RESEARCH NOTES

Research Note No. 20
May 1976

CATION EXCHANGE CAPACITY, CALCIUM, MAGNESIUM, AND pH CHANGES IN IRON TAILINGS AS AFFECTED BY VEGETATION

By

Joan M. Cryderman
Stephen G. Shetron

MICHIGAN TECHNOLOGICAL UNIVERSITY
FORD FORESTRY CENTER
L'ANSE, MICHIGAN 49946

Cation Exchange Capacity, Calcium, Magnesium, and pH Changes in Iron Tailings as Affected by Vegetation[1/]

Joan M. Cryderman and Stephen G. Shetron[2/]

ABSTRACT

Determination of cation exchange capacity (C.E.C.), pH, calcium and magnesium were made on iron mine tailings which had been stabilized from one to seven years. C.E.C. increased in the 0 to 1" surface layer with time for all particle size classes. On sands vegetated seven years C.E.C. had a seven-fold increase. Furthermore, C.E.C. decreased with depth regardless of particle size distribution. PH decreased for four years and then had a dramatic upswing soon after. Surface enrichment of calcium and magnesium also occurred.

INTRODUCTION

Iron mine tailings are finely ground waste rock from the beneficiation of low grade ore. They are deposited in man-made basins as a water-solid mixture resulting in a gradation of particle size from coarse to fine within the basin. Tailings are sterile and low in essential growth nutrients with the result that natural revegetation occurs slowly if it occurs at all. Seven years ago a program was set up between Michigan Technological University and the Cleveland-Cliffs Iron Company for a study on the possibilities of revegetating iron tailings.

Alfalfa was the major species used for this revegetation project because it grows well on a fine sand (major size fraction of the basins) and because of its nitrogen fixing capabilities. However, among the commonly grown forage legumes, alfalfa is one of the plants most sensitive to soil acidity. PH values between 6.5 and 7.5 has been shown to be ideal for maximum alfalfa production (Rhykerd et al, 1972).

Calcium is an important factor in the inoculation of rhizobia on the roots of alfalfa as well as other legumes. For example, experiments conducted on subterranean clover roots showed an increase in nodulation with increasing clacium levels, while yields of plant materials were not increased (Epstein, 1972). This is a reflection of increased calcium in the soil adjacent to the roots. Cation exchange capacity is important since it also is a measure of total exchangeable cations (Calcium, magnesium, potassium and sodium) in soil materials (Black 1968). It is, therefore, important to know what is happening to the tailings basins with respect to the C.E.C., pH and calcium. If these factors are known, management plans for the future can be developed and instituted.

PROCEDURE

Samples were collected at 0-1", 1-3", and 3-7" depths in various revegetated and non-vegetated locations on the Humboldt and Republic tailings basins in the summer of 1975. The plantings sampled were seven years old planted (1968) at the Republic Mine, four (1971), three (1972), and two (1974) years old at the Humboldt Mine. The samples were then tested for C.E.C., pH and exchangeable calcium and magnesium. C.E.C. was determined by using the Orion ammonia electrode according to procedures outlined by Bosenberg and Clemency (1973) and by Miller, Rjecken and Walter (1975). For pH-20 mls of deionized-distilled water was added to 20 grams of the sample. After stirring with a glass rod, the mixture was allowed to stand for one hour. Both C.E.C. and pH were determined with a Fisher Accumet Model 420 Digital pH/ion Meter. Calcium and magnesium - 10 grams of sample was placed in 50 mls of 1N NH_4OAc for 18 hours. The suspension was then filtered through a one micron millipore filter. An additional 25 mls of 1N NH_4OAc was used to rinse the flask and filtered. Finally, 25 mls of 1N NH_4Cl was then filtered through as an additional rinse.

Calcium and magnesium concentrations were determined on a Perkin-Elmer Model 360 atomic absorption spectrophotometer. A 1% solution of lanthanum was added to reduce interferences in the sample.

RESULTS AND DISCUSSION

Originally, Duffek (1969) found the pH of the iron tailings to range from 7.8 to 8.2 before revegetation. These same values are found where no vegetation presently are growing. However, as can be seen in Figure 1, the pH values for areas which now support vegetation have changed drastically with time. Four years after the first planting, pH had fluctuated from 8.0 to a low between 6.3 and 6.6. Seven years after the first planting, pH values were found to increase.

The same trend can also be seen in the calcium and magnesium levels. After four years, there is a definite change in the regime of these elements. Figures II and III show a surface enrichment effect of calcium taking place after the four year period. The surface layer shows an increase in the concentration of calcium and magnesium for the seven year measurement.

Magnesium also shows an increase after four years. Magnesium, like calcium, also shows a tendency for surface enrichment. (See Figure IV) The first and third year measurements show a decrease in the upper inch. The fourth year shows similarity in the contents of magnesium throughout the surface and rooting zone, but the seventh year shows considerable magnesium enrichment in the surface.

This shift after four years could be accounted for by one of three reasons or by some combination of them. The first possibility is the accumulation of materials blown in from adjacent unstabilized areas. These fine materials would be filtered out on the vegetation and consequentially become entrapped. The possibility of materials

Figure I pH Changes Related to Number of Years

Since Vegetation Was Established

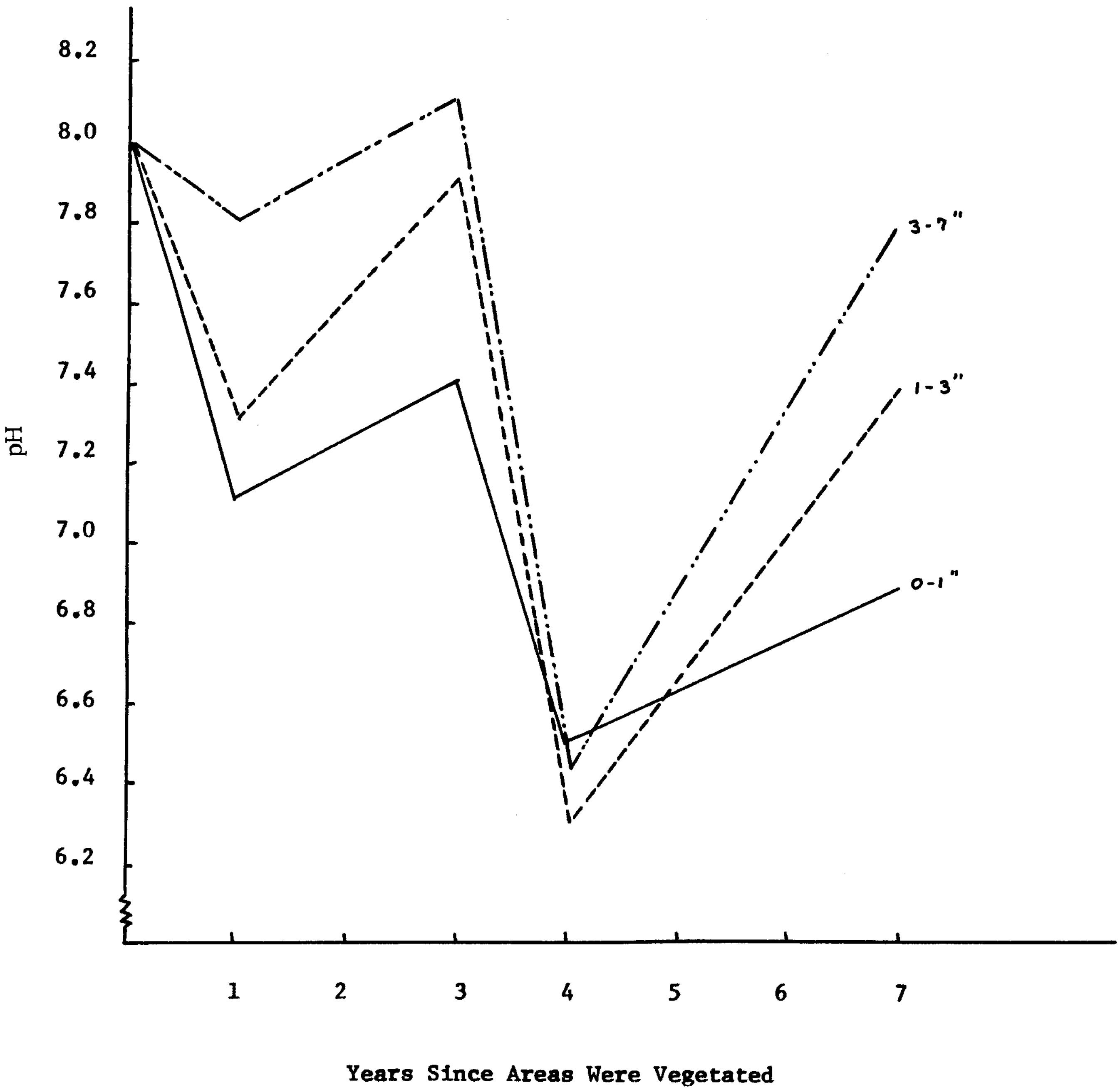


Figure II Calcium Levels on a Fine Sand Related to Number of Years Since Vegetation Was Established

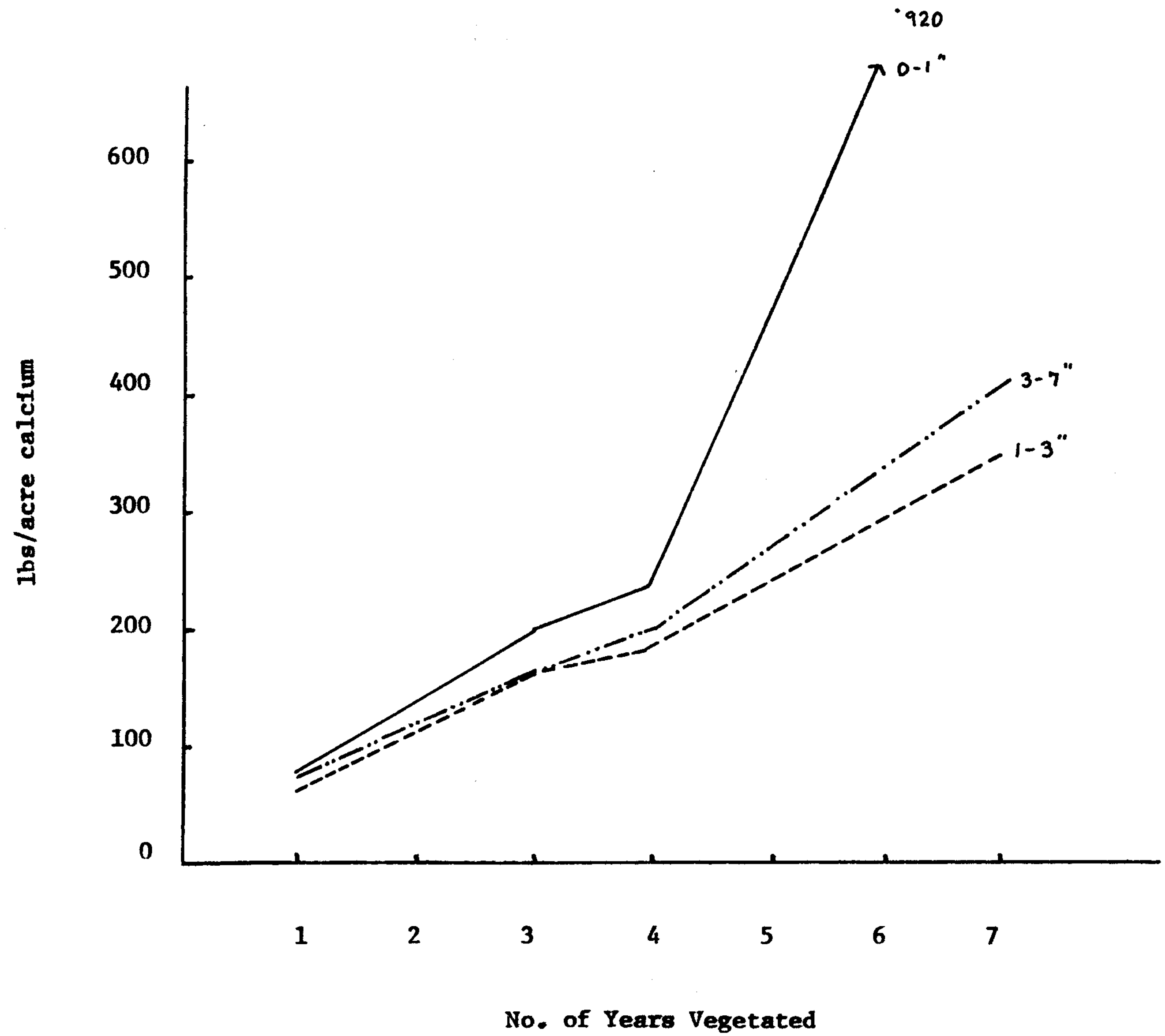


Figure III Depth Distribution of Calcium (lbs/acre) in a Fine Sand

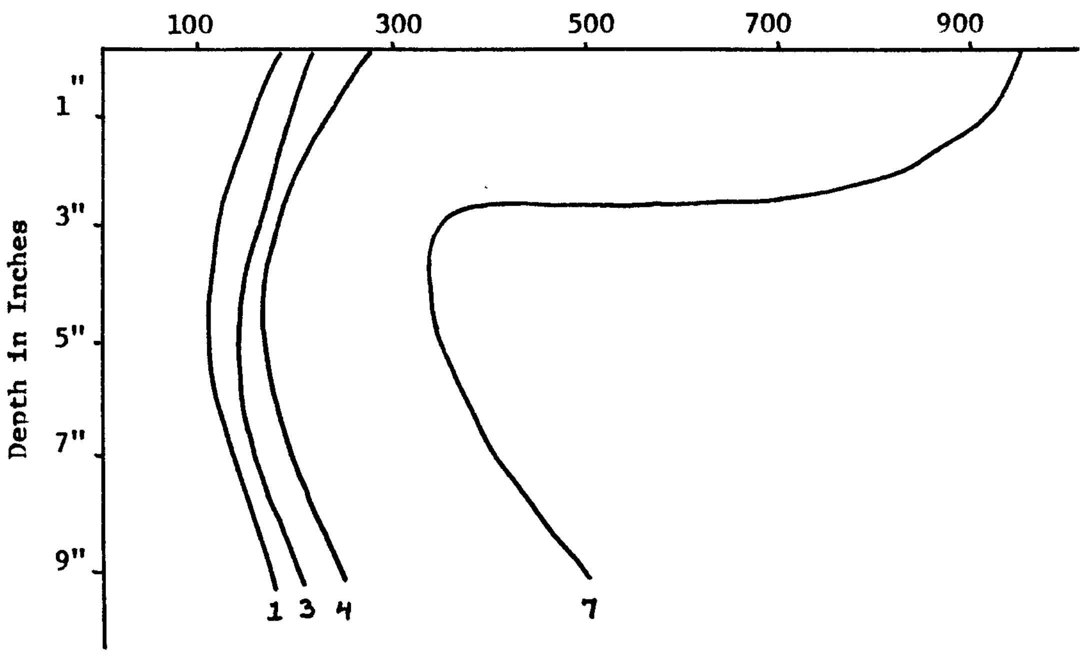
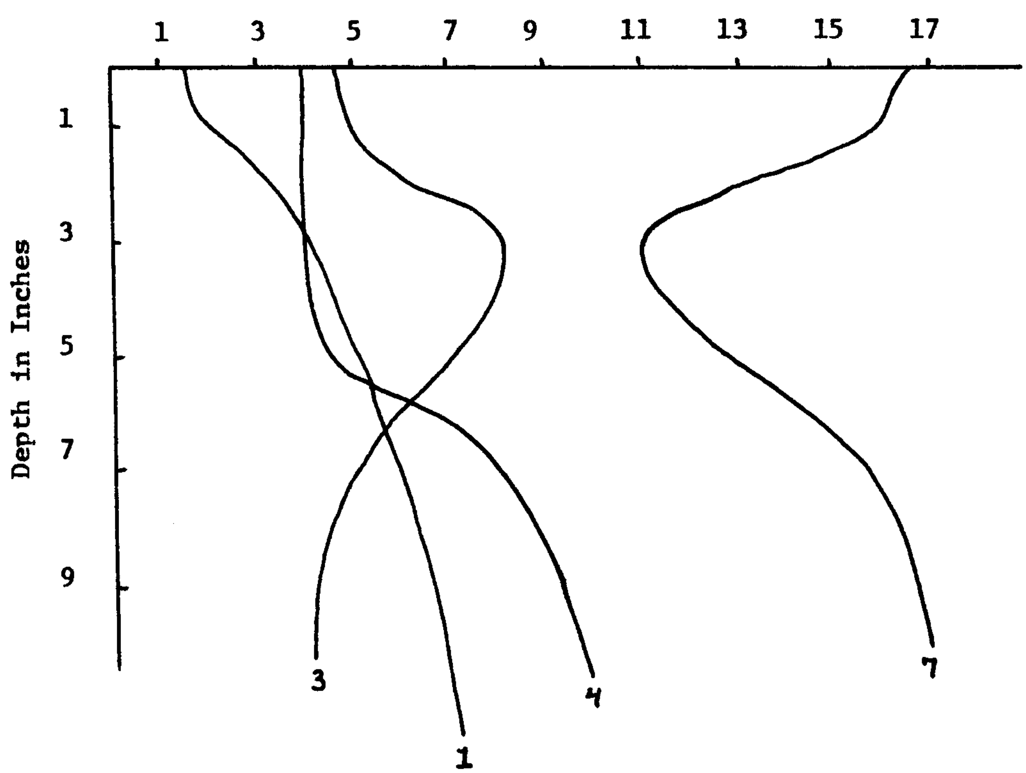


Figure IV
Depth Distribution of Magnesium (lbs/acre) in Fine Sand



being blown in and incorporated in the surface seems unlikely, however, due to the low initial calcium and magnesium levels of adjoining areas.

A second possibility is weathering of the finely crushed rock, since this is one of the most important processes in soil formation. Birkeland (1974) describes weathering as the process of rock and mineral alteration to more stable forms under the variable conditions of moisture, temperature and biological activity that prevail at the surface. It is likely that the vegetation would have an affect on the fine sand sized particles, resulting in the release of nutrients from within. Chemical and physical weathering could also account for a finer texture and therefore a higher cation exchange capacity.

The last consideration is the activity of the microbial population on the decomposition of accumulated organic matter. Before revegetation the tailings were essentially devoid of micro organisms due to the lack of organic matter. Revegetation supplied a food source that allows microbes to grow. Microbial decomposition is responsible for the release of nutrients held in an organic complex concentrated near the surface (Brady, 1974), and may, in part, account for the gradual enrichment of calcium and magnesium in the surface layer.

In support of this last assumption are direct comparisons of the study areas planted in 1971 and 1968. The root zone in the area planted four years ago showed little decomposition of dead roots while the root zone of the area planted seven years ago showed considerable rotting of the dead roots.

The C.E.C. in soils is associated with fine mineral particles organic matter and/or combinations of both. For the mineral fraction of a soil, C.E.C. increases with a decrease in particle size. Generally the colloid sized fraction contributes the most to a mineral particle C.E.C. properties. Soils contain a mixture of various minerals that differ chemically, and hence present difficult kinds of surfaces for C.E.C. Organic matter (colloidal) can have exchange capacity higher than an associated mineral fraction. Research has shown that C.E.C. of organic matter is a function of carboxyl groups, phenolic and enolic hydroxyl groups and amide nitrogen groups. (Black 1968).

Table 1 summarizes C.E.C., pH, Ca and Mg by depth for particle size and age under continuous vegetation. C.E.C. varies between size classes with slimes (finest texture) the highest and sands the lowest. Also C.E.C. was found to decrease with depth within each particle size class. Furthermore, C.E.C. increased with age of planting for the surface one inch. This is attributed to increased Ca and Mg and organic matter accumulation in the surface 0-1" layer. The greatest increase in C.E.C. occurs on the fine sands. Here a seven fold increase in C.E.C. has taken place. Whether or not weathering has commenced with the subsequent clay increase remains to be quantified.

Table 1. Summary of Cation-Exchange-Capacity pH, Available Ca, Mg for iron tailings between texture, age and depth.

Texture	Time in years since seeding	Cation Exchange Capacity Depth (inches) ME/100 gme			pH Depth Inches			Available Cal. #/Acre Depth Inches			Available Mg #/Acre Inches		
		0-1	1-3	3-6	0-1	1-3	3-6	0-1	1-3	3-6	0-1	1-3	3-6
Fine Sand	1	.43	.68	.79	6.7	6.3	7.3	80	60	75	1	2	3
	4	1.10	.78	.79	6.4	6.3	6.8	120	365	140	2	14	3
	7	3.70	.53	.50	6.7	6.7	7.7	690	150	150	9	4	5
Slimes	1	1.84	1.92	1.00	7.6	7.9	7.9	810	480	325	32	20	10
	4	4.00	1.08	1.33	8.1	8.3	8.4	30	770	840	1	27	27
	7	4.82	2.35	1.25	6.6	7.1	7.6	560	530	320	8	10	9
Medium Sand	1	.44	.31	.32	7.5	7.6	7.4	110	100	90	2	3	2
	4	.63	.28	.31	6.7	6.3	6.4	150	70	50	2	1	1
	7	1.87	.50	.82	6.9	6.2	6.4	230	180	150	5	6	5
Mixed Sand & Slime	1	.56	.56	.47	6.7	7.3	7.9	100	80	85	3	4	3
	4	1.60	1.05	.88	6.5	6.4	7.1	180	90	100	3	2	4
	7	2.35	.63	.50	7.1	7.5	8.2	230	170	320	7	5	10

CONCLUSION

This study has quantified changes in several chemical properties of iron tailings as a result of revegetation. C.E.C., calcium and magnesium show increases in the surface with increasing time since planting and between samples at 3 and 6 inches below the surface. PH, calcium and magnesium show first a decrease and then an increase with time. The fluctuation in the 0-1" surface layer properties is presumed to be caused by the withdrawal of Ca and Mg by plants. It is aided by organic matter accumulation, which begins releasing organic acids at about 4 years causing further pH decrease. Accumulations of Ca and Mg at between four and seven years contributes to the upward shift in pH. C.E.C. increases are a reflection of the continual additions of Ca, Mg and colloidal material resulting from the decomposition of organic matter.

Organic matter, calcium and magnesium effects have not penetrated the 1 to 3 and 3 to 6 inch sampling depths. These depths still reflect a rather stable pH and source of calcium and magnesium. Medium sands show lower pH values between age of stand and depth. Whether or not this is a rasult of acid leaching, organic matter decomposition, or plant uptake requires continued observation.

Establishment of vegetation has affected C.E.C., pH, Ca and Mg properties in iron tailings. Generally conditions for growth have improved except for the medium sands which have continued to acidify.

Literature Cited

Birkeland, P.W. 1974. Pedology, Weathering, and Geomorpholigical Research Oxford University Press. 285 pp.

Black, C.H. 1968. Soil Plant Relationships. John Wiley and Sons, Inc., New York 792 pp.

Brady, N.C. 1974. The Nature and Properties of Soils. 8th edition, MacMillian Publishing Company, Inc. 639 pp.

Busenberg, E. and C. V. Clemency. 1973. Determination of the Cation Exchange Capacity of Clays and Soils Using an Ammonia Electrode. Clays and Clay Minerals. Vol. 21:213-217.

Duffek, R. 1969. Vegetative Reclamation of Iron Mine Tailings. Masters Thesis. Michigan Technological University. 63 pp.

Epstein, E. 1972. Mineral Nutrition of Plants: Principles and Perspectives. John Wiley and Sons, Inc. 412 pp.

Miller, G.A., F.F. Riecken and N.F. Walter. 1975. Use of Ammonia Electrode for Determination of Cation Exchange Capacity in Soil Studies. S.S.S. Amer. Pro. Vol. 39:372-373.

Rhykerd, C.L. and Overdahl, C.J. 1972. "Nutrition and Fertilizer Use." Alfalfa Science and Technology Agronomy 15 American Society of Agronomy p. 437-468