

SPECIAL ARTICLES

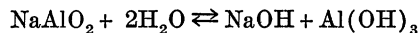
ALUMINUM HYDROXIDE AND THE "FREEZING UP" OF ALKALI SOILS DURING RECLAMATION

In the cultivation of irrigated soils in the west and southwest the chief adverse factor encountered is "alkali" (the presence of chlorides, sulfates and carbonates of sodium, and to a lesser extent, the chlorides and sulfates of calcium and magnesium). These soluble salts may have been present from the beginning or they may have been brought in by the use of saline irrigation waters. Large tracts of once productive lands are to-day alkali wastes, due to over-irrigation and seepage. During recent years reclamation measures on a large scale have been undertaken in many sections of California, Arizona, Utah and New Mexico. The common procedure has been to erect dykes or "borders," and apply large amounts of irrigation water to leach out the salts and permanently remove them from the land through under-drainage. In order for this procedure to be successful, it is, of course, necessary that the soils "take water" readily, *i.e.*, that good drainage be maintained throughout the washing process. It is a matter of common knowledge that water percolates freely through soils as long as they contain relatively large amounts of salts. When the solutes have been largely reduced, however, unless the irrigation water contains soluble calcium, the rate of percolation rapidly falls off and often reaches a point at which downward water movement ceases. In the words of the farmer, the soil "freezes up." When finally dried, such soils are hard, puddled and unfit for cultivation, and when rewetted "run together" and refuse to "take water." In fact, they are in worse physical condition than before reclamation operations were begun.

This "freezing up" of the soil has put an end to many alkali reclamation projects and has stimulated extensive investigation by soil chemists in arid countries. A number of theories have been advanced, but the "freezing up" is still unexplained. Recent contributions to the chemistry of alkali soils have added greatly to our understanding of the chemical reactions associated with the formation and properties of such types. We have reference to the work on soil zeolites by both American and European investigators. Some have given the impression that the soil zeolites (basic hydrated aluminum silicates) were directly associated with this phenomenon. It has been shown by two of the authors that the ratio of replaceable sodium to replaceable calcium has little or nothing to do with soil dispersion, also that the absolute amounts of sodium zeolite present bear little relationship to rate of percolation or degree of permeability.

As the concentration of sodium salts in the soil solution is reduced by leaching, the hydrolysis of the sodium zeolites present in varying proportions in all alkali soils yields hydroxyl ions in ever increasing amounts. The soil thus becomes more alkaline, and there has been much discussion as to whether the cation or anion is chiefly concerned in the accompanying increased dispersion. While the direct relationship of concentration of sodium zeolite or of sodium or hydroxyl ions to dispersion is open to question, it must be admitted that dispersion follows the hydrolysis and subsequent ionization of the sodium zeolite.

In soil investigations the amphoteric character of aluminum has rarely been considered. This element ionizes as a base when its normal salts are dissolved in water, and by hydrolysis yields an acid solution. On the other hand, it exhibits acidic properties, as the complex aluminate ion, when its solutions are made strongly alkaline, or when the hydroxide is dissolved in the solution of a strong base. Furthermore, the solution of any soluble aluminate always reacts alkaline due to hydrolysis, as shown in the following equation:



Within the range of reaction represented by pH 5 to 7.5 aluminum as the hydroxide is practically insoluble while above pH 8 its solubility as sodium aluminate rapidly increases. The latter may be considered just as truly a salt solution as borate or arsenate solutions, or as the normal acid aluminum salt solutions at reactions below pH 4. The physical properties of aluminum hydroxide vary greatly according to the conditions under which it is formed, being most colloidal when precipitated from dilute solutions and in the cold. Furthermore, the hydroxide may be formed both by reducing the alkalinity of an aluminate solution or by adding alkali to an acid aluminum-salt solution.

There is a definite difference between base replacement, soil reaction, colloidal dispersion and aluminum-hydroxide precipitation, although they all play an important part in the "freezing up" of soils during the reclamation process. It has been shown by us that this "freezing up" phenomenon is due to the precipitation of colloidal aluminum hydroxide within the washed soil complex simultaneously with the almost complete dispersion of the clay fraction, as the alkalinity is progressively reduced below pH 9.5 to 10. As will be seen, both the precipitation and the dispersion are largely governed by the reaction. The mechanism of the precipitation process is as follows: As we wash a highly saline soil, when the concentration of the sodium salts approaches a minimum, the alkalinity rapidly increases due to the formation of

sodium hydroxide by progressive replacement and hydrolysis of sodium zeolite. The sodium hydroxide, in turn, brings soil aluminum into solution as aluminate. On continued washing, the alkalinity is reduced. With this progressive reduction in OH-ion concentration, proportionally larger amounts of aluminum hydroxide are formed, accompanied by a corresponding reduction of the soluble aluminate. This, together with the almost complete dispersion of the clay colloids at these alkalinities, renders the soil practically impervious to water or air. As an example of such a soil we cite the case of an Arizona date orchard soil which before leaching was high in salines and gave a reaction of pH 8.8. After leaching out most of the neutral salts it showed a reaction of pH 11.05. The excess of aluminate over aluminum hydroxide is at a maximum at this latter reaction, but as the leaching operations were continued, the precipitation of aluminum hydroxide progressively increased with the lowered OH-ion concentration, and the soil finally became impermeable. Where "black alkali" soils (soils carrying sodium carbonate) are being reclaimed by leaching, the "freezing up" occurs as soon as the excessive alkalinity has been reduced to the precipitation point of aluminum hydroxide. Percolates from many "black alkali" soils have been examined and all show appreciable amounts of soluble aluminum as aluminate.

In our investigations to date we have obtained soluble aluminum by dialyzing black alkali soils. We have reproduced the "freezing up" phenomenon by the action of aluminum chloride solutions on an alkali soil of pH 10 in which the precipitation of aluminum hydroxide was produced by the reaction of the alkali within the soil. This was demonstrated by standing one-inch glass tubes of alkali soil in beakers of aluminum chloride solution of different normalities, noting the rate and height of capillary water movement, by the quantitative determination of the aluminum hydroxide deposited and by measuring the pH of the soil at varying heights in the soil column. Similar experiments were made with silica sand to which calcium carbonate and sodium carbonate had been added and similar results were obtained.

We further demonstrated the "freezing up" properties of aluminum hydroxide by mixing sodium aluminate with a neutral soil, placing in percolators, saturating with water, allowing the whole to stand several days for the reactions to come to equilibrium, and then percolating with water. In this case the precipitation was brought about by reducing the alkalinity of the aluminate. We have also determined the precipitation range of aluminum hydroxide by electrometric titration experiments and studied the properties of the aluminates formed. These experi-

ments not only showed a high solubility for sodium aluminate but also indicated that the solubility of calcium aluminate was appreciable at reactions usually found in alkali soils.

Further work has been done which correlates certain well-known peculiarities of aluminum hydroxide with soil behavior under reclamation. For example, if pure aluminum hydroxide is precipitated in a cold solution the precipitate is colloidal and filters very slowly. If, however, the precipitation is made in a hot solution, it is more granular and filters readily. When alkali soils are leached with cold water, they usually "freeze up" in a very short time. It has been found that, if these same soils are leached with hot water, they do not "freeze up," but percolate indefinitely.

If pure aluminum hydroxide is allowed to become perfectly dry it loses many of its colloidal properties which can not be restored fully by wetting or by pulverizing. We have shown that, if a "black alkali" soil is leached with pure water until it becomes impermeable and then dried out and cultivated, it takes water much more readily. The practical significance of this phenomenon is emphasized.

A complete discussion of this work, together with the numerical data obtained, will appear soon as Technical Bulletin No. 11 of the Arizona Agricultural Experiment Station.

W. T. McGEORGE

J. F. BREAZEALE

P. S. BURGESS

ARIZONA AGRICULTURAL EXPERIMENT STATION,
TUCSON, ARIZONA

THE ACTIVATION OF MOLECULAR HYDROGEN BY ELECTRON IMPACT

THE activation of molecular hydrogen by electron impact has been carried out under conditions in which the energy of the impinging electrons was known. The measurements were made in a four-electrode tube containing filament, grids and plate in the usual manner. A cylinder of copper oxide surrounding the space between the grids gave the activated hydrogen an opportunity to react. The water formed was frozen out in a liquid-air trap. The resulting pressure decrease was determined as a function of the accelerating voltage applied to the electron stream leaving the filament, and it was found that a sharp decrease in pressure occurs when electrons of 11.4 volts energy impinge on hydrogen molecules.

At the same time current-potential curves were taken by the Franck method and a kink in this curve occurred at the same voltage at which the pressure in the apparatus began to decrease.

The latest results of spectroscopy show that the