PART III.—THE NITRIFICATION OF AMMONIA IN STRONG SOLUTIONS.

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As explained in the introduction the object of these experiments was to ascertain whether by an application of the activated sludge principle, i.e., the circulation of appropriate bacteria in presence of air through a solution of the substances to be nitrified, solutions of nitrate could be produced sufficiently concentrated to make the recovery of the dissolved nitrates by evaporation economically possible.

Muntz and Lainé having stated that nitrifying organisms would tolerate 20 per cent. of nitrate, a preliminary experiment was made by bubbling air through a 15 per cent. solution of calcium nitrate containing an efficient activated sludge in suspension, and adding gradually a 4·5 per cent. solution of ammonium hydrate. No evidence of nitrification either by loss of ammonia or by development of nitrite was obtained. This result confirmed the observations of Roy (Part II), but is a little difficult to understand in view of the fact that under natural conditions nitrification appears to take place in slightly moist soils with the production of actual crystals of nitrate. Some condition present in nature evidently remains to be investigated.

Shortly after this failure the papers of Boullanger came to hand and were studied, and on proceeding further on the lines therein described, positive results were obtained. The general method of experiment was as follows :—500 c.c. of activated sludge in good 'condition' was mixed with 1500 c.c. of effluent in a tall narrow graduated cylinder of 2000 c.c. capacity. Air was drawn through by means of a filter pump and the solution to be nitrified slowly added from a tap funnel.

The effluent from the activated sludge installation originally contained ammoniacal and nitrous nitrogen but only traces of nitric nitrogen. In order to eliminate as far as possible all but the bacteria of nitrification, aeration was continued for 5 days, testing every day for ammonia and nitrites. At the end of 4 days nitric nitrogen only was present in solution to the extent of 2·6 parts per 100,000, equivalent to 0·015 per cent. calcium nitrate.

At this date, August 20th, a solution of ammonium sulphate was prepared containing 2·5 gms. per litre equivalent to 53 parts ammoniacal nitrogen per 100,000 which would give 318 parts per 100,000 of calcium nitrate on oxidation. To this solution precipitated calcium carbonate was added in the proportion of 5 gms. to each 2·5 gms. of ammonium sulphate. Before use this mixture was thoroughly shaken, and 120 c.c. placed in a dropping funnel. The suspended calcium carbonate was allowed to settle in the funnel and dropped into the aeration cylinder all at once, the remaining clear solution being slowly but continuously added during 3 to 5 hours, aeration continuing without intermission both day and night. The added ammoniacal nitrogen dissolved in 120 c.c. solution amounted to 0·06 gm., equivalent to 0·378 gm. calcium nitrate. Fresh additions were not made until ammoniacal nitrogen had completely disappeared. During the first days this generally occupied about 48 hours so that fresh additions were made on alternate days only. The procedure was to stop aeration for 1 hour daily in the morning between 9 and 10 a.m. to allow complete settlement. The supernatant liquor was tested for ammoniacal nitrogen by Nessler solution and for nitrite nitrogen by the Griess-Ilosvay reagent; in the event of complete oxidation, a volume of supernatant liquor was removed equal to the volume of ammonium sulphate solution to be added. Nitrous nitrogen was still present at the end of 48 hours, but this was disregarded at first. By the 31st September both the ammoniacal and nitrous nitrogen present in the 120 c.c. of solution added were completely nitrified.

From September 1st to 15th both days inclusive the daily volume of ammonium sulphate added was gradually increased until at the end of this period it amounted to 400 c.c. per day. No increment was made until the rate of nitrification had maintained itself unimpaired for 3 or 4 days, an additional 50 c.c. of solution being then added. Under these conditions the oxidation proceeded very smoothly. It was noticed however, as a general observation that if the increment exceeded the established limit of oxidation at the concentration reached, nitrites as well as ammonia were found in solution in quantity. It was further observed that even if the normal daily dose was added irregularly the oxidation was not completed within 24 hours. Thus if 400 c.c. were normally oxidised during 3 to 5 hours the process was checked if 100 c.c. was added all at once.

From 16th to 27th September both days inclusive the solution of ammonium sulphate added was doubled in strength, an equivalent increase in the calcium carbonate being made simultaneously. The solution thus contained 100 parts of ammoniacal nitrogen per 100,000. This strong solution was added gradually, 100 c.c. only being used on the first day and the additions gradually increased to 250 c.c. per day by the last two days of the period. At this stage 265 mgms. of ammoniacal nitrogen were being oxidised in a volume of two litres per 24 hours.

On the 28th September a further increase of concentration was made in the solution, viz., from 5 gms. to 7·5 gms. of ammonium sulphate per litre with an accompanying 11·5 gms. calcium carbonate. This solution contained 157 parts ammoniacal nitrogen per 100,000. By the 8th October 150 c.c. of this, i.e., 237 gms. of ammoniacal nitrogen were being oxidised per day.

The important observation was made that these higher concentrations of ammonium sulphate could be oxidised quite smoothly provided that when a change was made from a weaker to a stronger solution, the actual quantity of nitrogen added was slightly lower than the quantity which was previously being oxidised, the full additional quantity not being added till 2 or 3 days had elapsed, otherwise, although oxidation did not actually cease, the amount of nitrogen oxidised in 24 hours diminished, nitrites being sometimes present for 48 hours. At this stage it was decided to add ammoniacal nitrogen in the form of ammonium nitrate rather than in the form of ammonium sulphate.

The advantage of this procedure, as pointed out by Boullanger, is to eliminate the formation of calcium sulphate which, in his case, tended to block up the filters and, in the present case, to deposit as heavy mud which was liable to impede aeration. Moreover by using ammonium nitrate the rate of concentration of nitrogen in the solution was hastened and the limit, which it was desired to determine, more quickly reached. A solution of ammonium nitrate was prepared containing 8·266 gms. per litre or 150 parts of ammoniacal nitrogen and 150 parts of nitric nitrogen per 100,000; 10·33 gms. calcium carbonate were added to a litre of this solution.

The addition of ammonium nitrate to the oxidising medium was begun on the 9th October at which time 237 mgms. of ammoniacal nitrogen were being oxidised in 2 litres of medium. The ammonium nitrate solution was added cautiously and it was not until the 11th day, i.e., 21st October that 100 c.c. of the solution was oxidised in 24 hours. Thus although at the beginning of this period 237 mgms. of ammoniacal nitrogen as ammonium sulphate were being oxidised in 24 hours, only 150 mgms. of ammoniacal nitrogen in the form of ammonium nitrate could be oxidised in 24 hours after 10 days acclimatisation. After 10 days further work an increase of 25 per cent. on this figure was possible, but it was not until the 15th December that 200 c.c. of ammonium nitrate, i.e., 300 mgms. of ammoniacal nitrogen together with 300 mgms. of nitric nitrogen were being easily oxidised per 24 hours.

Up till then as much liquid had been withdrawn from the cylinder as had been added. In order to obtain a real increase in the concentration of the calcium nitrate it was clearly necessary that the ammonium nitrate should be actually dissolved in a portion of the supernatant liquid from the cylinder and this solution returned to the vessel. This was accordingly done, 2·86 gms. ammonium nitrate or 500 mgms. ammoniacal nitrogen being dissolved in 100 c. c. of the supernatant liquor which was then slowly returned to the cylinder through the tap funnel. The equivalent amount of calcium carbonate was added to the cylinder separately.

The additional quantity of ammoniacal nitrogen could not, however, be at once oxidised and it took nine days for every trace of ammonium nitrate to disappear. The rate of oxidation gradually increased till January 14 when, through an unfortunate accident owing to a loss of water pressure during the night, aeration practically ceased, resulting in the production of a large quantity of ammonia and of nitrite. This led to a loss in activity from which the solution did not recover, and it appeared that it would be necessary to rebuild a special activated sludge. It had, however, been demonstrated that 300 mgms. of nitrogen could be readily oxidised daily in a volume of 2 litres, and a rate of 500 mgms. of ammoniacal nitrogen oxidised per 2 litres had just been attained when the unfortunate set-back occurred. The concentration of calcium nitrate at that date was 2·5 per cent.

Shortly after these difficulties were encountered the writer left to take up an appointment and further study of the subject passed to other investigators whose results are recorded in Part IV. The results described in the present paper are summarised in the tabular statement attached. It should be noted that no appreciable loss of ammonia from the solution could be found when the air drawn through the cylinders was passed through decinormal sulphuric acid and the acid tested for the presence of ammonia at the end of a month.

TABULAR STATEMENT OF RESULTS OBTAINED, AUGUST—JANUARY.

Date.	1923.											1924.
	Aug. 8.	Aug. 27.	Sept. 1.	Sept. 7.	Sept. 11.	Sept. 22.	Sept. 26.	Oct. 1.	Oct. 16.	Oct. 23.	Nov. 1.	Jan. 14.
Nature of Am. salt	Sulphate.	Do.	Do.	Do.	Do.	Do.	Do.	Do.	Nitrate.	Do	Do.	Do.
Percentage of Am. salt ...	0·25	0·25	0·25	0·25	0·25	0·5	0·5	0·75	0·826	0·826	0·826	0·826
Volume in c.c. added ...	120	120	120	200	300	250	250	150	100	100	125	...
Am. Nitrogen added in mgms.	63	63	63	106	159	265	265	240	151	151	189	...
Percentage of Calcium nitrate.	0·015	0·06	0·12	0·24	0·30	0·35	0·62	0·72	1·17	1·8	1·95	2·5

Note.—From December 22 to January 14 the percentage of calcium nitrate in solution gradually rose to 2·5 as no liquor was taken out but the solid ammonium nitrate was dissolved in a portion of the supernatant liquor which was slowly returned to the main volume.