine Wastes and Tailings in the Southwest, Tucson.

Hanlon, Jr., E. A. 1977. Use of clear residue of modify alkaline tailings environment for revegetation. M.S. Thesis, Univ. of Arizona.

Hicks, C. R. 1973. Fundamental concepts in the design experiments, 2nd ed. Holt, Rinehart and Winston, New York.

Jenny, Hans. 1941. Factors of soil formation. McGraw-Hill Book Co., Inc., New York.

Jones, Ulysses S. 1979. Fertilizers and soil fertility. Reston Publishing Company, Reston, Va.

Little, T. M. and F. J. Hills. 1978. Agricultural experimentation. John Wiley and Sons, New York.

Ludeke, K. L. 1972. Soil properties of soil materials in copper mine tailing disposal berms. M.S. Thesis, Univ. of Arizona.

Marshall, C. E. 1977. The Physical chemistry and mineralogy of soils. Vol. 2. Wiley-Interscience Publication, New York.

Matter, Fred S. 1974. A balanced approach to resource extraction and creative land development associated with open pit copper mining in Southern Arizona. College of Architecture and College of Mines; University of Arizona, Tucson.

Michelutti, R. 1974. How to establish vegetation on iron-sulfur mine tailings. Can. Mining J. 95: 54-58.

Millar, C. E., L. M. Turk and H. D. Foth. 1965. Fundamentals of soil science. John Wiley and Sons, Inc., New York.

Palmer, M. E. 1978. Acidity and nutrient availability in colliery spoils. p. 85-126. In G. T. Goodman and M. J. Chadwick (eds.), Environmental management of mineral wastes. Sijthoff & Noordhoff, Alphen aan den Rijn.

Rajan, S. S. S. 1979. Absorption and desorption of sulfate and charge relationship in allophanic clays. Soil Sci. Soc. Amer. J. 43: 65-69.

Sauchelli, Vincent. 1965. Phosphates in agriculture. Reinhold Publishing Corp., New York.

Sinkankas, John. 1964. Mineralogy for amateurs. Van Nostrand Reinhold Company, New York.

Smith, G. Armstrong. 1970. Primary copper: A review of methods, production and quality control. p. 9-13. In copper and its alloys, Proceedings of an International Conference of the Institute of Metal, Amsterdam, Sept. 21-25, 1970. The Institute of Metals, London.

Soil Conservation Service. USDA. 1977. Revegetating lands disturbed by mining in the Southwest. Soil Conservation Service, Portland.

Strip and Surface Mine Study Policy Committee. 1967. Surface mining and our environment. Department of Interior, Washington, D.C.

Thompson, L. M. and F. R. Troeh. 1973. Soils and soil fertility. McGraw-Hill Book Co., New York.

Tisdale, S. L. and W. L. Nelson. 1975. Soil fertility and fertilizers, 3rd ed. MacMillan Publishing Co., Inc., New York.

Tucson Metropolitan Chamber of Commerce. 1980. Unpublished data.

United States Salinity Laboratory Staff. 1954. Methods for soil characterization. In R. A. Richards (ed.) Diagnosis and improvement of saline and alkali soils. Agric. Handb. no. 60, USDA, U.S. Government Printing Office, Washington, D.C.

Vallentine J. F. 1971. Range development and improvements. Brigham Young Univ. Press, Provo, Utah.

Van Breenan, N. 1975. Acidification and deacidification of coastal plain soils as a result of periodic flooding. Soil Sci. Soc. Amer. Proc. 39: 1153-1157.