

exposure which was too short to register any of the normal reflections.

The writer has prepared Laue photographs with the X-rays passing either parallel to or making small angles with the normal to a (100) face. They have been taken both with a crystal-to-plate distance of 2.5 centimeters and with the more commonly employed distance of five centimeters. Some of the exposures were at least ten times greater than necessary for the detection of the ordinary reflections from crystal faces. Four crystal specimens were used; their refractive index was determined to agree within 0.001 with that which has been assigned to pure potassium iodide.<sup>5</sup> Several voltages were used in the preparation of these photographs. The minimum wave length present was directly determined for a particular experiment (1) by calculating from an analysis<sup>6</sup> of the photograph the wave lengths of the rays giving rise to different spots and (2) by taking, under the same conditions of experimentation, a reflection photograph from a calcite crystal. In some photographs reflections were present from wave lengths as low as 0.23 A. U. (the critical absorption limit for the K-series of iodine<sup>7</sup> is 0.374 A. U.). In no instance was anything found upon the photographs at the points which both the published Laue photograph and the accompanying spectrometer measurements indicate as the locations of the X-peaks. Furthermore the general aspect of the Laue photographs is such that there can be no possibility of a confusion of these X-peak spots with the regular reflections occurring upon good photographs.

Potassium iodide, in common with certain other crystals, of which tin tetraiodide<sup>8</sup> is typical, gives hazy diffraction phenomena which are not to be directly accounted for as reflections from planes in perfectly constructed crystals. These diffractions, though they seem to occupy the same positions in different specimens, are not sharply defined; furthermore they are relatively very weak and occur at much smaller angles of deviation than obtain for the X-peaks. As a consequence it is impossible to identify the two.

These hazy diffractions seem related to the well-known "asterism" phenomenon<sup>9</sup> which shows itself as diffraction stripes passing along principal zones of planes in distorted crystals. A number of crystalline substances which deform readily, among which the

alkali halides are conspicuous, will usually if not always show some striping from specimens which have not been subjected to external deforming forces. The observed effects with potassium iodide differ from those with other alkali halides in that, instead of a continuous stripe, the intensity is largely localized. Had it been possible to identify these hazy diffractions with the X-peaks, then a proof that the latter were due<sup>2</sup> to X-rays having the frequency of the characteristic radiation of iodine would have led to the possible explanation that the hazy diffractions arise from resonance iodine radiation.<sup>10</sup>

The writer has reexamined photographs of caesium dichloroiodide;<sup>11</sup> Laue exposures also have been made from a number of other crystals which, containing atoms that could emit their characteristic radiations under the action of the primary X-ray beam, might be expected to show X-peak spots. Among the photographs thus produced were ones from barite, barium nitrate and silver nitrate. On none of these was any evidence found pointing to the existence of other than the normal planar reflections.

More details of these experiments, together with reproductions of Laue photographs, will be published soon in the *American Journal of Science*.

RALPH W. G. WYCKOFF

GEOPHYSICAL LABORATORY,  
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### THE BIOCHEMICAL SULFUR OXIDATION AS A MEANS OF IMPROVING ALKALI SOILS<sup>1</sup>

THE problem of reclaiming alkali soils, especially black alkali, has been studied at various experiment stations and methods for amelioration of the alkali conditions have been suggested. The methods might be divided into mechanical and chemical. The former consists in either surface washing off of the salts or leaching out. The chemical method consists in treating the soil with gypsum whereby the conversion of the carbonates and bicarbonates into sulfates takes place. Recently Lipman suggested a biochemical method whereby the oxidation of sulfur by microorganisms and the production of sulfuric acid might be utilized in converting the carbonates into sulfates. The advantages of this method over the gypsum method is the difference in the reversibility of the reactions in

<sup>5</sup> The writer is greatly indebted to H. E. Merwin for this determination.

<sup>6</sup> R. W. G. Wyckoff, *Am. J. Sci.*, 50, 317 (1920).

<sup>7</sup> W. Duane, *Bull. Nat. Research Council*, 1, 389 (1920).

<sup>8</sup> R. G. Dickinson, *J. Am. Chem. Soc.*, 45, 958 (1923).

<sup>9</sup> G. Aminoff, *Geol. För. Förh.*, 41, 534 (1919); E. Hupka, *Physikal. Z.*, 14, 623 (1913); F. M. Jaeger, *Proc. Roy. Soc. Amsterdam*, 18, 3; F. Rinne, *Ber. Sächs. Akad. Wiss. Leipzig (Math.-phys. Klasse)*, 67, 303 (1915).

<sup>10</sup> G. L. Clark and W. Duane, *Proc. Nat. Acad. Sci.*, 9, 126 (1923).

<sup>11</sup> R. W. G. Wyckoff, *J. Am. Chem. Soc.*, 42, 1100 (1920).

<sup>1</sup> The authors share equal responsibility and credit for the work reported.

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the respective chemical systems. In the gypsum method a large preponderance of it is necessary to force the desired reactions in one direction and even then reversion will take place. In the sulfur treatment the sulfuric acid produced introduces in the system the unstable carbonic acid which is eliminated from the system and the chances for reversion are reduced to a minimum. The conversion of the black into white alkali does not solve the problem in its entirety, since in some white alkali soils the concentration of the soluble salts inhibits plant growth. A combination of mechanical and chemical or biochemical methods must therefore be practiced, the mechanical method as a rule to follow the others, depending on conditions. The drawback of the leaching method is the fact that alkali soils due to colloidal silicates, or other compounds, and peptization of organic matter are impermeable to water.

The work given below is merely a progress report of an investigation conducted at the New Jersey Experiment Station with the purpose of utilizing the biochemical oxidation of sulfur in reclaiming alkali soils. The study takes up the effect of sulfur application on the physical, chemical and biological structure of alkali soils. The soils under investigation were obtained from the California Experiment Station at Riverside. In texture it is a sandy loam, strongly alkaline, having a pH varying from 8.8 to 9.6. The soda odor is quite pronounced. The carbonates run up to about 500 pounds per acre, calculated as  $\text{Na}_2\text{CO}_3$ , the bicarbonates about 1,700 pounds, calculated as  $\text{NaHCO}_3$ , the chlorides run up to 7,000 pounds, calculated as Cl per acre on the basis of two million pounds of soil per acre. This soil is extremely unfavorable for plant growth not only from the standpoint of its alkali content but even from its chlorine content.

Various applications of sulfur were made running from 2,000 pounds to 6,000 pounds per acre. The sulfur was inoculated with a culture known for its strong sulfur-oxidizing capacity. After 18 days of incubation the soil cultures with 6,000 pounds and 4,000 pounds of sulfur were changed considerably; the capillary rise of water was considerably faster in the sulfur treated than in the untreated cultures. The reaction in terms of pH values went down from a pH 9.0 to 8.0; the carbonates disappeared, the bicarbonates were reduced 66 per cent. This was accomplished by the sulfuric acid produced by the oxidation of 33 per cent. of the sulfur. The bacteria content did not change, although a tremendous chemical change had taken place. After 60 days of incubation the physical condition of the soil was improved considerably, as was demonstrated by the capillary rise and speed of leaching through. The capillary rise in the treated soils was 18 inches in 72

hours, in the untreated only 7 inches. The chemical nature changed but slightly; the bicarbonates still persisted even in the cultures with the highest sulfur application; the oxidation of sulfur decreased in most cultures; still the reaction went down to a pH 7.3. No change in the numbers of bacteria took place. It seems as if the concentration of the different soluble salts, especially calcium, magnesium, sodium and iron, had reached a maximum, inhibiting bacterial activities. To test out this hypothesis some soil cultures were leached after 18 days of incubation and allowed to incubate further. After 48 days the cultures were examined again and a tremendous rise in the number of bacteria took place. While the check had only 400,000 bacteria per gram of soil, some of the sulfur treated had as high as 7 millions. That sulfur oxidation had proceeded again at a reasonable rate and that the physical condition was improved still more was demonstrated by the speed and amount of water leached through. The check after 36 hours had only 80 cc. leached through (400 cc. was applied to all cultures), while the sulfur treated had close to 300 cc. leached through. The checks became waterlogged and allowed no water to pass through. It seems as if the gelatinous-like colloidal silicates and peptized organic compounds produce a sponge-like effect. The reaction of the leachings in the untreated cultures remained the same, while in the treated the pH was approaching 7.0. It was also noticed that in some of the treated cultures some vegetation began to appear.

In connection with the study of treating alkali soils with sulfur several cultures were also made up applying alum at the rate of 40 tons of the crude material per acre as suggested by Scofield. The results seem to indicate that alum does not ameliorate the condition, since the colloids, after being precipitated, come back, leaving the soil practically in the same condition as in the checks. A more detailed analysis of the reactions involved will be given at a later date.

The outstanding features of the investigation may be summed up as follows: (1) Sulfur oxidizes rapidly in the early period of incubation; (2) The acid produced coagulates the colloids, destroying the impermeability of the soils and thus allowing leaching operations; (3) Indications seem to point to the possibility of bringing black alkali soils of the most hopeless character back to productivity by treating with sulfur and following by leaching. The details of the procedure as well as a more thorough understanding of the exchange of ions due to the oxidation of sulfur will be reported later as the data accumulated is tabulated.

J. S. JOFFE

H. C. McLEAN

NEW JERSEY AGRICULTURAL EXPERIMENT STATION