

WEATHERING ACCORDING TO THE CATIONIC BONDING ENERGIES OF COLLOIDS¹

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ABSTRACT

A study was made of the energy changes of several colloidal systems in relation to weathering.

The total energy change associated with pH, total hydrogen, and bonding energy involved in the weathering of natural phosphates was established by mixing particles of apatite with hydrogen systems of amberlite (I.R. 120), bentonite clay, Putnam clay, kaolinite, and humus. Mixtures of potassium-saturated bentonite, sodium-saturated bentonite, and powdered rock phosphate were also investigated for weathering changes.

The amount of phosphorus weathered was related to hydrogen bonding at the outset and to calcium bonding energy of the colloidal system. H-amberlite, which has the highest bonding energy for calcium of the systems studied, was most effective in weathering phosphate minerals. H-humus, which has the lowest bonding energy for calcium was least effective as a weathering agent. The clay minerals weathered according to the relative energy levels resulting from the consideration of both hydrogen and calcium bonding energies. Bentonite clay was the most effective weathering agent; Putnam clay intermediate, and kaolinite the least effective. Bentonite clay saturated with potassium or sodium was effective as a phosphate mineral weathering agent.

INTRODUCTION

The chemical weathering of rock and minerals and its relation to the nutrition of our crops has been studied in many ways since the beginnings of soil science. It is now evident that the acidity in soil created by plant roots (and by soil microbes) is one of the major chemical reagents for processing mineral fragments and converting their content of plant nutrients into available forms. The clay is the means of passing the acid, accumulated from the roots, on to the minerals; and, in turn, of passing the nutrients in the opposite direction from the mineral to the clay surface and then to the plant roots. The exchangeable, i.e., the surface-adsorbed nutrients on clay, may start a crop to grow and produce for a few years. However, if the soil is to remain productive over periods of time it must contain reserve nutrients which commonly are associated with rather stable minerals. It is these reserve minerals that are sustaining the fertility of our major, regularly productive soils.

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It is necessary in our research on soils that we obtain (a) an inventory of soil reserve minerals, (b) some conception of whether nutrients contained in a mineral will be converted from the more insoluble, unavailable forms to those more available, and (c) some idea of the rate at which conversion of these mineral reserves will proceed.

The effectiveness of hydrogen-saturated colloidal systems as weathering agents has been demonstrated (Graham, 1940; 1941). Various primary minerals were mixed with different types of clay, and observations were made of the breakdown after a few months of weathering. In these experiments some differences due to pH as well as to the nature of the colloidal system were observed. H-bentonite, with initial pH below 3.0, usually was a more rapid weathering agent than H-Putnam (beidellite) which had an initial pH above 3.0. Yet observations on some H-humus clay systems of pH equal to, or lower than, H-Putnam revealed the H-Putnam as a more efficient weathering agent than H-humus.

Observations on the agronomic response of plants to rock phosphate cannot be explained on a basis of pH alone. In Missouri and Illinois, soils with a pH of 5.0 respond well to treatments of rock phosphate and result in improved plant conditions and growth. Yet in Australia many soils with pH values of near 5.0 fail to respond to rock phosphate treatments. It is therefore apparent that factors other than the initial pH of a colloidal system are important in weathering minerals in the soil.

Marshall (1950), in his studies of the electrochemistry of clay minerals, has suggested that the properties which determine the extent of ionization at silicate surfaces and hence also control conductance, exchange reactions, surface migration of ions, and contact exchange between ionic atmospheres, might well exert powerful influences upon soil-forming processes and other physico-chemical phenomena as well. A study of the extent of ionization at the silicate surfaces of clays, or the surface of organic colloids, necessarily involves consideration of the bonding energies of the cations toward the surfaces. It has been suggested for some time that hydrogen bonding varies with different clays and other colloidal systems. Marshall (1950) has demonstrated that other cations such as calcium, magnesium, potassium, and sodium show different bonding with different clay systems.

Marshall (1950) suggests that it is natural to think of the fraction of the total exchangeable cations measured by electrometric methods as analogous to activity coefficients in true solutions. For clay systems the term "fraction active, or $\frac{a_1}{C}$," is suggested to designate this. Therefore, the mean free bonding energy of a given cation may be written $\Delta F (\text{cation}) = RT \ln C/a$, where a represents the measured activity, and C that which would be given for complete ionization, or the total concentration of the cation. Since the fraction active = $\frac{a_1}{C}$, then:

$(\Delta F)_{\text{cation}} = RT \ln 1/f$, or $(\Delta F)_{\text{cation}} = 1,363 \log_{10} 1/f$ at 25°C

Therefore whenever a_1 can be determined the $(\Delta F)_{\text{cation}}$ or the molar free bonding energy of the total cation employed can be calculated. The value per equivalent may then be obtained by dividing by the valence.

In this investigation a study was made to determine what relationship existed between the cationic bonding energy of a given colloidal system and its effectiveness as a weathering agent.

PLAN AND PROCEDURE

Hydrogen-saturated suspensions of Wyoming bentonite, Putnam clay, and kaolinite were prepared by using a cation exchanger IR - 100 amberlite. The amberlite was saturated by mixing it with normal hydrochloric acid in a beaker and then washing with distilled water until the supernatant liquid was free of chlorides. The suspended clays were allowed to percolate slowly through about two hundred grams of this amberlite held in two large filter funnels, each prepared with silk bolting cloth to hold the amberlite. The H-saturated suspensions thus prepared by percolation through the acid amberlite were checked for chloride content using a silver-silver chloride electrode. They were found to be free of this element. Hydrogen-saturated systems of amberlite IR 120 as prepared by Upchurch (1953) were used as the colloidal system for this experiment. They were prepared by grinding to colloidal size in a ball mill and electro dialyzing until free of adsorbed bases. Hydrogen-saturated humus was prepared by extracting Wisconsin peat with sodium hydroxide and then electro dialyzing until free of bases.

The titrated hydrogen, initial pH, and the concentrations of the clay, resin, and humus suspensions were measured. Volumes of the suspension of each colloidal system, so chosen that each volume would furnish 2.0 meq of hydrogen, were placed in 300-ml flasks. Then 100 mg of washed apatite (particle size: through a 40-mesh screen and remaining on a 100-mesh screen) were added to each system. The mixtures thus prepared were allowed to stand for 48 hours after which the entire mixture was screened through a 300-mesh screen to remove the unweathered apatite. The suspensions of clay and humus were then treated with Bray's (1948) reagent, the systems were centrifuged, and the clear supernatant liquid was analyzed for phosphorus. The suspension of amberlite was filtered through a collodion filter under pressure and the clear liquid analyzed for phosphorus. A sample of each colloidal system was analyzed for phosphorus using the same extracting solution and reagents previously used, so that corrections could be made for any phosphorus carried by the colloidal systems. A sample of the apatite was mixed with distilled water and allowed to stand for the same time interval as the colloidal apatite mixtures. The supernatant liquid of the apatite-water mixture was analyzed for phosphorus so that corrections could be made for any phosphorus released by the action of water.

Mono-ionic systems of Wyoming bentonite saturated with calcium, potassium, and sodium separately were prepared as follows: A hydrogen system of the clay was prepared as described above, then a given volume of the suspension was titrated to a pH near 7.5 using standard solutions of calcium hydroxide, potassium hydroxide, and sodium hydroxide respectively. A constant amount of clay was used as well as 1 meq of each base. This resulted in slightly different pH readings. However, all were above a pH of 7.0 at the outset. To each of the suspensions of Ca-Clay, K-Clay, Na-Clay, 0.5 gram of 200-mesh rock phosphate was added. These mixtures were allowed to stand for one week. After this time interval, all mixtures had flocculated. The supernatant liquids from the mixtures were removed and analyzed for their phosphorus contents.

EXPERIMENTAL RESULTS

The results of hydrogen analysis as presented in Table 1 show that the Wyoming bentonite had the highest fraction of its hydrogen active, with a correspondingly low mean free bonding energy of hydrogen. The other systems studied were very similar. The kaolinite suspension showed the lowest fraction of the hydrogen active, resulting in the highest mean free bonding energy.

TABLE 1. — INITIAL pH FRACTION ACTIVE AND HYDROGEN CATION BONDING ENERGY OF CLAYS, AMBERLITE, AND HUMUS

Colloidal system	Volume, ml	Initial pH	Total titrated hydrogen, meq	Fraction active	$\Delta F H$ Cationic mean free bonding energy, cal./mole
Amberlite Wyoming Bentonite	20	2.5	2.0	.0315	2048
Putnam	90	2.6	2.0	.1130	1281
Kaolinite	70	2.9	2.0	.0440	1850
H-Humus	333	3.8	2.0	.0263	2152
	40	2.7	2.0	.0399	1908

The data assembled in Table 2 show that the mean cationic bonding energy values for calcium in the colloidal suspensions arrange themselves in the order from high to low as follows: amberlite, Putnam, kaolinite, bentonite, and humus.

The results of the phosphorus analyses, presented in Table 2, show that significant amounts of phosphorus were weathered out by each colloidal system. The portion of the total phosphorus weathered from the apatite during the 48 hours was 74 percent by H-amberlite, 28 percent by H-bentonite, 12 percent by H-Putnam, 8 percent by H-kaolinite, and 3 percent by H-humus.

The results of the phosphorus analysis of the water extracts of the saturated systems of bentonite are presented in Table 3. The water extract of the Ca-bentonite system contained no phosphorus; the extract of the

TABLE 2.—CALCIUM BONDING ENERGY (McLean, 1948; Upchurch, 1953; Barber, 1949; Marshall and Patnaik, 1953), RELATIVE DRIVING ENERGY AND THE PHOSPHORUS WEATHERED BY HYDROGEN SYSTEMS OF CLAYS, AMBERLITE, AND HUMUS FROM APATITE

Colloidal system	Ca bonding energy near 60% saturation, cal./mole	$\Delta F \frac{1}{2}Ca - \Delta F H$, cal./mole	Relative driving energy cal./mole	Phosphorus weathered, mg
Amberlite	6000*	— 952	2351	13.35
Wyoming Bentonite	2415	— 72	1325	5.03
Putnam	3440	— 130	1269	2.16
Kaolinite	2450	— 927	472	1.50
H-Humus	1019	—1399	0	.62

* The data for Ca bonding at 60 percent saturation are not available. This figure is estimated from data obtained on Ca-H systems at higher saturations.

K-bentonite system revealed 3.0 parts per million phosphorus; and the extract of the Na-bentonite system was found to be 2.8 parts per million phosphorus.

DISCUSSION OF RESULTS

The results of this study and one on the weathering of anorthite (Graham, 1941a) show that in addition to the dissociation of hydrogen, the dissociation of the calcium from the colloid is also important. The importance of the dissociation difference of various ions other than hydrogen is demonstrated by the weathering obtained when rock phosphate was treated with either a sodium- or potassium-saturated Wyoming bentonite. The advantage of Marshall's (1950) approach to the cationic energy

TABLE 3.—CALCIUM, POTASSIUM (McLean, 1948) BONDING ENERGY (Marshall, 1950), AND RELATIVE DRIVING ENERGY IN RELATION TO THE PHOSPHORUS WEATHERED FROM RAW ROCK PHOSPHATE BY COLLOIDAL SYSTEMS OF BENTONITE

System	Ca bonding energy at 50 percent Ca saturation, cal./mole	K or Na bonding energy at 50 percent K saturation, cal./mole	Relative driving energy ($\Delta F \frac{1}{2}Ca - \Delta F K$) ($\Delta F \frac{1}{2}Ca - \Delta F Na$)
Ca-K Bentonite	3421	660	1055
Ca-Na Bentonite	3421	600*	1115

System	Initial pH	Water extract phosphorus concentration p.p.m.	Phosphorus weathered mg (ms)
Ca-Bentonite	7.5	.0	.00
K-Bentonite	7.5	3.0	.48
Na-Bentonite	7.5	2.8	.46

* The data for the Na-Ca system of bentonite are not available. This figure is estimated from the value of the Na-H system at 55 percent saturation.

involved in the various colloidal systems was well demonstrated by this study.

The importance of colloidal clay as an agent in weathering primary minerals and in transferring nutritive cations from mineral to plant has been demonstrated (Graham, 1941). The present study reveals the importance of clay and its cationic saturation in the weathering of the nutritive anions out of minerals and their availability to plants. These findings when related to other soil measurements will help to explain many of the ionic behaviors associated with the problem of plant nutrition in the soil.

SUMMARY AND CONCLUSIONS

A study of the weathering of apatite by colloidal systems having different levels of cationic bonding energy revealed the following items of importance.

In 48 hours, H-amberlite weathered 20 times as much phosphorus from apatite as H-humus weathered for the same time interval although the initial pH values were nearly the same and the total amounts of the acids were the same. H-Wyoming bentonite weathered two times as much phosphorus from apatite as did H-Putnam, and four times as much as did H-kaolinite.

The weathering of raw rock phosphate occurred in the absence of hydrogen when rock phosphate was treated with potassium- or sodium-saturated Wyoming bentonite.

The relative driving energy was calculated by considering the cationic mean free bonding energy of both. Cationic calcium and cationic hydrogen gave an excellent correlation with the amount of phosphorus weathered from the apatite.

The relative driving energy calculated by considering the cationic mean free bonding energy of both calcium and potassium and for calcium and sodium gives some explanation of how weathering may occur in neutral or alkaline systems.

REFERENCES CITED

- Barber, S. A. (1949) *Studies of cationic activities on clay minerals*: University of Missouri, Ph.D. Thesis.
- Bray, R. H. (1948) *Diagnostic techniques for soils and crops*: The American Potash Institute, Washington 7, D. C., p. 53-85.
- Graham, E. R. (1940) *Primary minerals of the silt fraction as contributors to the exchangeable base level of acid soils*: Soil Science, v. 49, p. 277-281.
- (1941) *Calcium transfer from mineral to plant through colloidal clay*: Soil Science, v. 51, p. 65-71.
- (1941a) *Colloidal organic acids as factors in the weathering of anorthite*: Soil Science, v. 52, p. 291-295.
- Marshall, C. E. (1950) *The electrochemistry of the clay minerals in relation to pedology*: International Congress Soil Science, v. 2, p. 71-82.
- Marshall, C. E., and Patnaik, N. (1953) *Ionization of soils and soil colloids, IV, Humic and hmatomelanolic acids and their salts*: Soil Science, v. 75, p. 153-165.

- McLean, E. O. (1948) *The measurement of potassium activities by means of clay membrane electrodes in homoionic and polyionic systems including plant cultures*: University of Missouri, Ph.D. Thesis.
- Upchurch, W. J. (1953) *An experimental study of the chemical factors in cation exchange between root surface and nutrient media*: University of Missouri, Ph.D. Thesis.