LXXIV.—*On the Action of Gypsum in Promoting Nitrification.*

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IN a communication recently made to the Chemical Society ("Nitrification, Part III," Trans., 1884, 637), I pointed out that the existence of more than a certain small proportion of soluble alkali in a solution entirely prevented nitrification from taking place. This prejudicial action of an excess of alkali was shown by disodium carbonate, by monosodium carbonate, and by ammonium carbonate, the quantity of disodium carbonate sufficient to prevent nitrification being smaller than that of the other carbonates named. Experiments were made in each case with a graduated series of solutions containing increasing quantities of soluble alkali. With monosodium carbonate as the alkali, nitrification was obtained, after many days, when the alkalinity equalled 350 parts of nitrogen as ammonia per million of solution; nitrification did not occur in the solutions of greater alkalinity. With ammonium carbonate as the alkali, nitrification took place after a considerable time when the alkalinity equalled 368 parts of nitrogen per million of solution; in the stronger solutions, nitrification did not take place. In a series of experiments with diluted urine of graduated concentration, nitrification was obtained after many days in a solution containing 12 per cent. of urine, the alkalinity of which (due to ammonium carbonate) at the commencement of nitrification was equivalent to 368 parts of nitrogen per million. Stronger solutions of urine did not nitrify.

All the solutions referred to above have been preserved up to the present time, but although the experiments have now continued considerably more than a year, nitrification has not occurred (with perhaps a single exception) in any solution of greater alkalinity than that named above. The possible exception is that of a 14 per cent. urine solution, belonging to the series above named. To the whole series of these solutions, 1 gram of soil was added on May 6, 1884. In the weaker solutions nitrification commenced in a few days. In the 10 per cent. solution, nitric acid was first found on July 7 (62 days). In the 12 per cent. solution, nitric acid appeared on August 4 (90 days). In the 14 per cent. solution, no nitrification had taken place on January 23, 1885 (262 days); nevertheless when examined in July, 1885, nitrification was found to be pretty far advanced. Of the alkalinity of this solution at the time when nitrification commenced, we have no knowledge, but in the previous September the alkalinity was equal to 412 parts of nitrogen per million. If we assume that the amount of ammonium carbonate found in

September continued unaltered at the commencement of nitrification, the limit of alkalinity already given (368 per million) will not be very seriously affected. In truth, however, the alkalinity of the solution must have been steadily diminishing, the diluted urine being kept in wide-mouthed loosely-stoppered bottles, less than half-filled ; opportunity was thus afforded for the access of air to the solutions, and for the gradual escape of the ammonium carbonate. It seems most probable, therefore, that the alkalinity of the solution slowly diminished, and that nitrification commenced when alkalinity had sunk to something like the point already mentioned. No nitrification has commenced in the 16 per cent. urine solution, although 16 months have elapsed since the experiment was started.

As the result of all the experiments, we may probably conclude that nitrification will not take place in solutions having an alkalinity of about 400 parts of nitrogen as ammonium carbonate per million of fluid ; whilst with an alkalinity of 368 parts per million nitrification may occur. An alkalinity somewhat above 400 per million does not, however, destroy the nitrifying organism, but merely suspends its action, as is shown by the last quoted experiment.

In the last communication to the Society, it was further shown that the degree of concentration of the solution had a considerable effect in retarding nitrification. This hindrance was, however, far less than that produced by the presence of soluble alkali. Thus while nitrification will not commence in the presence of 400 of nitrogen per million as ammonium carbonate, a solution containing more than 1000 per million of nitrogen as ammonium chloride has been completely nitrified, and nitrification is in progress in solutions of much greater concentration. In the case of solutions of ammonium chloride, a small amount of alkalinity was maintained by the presence of an excess of calcium carbonate.

From these results, it appeared highly probable that the limit of concentration (about 12 per cent.), beyond which urine ceased to be nitrifiable, might be greatly extended if measures were taken to prevent the production of a large quantity of ammonium carbonate in the early stages of the action. It was suggested in the last communication that this might be accomplished by the addition of gypsum to the urine ; the results of experiments in this direction will now be described.

On September 8, 1884, four urine solutions were prepared, containing respectively 15, 20, 30, and 50 per cent. of urine ; all of the solutions were thus above the strength previously found to be nitrifiable. 100 c.c. of each solution were placed in a short wide-mouthed bottle, similar to that used in the former experiments, and 22 mgrms. of precipitated gypsum added for each cubic centimetre of urine present ;

the quantity of gypsum was calculated from the amount of alkalinity shown by the fermented urine in the previous experiments. Each solution was finally seeded with 1 gram of soil. The solutions were agitated from time to time, to renew contact with the gypsum. The bottles were closed with cotton-wool.

As ammonium carbonate was developed in the solutions, the solid gypsum disappeared, and crystalline rounded masses (probably of calcium carbonate) were deposited on the sides of the bottles. As nitrification progressed these crystalline masses were again taken up by the liquid.

No nitrification was observed in any solution up to December 10, and fearing that the nitrifying organism might have been injured during the energetic changes which had taken place during the fermentation of the urine, a fresh seeding of soil was added on that date. The fear was probably groundless, for when next examined on January 23, 1885, nitrification was found to have made distinct progress in the 15, 20, and 30 per cent. urine solutions. The 50 per cent. solution showed no signs of nitrification on February 16, but on March 26 nitrification had distinctly commenced. The whole of the urine solutions treated with gypsum were thus found susceptible of nitrification.

Before the conclusion of the above experiments, and while it seemed doubtful whether the 50 per cent. urine solution would nitrify, a fresh series of trials was commenced. The solutions in this series contained respectively 15, 20, 30, 40, and 50 per cent. of urine; gypsum was added in the same proportion as before, but one solution containing 15 per cent. of urine was purposely left without gypsum. On February 7, 1885, a few particles of soil were added to each bottle, to set up the ammoniacal fermentation; when this stage was apparently completed, 1 gram of soil was added to each solution on March 13. The dates of the appearance of nitric or nitrous acid in each solution are given in the following table.

Commencement of Nitrification in Diluted Urine of various strengths, containing Gypsum, seeded with Surface Soil March 13th, 1885.

Urine in 100 of solution.	April 23, 41 days.	May 5, 53 days.	May 20, 68 days.	May 30, 78 days.	June 27, 106 days.	July 20, 129 days.	Aug. 11, 151 days.
15	none	distinct	—	—	—	—	—
20	"	none	distinct	—	—	—	—
30	"	"	trace	distinct	—	—	—
40	"	"	none	none	none	distinct	—
50	"	"	"	"	"	none	distinct

It will be noticed that nitrification occurred pretty soon in the case of the three weaker solutions, whilst an interval of 51 days elapsed between the nitrification of the 30 per cent. and 40 per cent. solutions. In the case of the 40 per cent. and of the 50 per cent. solutions, the sediment at the bottom of the bottle became for a time partially dark, and until this phase had passed over and the sediment resumed its normal colour no nitrification took place.

In this series of experiments, as in the former, the whole of the solutions treated with gypsum were found to be susceptible of nitrification. Nitrification commenced indeed in the stronger solutions only after a very considerable time, but a lengthening of the so-called period of incubation we have already learnt from numerous experiments always accompanies any increase in the concentration of the nitrifying fluid.

The 15 per cent. urine solution, which had not been treated with gypsum, but seeded equally with the others with 1 gram of soil, has remained unnitrified up to the present time.

The action of gypsum shown in these few experiments is quite in accordance with the observations of others. Thus Pichard (*Ann. agronom.*, 1884, 302), experimenting on the nitrification of earthnut-cake mixed with sand, found that by far the largest amount of nitric acid was produced when gypsum was added to the mixture; he supposes, however, that the sulphate of calcium had acted simply as an oxidising agent, and that its effect was due "à sa facilité d'être déoxydé au contact des matières organiques et réoxydé au contact de l'air." Joulie also, in his experiments on the loss of nitrogen during the fermentation of farmyard manure (*ibid.*, 289) found a formation of nitric acid only in those cases in which gypsum had been added to the mixture.

As the use of gypsum so greatly extends the limits of nitrification in the case of substances rich in ammonium carbonate, or other alkali, it seems probable that this property might be put to practical use if ever the artificial production of nitre were again to become remunerative, a state of things which must remain impossible while the present low price of sodium nitrate continues. Gypsum would probably be found a valuable ingredient of nitre-beds; it must also increase the oxidising power of the soil used in earth-closets. In cases also where strong sewage from factories or other large establishments is to be treated by application to land, the addition of gypsum would avoid the necessity of great dilution of the urine, and probably would enable oxidation to be effected by a smaller area of land.

In agriculture, the activity of dressings of farmyard manure would probably be increased by the addition of gypsum to the soil.

The experiments here described were carried out in the Rothamsted Laboratory.