samples of milk from the same barns, it is clear that much remains to be done in the perfection of the technique of sampling and bacteriological analyses of milk.

These data show how flimsy is the basis for the common belief that there is a relation between the score of a dairy and the quality of the milk produced by it, and how premature the official sanction for the grading of milk by means of dairy scores.

J. Arthur Harris

"SOIL ACIDITY AND METHODS FOR ITS DETECTION"[1]

In a previous issue of Science, J. E. Harris[2] published an article entitled similarly as above. In this article Harris states that two theories have been advanced to explain soil acidity, viz., the humic-acid theory and the colloid absorption theory. This same investigator also makes reference to an article published by the present writer on a new method for the determination of soil acidity,[3] and after quoting the writer in regard to the use of calcium chloride in this method, says:

> This statement brings out very clearly the absurdity of the position of those who accept the humic acid theory. These humic acids are supposed to be strong enough and soluble enough to liberate hydrochloric acid from calcium chloride, but not strong enough or soluble enough to liberate hydrogen sulphide from zinc sulphide. It is also suggested that this method be made the basis for a quantitative determination of the lime requirements of the soil. The writer does not believe this is possible because he has shown[4] that acid soils do not absorb equivalent amounts of different ions.

Although Harris apparently assumes that the writer believes soil acidity in upland soils is due largely to the so-called humic acids, yet the writer has never published such views or believed that such was the case. The writer also wishes to state that he is even more adverse to accepting the colloid absorption theory as an explanation of soil acidity, than he is to accepting the so-called humic acid theory. The acidity of peat and muck soils is undoubtedly due in part to organic acids. There are upland soils, however, which are practically free of organic matter and still they react strongly acid. Similar soils containing considerable organic matter appear to retain all their acid properties even after the organic matter is destroyed with hydrogen peroxide. What is this inorganic acidity due to? Harris and many other investigators have assumed that it is due to absorption of bases by soil colloids. They have arrived at this conclusion because by their methods of experimentation, acid soils do not take up chemically equivalent amounts of the different bases. Colloids exhibit similar properties as to the absorption of bases, and hence they conclude that soil acidity is due to colloids. Let us carefully examine the facts and draw our conclusions accordingly:

Upland soils consist of from 75 per cent. to over 95 per cent. of silicates and silica. Silicates are salts of various silicic and alumino-silicic acids. The water solution in the soil slowly reacts with these silicates, forming with the bases of the silicate a soluble hydroxide or salt, which is taken up by plants or removed in the drainage water. The other product, an acid silicate, being comparatively insoluble, accumulates in the soil and gives rise to an acid condition. The writer and assistants have treated powdered basalt, granite, feldspar and other minerals with carbonated water, and after filtering have obtained residues which are acid to litmus and other tests. This is essentially comparable to the weathering process going on in soils. Acid soils treated in this way are made more acid.

If soil acidity is due to true acids and acid salts such as acid silicates, why have investigators not been able to show that acid soils take up equivalent amounts of the different bases from salt solutions? This is due to the fact that the acid silicates and their neutralized products are only very slightly soluble, and the solubility of the neutralized silicates varies according to the base that effects the neutralization. The law on which the ad-

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[1] Published with the permission of the director of the Wis. Expt. Station.

[2] Science, 40 (1914), 49.

[3] Science, 40 (1914), 246.

[4] *Jour. Phy. Chem.*, 18 (1914), 355.

herents of the colloid theory base their conclusion reads as follows: The relative affinity of the acids is independent of the nature of the base. *It must be carefully noted that this law only holds when all the reacting substances are in a true solution, or if there are partially soluble substances formed, then in any series of comparisons, the solubility of the corresponding substances must be of the same order. The opportunity for secondary or side reactions must also be eliminated or made comparable. In the soil there is almost unlimited opportunity for these side reactions to occur. Most previous investigators of soil acidity and absorption have entirely overlooked and ignored these most important considerations and hence have accordingly arrived at erroneous conclusions.*

In order to overcome these difficulties and make the conditions more comparable, the writer has proceeded as follows: Small amounts of very finely powdered soil were thoroughly shaken with comparatively large amounts of the respective salt solutions for a short period and then quickly filtered, and the acidity of the filtrate determined. *When this was done the soil took up very nearly equivalent amounts of different bases from salts having a common acid ion.* The use of very finely powdered soil and the procedure of thoroughly shaking made the conditions more like those of a true solution than was the case of other investigators. The use of an overwhelming mass of salt solution in comparison to the soil used equalizes the side reactions to a large extent. The main reaction takes place almost instantly, and hence the treatment should be short in order to prevent further side reactions. The results of these experiments point strongly to the existence of true acid substances as the cause of soil acidity.

Besides this active acidity, there is in soils usually a considerable amount of inactive acidity, which comes into play on continued treatment with salt solutions or basic materials. The writer has evidence, though not conclusive, which indicates that kaolin is a substance which may exist as either an active or an inactive acid. It is possible that rearrangements of the molecule, or polymerization may be the cause of this. In contact with basic material, kaolin gradually takes up more and more base, which may be due to the gradual change of kaolin to the active acidic form. Treatment with carbon dioxide or other acids also seems to cause a change to the active form.

The writer and assistants have perfected a new quantitative method for soil acidity. In this method 25 g. of soil are moistened in a casserole with 35 c.c. of water and then treated with an excess of barium hydroxide solution. This is allowed to act for *one minute* with constant stirring and then carbon dioxide is immediately passed in, changing the excess of hydroxide to the carbonate. The material is evaporated to complete dryness on a steam bath, and then the excess of hydroxide is measured by determining the carbonates present. A special form of apparatus has been devised for making this carbonate determination. It can also be used for determining carbonates in non-acid soils. When the determination is made by this method, it makes little difference whether calcium, barium or sodium hydroxide is used to neutralize the acidity. If soil acidity is due to colloids, then according to the properties of colloids it should take different chemical equivalent amounts of sodium, barium and calcium hydroxide. This, again, indicates very strongly that soil acidity is due to true acids and not colloids. The writer has a considerable amount of other data which bears on the subject at various angles, but always supports the existence of true acids as the cause of soil acidity.

There is no question but what colloids exist in soils. Some colloids absorb bases and others absorb the acid ion. The amount of absorption, however, in the case of the pure colloids which have been worked with in the laboratory is very small in comparison to the phenomena going on in acid soils. The absorption capacity of these colloids is practically negligible as far as soil acidity is concerned. The wrongly so-called selective absorption of bases in soils has received a large amount of attention during the past fifty years, but the explanations of the phenomena have never been satisfactory. It is for the most part not an absorption phenomenon but a true chemical reaction consisting of an exchange of bases between a soluble salt and silicate, or else a neutralization of acid substances by the base of a salt giving rise to a soluble acid, as in the case in acid soils. In the case of peats and soils high in organic matter, organic compounds may cause similar phenomena. The writer has been unable to obtain or find any data which on careful consideration would lend support to the colloid absorption theory of soil acidity.

The new test for soil acidity which the writer had previously described[5] has now been tried on a very large number of soils and found entirely satisfactory. As is obvious, it is absolutely necessary to use *neutral* calcium chloride and zinc sulphide in the test. Merck's reagents have given perfect satisfaction. In reply to Harris,[6] the writer wishes to state that acid soils react without the use of calcium chloride and hence his comment does not apply.

Although soils are composed for the most part of silica and silicates, yet the function of the silicates in soil fertility has been almost entirely ignored. Their function in the inorganic world is analogous to that of the proteins and carbohydrates in the organic world. The complex nature and behavior of the silicates makes possible the great regulatory processes going on in soils. The property of certain silicates by means of which they change from an active acidic state, a condition in which they actively take up bases from solution, to a condition of inactivity, and also the change in the reverse direction, is of the greatest importance. This property makes possible the presence of an enormous amount of such silicates which prevent undue loss by leaching without giving rise to the excessively acid condition which would otherwise be necessary. The root hairs of plants are probably among the most delicate of all external organs in either plant or animal life. In the soil there are a great variety of processes going on, resulting undoubtedly in the formation of not only beneficial substances, but also of some harmful ones. If this is the case, it is probable that nature has made some provision for inhibiting the deleterious action of the harmful substances on the delicate root hairs. It seems possible that the silicates may form temporary combinations with these substances and thus prevent unfavorable action on the root hairs. The wonderful influences, in other than physical ways, of a small amount of such silicates commonly called clay, on the fertility of sandy soils has been known for a long time, and a consideration of the above aids greatly in its explanation. The writer has in preparation a detailed paper dealing with the subject of soil acidity and related phenomena.

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A NEW METHOD OF MEASURING THE CONCENTRATION OF THE SOIL SOLUTION AROUND THE SOIL PARTICLES

IN conducting a thorough investigation on the general subject of soil temperature the influence of soluble salts on the lowering of freezing point of soils was also studied. It was observed that the phenomena of supercooling and freezing behaved in moist soils exactly the same way as in solutions. These facts suggested the ideas that the freezing point method might be employed to measure the concentration of the soil solution around the soil particles. In order to ascertain whether or not this could possibly be done a series of experiments was instituted, using different classes of soil with various moisture contents, or known concentration of solutions. It has been found that the freezing point of the soil solution around the soil particles can be determined with great ease. Solidification can be started when the soil mass is supercooled to only about 0.2° C., by simply moving the thermometer in the soil. The starting of the solidification is far easier in soils than in solutions. The freezing point of soils can be determined even when the moisture con-

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[5] *Loc. cit.*

[6] *Loc. cit.*