A more detailed report is being prepared.

G. J. Bouyoucos

Michigan State College

SPECIAL ARTICLES

ZEOLITE FORMATION IN SOILS

THE presence, in soils, of zeolites (basic hydrated aluminum silicates) possessing the property of base replacement, has been known and studied by chemists for a great many years. The source or origin of these chemical compounds is unknown, although most authorities, either by direct statement or by intimation, have given us the idea that, as they make up an important part of the clay fraction of soils, they are chiefly formed by the slow natural processes of decomposition, hydration and trituration under water, over long periods of time and are of great age.*

During the researches being conducted in this laboratory upon the aluminates and silicates occurring in alkali soils, the following question arose. Having shown that black alkali soils contain sodium aluminate and sodium silicate in the soil solution and having found that these two compounds will unite in the cold to form sodium zeolite, may we not consider such a union possible within the soil complex under natural conditions? The present paper constitutes a brief summary of detailed work which shows to our satisfaction that the zeolites now present in soils have not necessarily existed for untold ages but may be of very recent origin—in fact, may even now be in process of formation.

In preparing a synthetic zeolite by the above method, namely, from solutions of sodium aluminate and sodium silicate in the cold, the resulting colloid was found to possess extremely active base replacement properties. Also, upon adding small amounts of solutions of the above compounds to soils and allowing the latter to dry in the air at room temperatures we obtained a notable increase in their zeolitic content as indicated by quantitative base replacement studies. We have thus built up the zeolite content of a soil by adding the two compounds which we had previously shown would combine to form a zeolite, and which two compounds we have also shown to be present and to be often in process of formation within black alkali soils.

On mixing concentrated solutions of sodium alumi-

* Gedroiz claims that more recent "secondary absorbing complexes" in the form of "absorption compounds" may be formed by the union of particles of colloidal silicic acid carrying negative charges with those of colloidal aluminum hydroxide carrying positive charges, but that such "new formations" are extremely unstable, "decomposing easily into their constituent parts."

nate and sodium silicate the resulting solution will almost instantly solidify to a gel. Dilute solutions, N/50 for example, showed no gel formation even on long standing. By titrating such a dilute solution with acid, however, it was found that zeolite formation occurred and, in dilute solution, is a function of reaction. Continuing this line of experimentation, we found that at strongly acid or strongly alkaline reactions a high concentration (due to high solubility) is essential to the formation of the colloidal zeolitic gel, while in dilute solutions the components combine within a definite pH range only. The maximum precipitate, or range of lowest solubility, is on the acid side of neutrality, pH 5 to 7. At pH 3.6 the zeolite was completely soluble. Our results to date indicate that it is far less soluble in alkaline than in acid solutions, although it has an appreciable solubility in both.

We thus obtained data in the above titrations showing that zeolites are completely soluble in dilute acids.[1] On titrating back with alkali, however, the colloid was again formed and its typical base replacement property restored. To prove that the colloidal zeolite molecule had been broken down into its acidic constituents (silicic acid, aluminum chloride and sodium chloride) an acid solution of the zeolite was dialyzed through a paraloidion membrane, the dialyzed solution neutralized to a reaction of pH 6.0, and evaporated until a gel was again formed. This zeolitic gel had reacquired its base replacement property.

After having formed the basic zeolite from its alkaline constituents, which we have shown to be present in black alkali soils, the acid zeolite was then synthesized from the acid constituents which are known to be present in acid soils. These are silicic acid and soluble aluminum and sodium[2] salts (chlorides). The physical and chemical properties of all of these zeolites are being studied and their formulae determined.

The next step in our investigations was to extract the components of the zeolites from both alkaline and acid soils and cause them to recombine to again produce zeolites. Thus, a soil was leached with 3 per cent. hydrochloric acid, the leachings evaporated upon the water bath to a gel, and this gel shown to possess the property of base replacement. A similar experiment using water or a solution of sodium hydroxide was carried out with a black alkali soil, with the same typical property of base replacement showing in the colloid obtained. In the latter case there

[1] This would confirm the results obtained by Kelley, Gedroiz and others who have shown that in attempts to use acids as a carrier of H ions in base replacement there is a disruption of the zeolite molecule.

[2] Soluble potassium, calcium or magnesium salts may be used.

may not be a destruction of the zeolite molecule during extraction, as the leachings from a black alkali soil will often contain sufficient soluble aluminates and silicates to recombine under proper reaction conditions to form the insoluble zeolite with replaceable base properties, without evaporation. As stated above, our work shows that the zeolite molecule is most stable under alkaline conditions. This is doubtless due to the excess of OH ion present, which prevents hydrolysis. It is also very stable in the presence of an excess of the common metallic ion.

This work indicates that there is a great similarity between the soil zeolites as prepared either from acid or alkaline soils (acid extracts of the former and both water and alkaline extracts of the latter), and those artificially prepared on the one hand from aluminum chloride, silicic acid and sodium chloride and on the other from an alkaline aluminate and silicate. In fact, we are inclined to consider them as practically · identical.

The small amounts of soluble aluminum present in acid soils probably result from the solution, with accompanying decomposition, of previously formed zeolites which are slightly soluble at hydrogen-ion concentrations below pH 5.0.

It is a widely known fact that black alkali (sodium carbonate) may be formed by the interaction between calcium carbonate and either sodium sulfate or sodium chloride. It may also be formed by the natural weathering of basaltic rocks. We are inclined to attribute the formation of zeolites in alkaline soils to the presence of black alkali formed as above (with attendant high pH), rather than consider black alkali as usually derived from sodium-zeolite hydrolysis. This latter explanation of black alkali formation appears to us to be putting the cart before the horse, for the major trend of chemical reactions in soils will be in the direction of synthesis of the least soluble product, which here, most assuredly, is the zeolite. That sodium hydroxide may be formed by the hydrolysis of sodium zeolite, after the latter has been formed, is of course well known, but the importance of this reaction in black alkali formation in soils is open to question.

To recapitulate briefly, our work thus far indicates that the steps in zeolite formation in alkaline soils are somewhat as follows: Sodium carbonate is formed from the interaction between white alkali and calcium carbonate; the sodium carbonate hydrolyzes to give sodium hydroxide,[3] which ionizes to produce a solution of high alkalinity (pH 10 to 11.5); sodium silicate and sodium aluminate are formed under these conditions from the more readily soluble aluminum silicate minerals; as the pH is lowered, due to washing out by rains or irrigation, or as the soil dries out, the sodium silicate and sodium aluminate combine to form sodium zeolite, which may remain as such or be converted into other zeolites, depending upon the salt concentrations within the soil solution.

A detailed account of this work soon will appear in the technical bulletin series of this experiment station.

P. S. BURGESS,[4]
W. T. McGEORGE

ARIZONA AGRICULTURAL EXPERIMENT
STATION, TUCSON

GROWTH AND GROWTH FORMULAS IN PLANTS

FOR some years the writer has been engaged in an investigation of the growth of plants under constant, controlled conditions, and especially of wheat, at the Food Research Institute of Stanford University. In the winter of 1925–26 he reached the conclusion that the first part of the growth cycle can not be represented by an autocatalytic reaction equation, while the later part of the cycle is only approximated by such an equation. These results were presented at the meeting of the Pacific Coast Branch of the American Association for the Advancement of Science in June, 1926. Since that time the writer has become acquainted with a paper by Gregory[1] in which the position is taken "that only the second part of the growth cycle can be represented by an autocatalytic reaction equation." As the full publication of the writer's work can not appear for some time and as his conclusions, while resembling those of Gregory in certain respects, differ in others, it seems of interest to students of growth to present at this time the writer's method of analyzing growth data.

Of the different theories and formulas which have been advanced in order to express growth of plants mathematically, the compound interest law of Blackman and Robertson's formula, which is identical with that of the autocatalytic reaction of chemistry, are the only ones which express growth as the effect of internal processes. As the latter formula

$$\frac{dx}{dt} = kx(a - x), \qquad (1)$$

in which a is the final length or final dry-weight, k, a constant and x, the length or dry-weight observed at a time t, can be written

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[3] In dilute solutions (N/20 or less), sodium carbonate is hydrolyzed to the extent of 65 per cent. or more.

[4] The authors are equally responsible for the presentation of this paper.

[1] Gregory, F. G., *Ann. Bot.*, 40: pp. 1–26 (1926).