REVIEW OF LITERATURE

The work done on ammonium fixation in soils has been briefly reviewed under the following heads:

1. Forms of nitrogen in soils;
2. Nature of ammonium fixation in soils;
3. Factors affecting ammonium fixation in soils;
4. Ammonium fixation capacity of soils;
5. Methods for the determination of ammonium fixation in soils;
6. Availability of fixed ammonium to nitrifying bacteria and plants.

1. Forms of nitrogen in soils - The total nitrogen content present in a soil depends on several factors, such as, temperature, rainfall, soil texture, the type of minerals present and vegetation. According to Schreiner and Brown (1957) the nitrogen content of soils in various parts of the United States varies from 0.05 to 0.30 per cent. In the Punjab soils also the nitrogen content shows a great variation, according to climate.

   The soil nitrogen can be divided into two main categories:

   (i) Organic form - Most of the nitrogen exists in soils in the organic form. Our knowledge of the organic form of nitrogen is inexact, because widely varying types of nitrogenous compounds gain entrance to the soil and soon start decomposition. Protein and amino acids are believed to be the chief forms of organic nitrogen in soil. Other important organic materials, which contain nitrogen, are chitin, purines, pyrimidines and nucleic acids. The availability of organic nitrogen to plants depends on the rate of its mineralisation.

   (ii) Mineral nitrogen - The mineral nitrogen in soil is present either as ammonium or as nitrate ions. This form of nitrogen generally comprises less than 5 per cent of the total nitrogen.
Nitrate nitrogen - The nitrates are all dissolved in soil solution, unless the soil dries out. According to Russell (1956) the nitrate content in normal arable soils ranges from 2 to 20 ppm and varies with the season and growth of crops. This form of nitrogen is considered readily available to plants, but the quantity present is generally small.

Ammoniacal nitrogen - The ammoniacal nitrogen is held on the soil exchange complex. Many soils can hold ammonium nitrogen so tenaciously, that it is released slowly to micro-organisms and plants. Therefore, ammoniacal nitrogen can be divided into exchangeable ammonium, which is readily available to plants, and fixed ammonium, which is slowly available to plants. According to Bremner (1959) exchangeable ammonium in 15 Rothamstead soils ranges from 3 to 27 ppm with an average of 11.5 ppm. The fixed ammonium is described in detail later on.

2. Nature of ammonium fixation in soils

The mechanism of ammonium fixation in soils appears to be the same as that of potassium fixation (Chaminade and Drouneau, 1936; Levine, 1941; Page and Faver, 1940; Stanford and Pierre, 1947; and Pocor, 1950). Prior fixation of ammonium or potassium has a depressing effect on the subsequent fixation of the other, in case of bentonite (Joffe and Levine, 1947), vermiculite (Barshad, 1948), and illite (Wikander, 1950). Stanford and Pierre (1947) found a correlation coefficient of 0.87 between ammonium and potassium fixation capacities of Webster high lime soils (U.S.A.) under moist conditions.

Barshad (1948, 1951, 1954) indicated that ammonium ions replace inter-layer cations, such as calcium, magnesium, etc., in the expanding lattices of clay minerals and this causes contraction of the crystal lattice and entrapment of inter-layer ammonium ions, which are considered as fixed. Wikander (1954) concluded that ammonium ions having similar size and valence as potassium ions, show the same behaviour and are fixed in the normal
potassium positions in the weathered micaceous minerals. It will be interesting to find out the relationship between ammonium and potassium fixation in the Punjab soils.

3. Factors affecting ammonium fixation in soils

(i) Clay minerals - The nature and amount of clay minerals in soils are known to play a dominant role in ammonium fixation. The clay minerals, chiefly responsible for ammonium fixation in soils, are of an expanding type. The observations of some important workers, in this connection, are noted below:

Fixation of ammonium by bentonite upon drying was observed by Page and Baver (1940), Joffe and Levine (1947) and Hanway (1956), but not by Wear and White (1951). Hanway (1956) reported that bentonite did not fix ammonium under wet conditions. Allison et al. (1951) concluded that in Harpster clay loam soils ammonium fixation under moist conditions was due to illite, whereas, under dry conditions it was due to both illite and montmorillonite. Aomine and Wada (1952) reported that in the Lukusa sandy soils (Japan) ammonium fixation was caused by vermiculite in interstratified layers of mica and vermiculite.

Allison et al. (1953) concluded that clay minerals, chiefly responsible for the fixation of ammonium in soils, are vermiculite, montmorillonite and illite. Vermiculite soils fixed more ammonium under moist or air-dry conditions; but when heated, illitic soils absorbed more ammonium. In soils where montmorillonite was predominant, the fixation values were about half of those for illite soils. Allison and Roller (1955) found, that montmorillonite fixed 6.3 m.e. ammonium per 100 grams and illite and metabentonite 1.0 m.e. ammonium per 100 grams, when leached with normal ammonium chloride solution and heated at 100°C. They concluded that high fixation of ammonium in many
soils was due to vermiculite and montmorillonite formed from illite as a result of weathering and with accompanying loss of potassium.

Harada and Kutsuna (1955) concluded that ammonium fixation by residual soils from crystalline schists at Yokatahama was due to degraded vermiculite apparently developed from chlorite during weathering of schist. Stevenson and Dhariwal (1959) reported that naturally fixed ammonium in great soil groups was related to the amount and kind of clay minerals present and order of ammonium fixation was illite $\rightarrow$ montmorillonite $\rightarrow$ kaolinite.

It may be concluded that the clay minerals mainly responsible for ammonium fixation are illite, vermiculite and montmorillonite in the given order.

(ii) Ammonium concentration - The increase in the concentration of $NH_4^+$ ions in soil solution generally leads to an increase in its fixation, because of the mass action. Aomine (1951) found a correlation coefficient of $+0.69 \pm 0.05$ between the fixed and adsorbed ammonium. Allison et al. (1951) observed that under wet and dry conditions the amount of ammonium fixation increases, but the percentage fixation decreased when the amount of ammonium added to Harpster clay loam was increased. Harada and Kutsuna (1954) reported that under moist conditions the increase in the amount of ammonium added to Yahatahama soils (Japan) increased the fixed ammonium. Nomiki (1957) reported that in heavy clay soil the total ammonium fixation increased and percentage fixation decreased with the increase in the concentration of $NH_4$ from 1-40 m.e. per 100 grams. It may be concluded that the increase in ammonium concentration in soil leads to an increase in its fixation, though little is known about the exact relationship between its concentration and fixation in soils.

4. Ammonium fixation capacity of soils

The ammonium fixation capacity of a soil varies with the method used
for its determination and it is not desirable to compare the results reported by various workers, using different methods. However, the values obtained by various workers are given below:

Bower (1950) reported that twenty-one soils of the semi-arid regions (California) fixed nil to 6.2 m.e. ammonium per 100 grams of soil under moist conditions and thirteen soils out of these fixed more than 1.1 m.e. per 100 grams of soil. Allison et al. (1951) observed that Harper soil, clay loam soil of Iowa fixed one milliequivalent ammonium per 100 grams, when moist and about 6.0 m.e. per 100 grams of soil, when dried at 100°C. Allison et al. (1953) found that representative soils of U.S.A. fixed 1.6 to 4.0 m.e. ammonium per 100 grams on air drying and 3.1 to 6.3 m.e. per 100 grams on heating at 100°C. In general sub-soils fix more ammonium than the surface soils (Bower, 1950; Aomine, 1951; Allison et al. 1951).

It has been noted that many soils have considerable amounts of their nitrogen in the form of fixed ammonium. Rodrigues (1954) reported that in profile samples of tropical soils 14-78 per cent nitrogen was in the form of fixed ammonium. Bremner (1959) observed in Rothamsted soils that on an average 5.6 and 21.5 per cent of nitrogen in the surface and sub-soils respectively was in the form of fixed ammonium. Stevenson and Dhariwal (1959) reported that the naturally fixed ammonium in sub-soils ranged between 0.05 m.e. per 100 grams in podzols and ground water podzols and 1.5 m.e. per 100 grams in grey-podzols, with intermediate values in grass-land, brunozems planosol, chernozem and chestnuts. Walsh (1959) found that Wisconsin soils contained 0.5 to 1.0 m.e. of native fixed ammonium per 100 grams soil. It may be concluded that many soils have considerable amounts of their nitrogen in the form of fixed ammonium and have the capacity to fix more ammonium nitrogen.

5. Methods for the determination of ammonium fixation in soils

The methods of the estimation of ammonium fixation in soils are of
empirical nature. The ammonium held in the difficult exchangeable form on the soil exchange complex are considered as fixed. The methods proposed by various workers are briefly reported below:-

Bower (1950) proposed a method, in which known amounts of ammonium are added to a soil and the ammonium not replaced by normal potassium chloride is considered as fixed. Barshad (1951) proposed an alkaline distillation procedure in which the soil sample is distilled with sodium hydroxide and a duplicate sample is distilled with potassium hydroxide. The amount of fixed ammonium is calculated from the difference between the amounts distilled by sodium hydroxide and by potassium hydroxide. Allison et al. (1951) proposed a method in which the soil is saturated with ammonium ions, and, then, free and readily exchangeable ammonium ions are removed with normal potassium or calcium chloride solutions. The difference in the total nitrogen of the ammonium treated and control samples is considered as fixed ammonium. Rodrigues (1954) proposed a method in which soil is treated with 4:1 mixture of 40 per cent hydrochloric acid and 50 per cent sulphuric acid for one hour. The ammonium thus released is considered as fixed ammonium. Bremer (1959) reported that the difference in the amounts of ammonium released from soil on treatment with normal HF + normal HCl and with normal KCl is the fixed ammonium.

Thus it is evident that the ammonium fixation capacity of soil will vary with the method used.

6. Availability of fixed ammonium to nitrifying bacteria and plants

The practical importance of ammonium fixation lies in its unavailability to plants, because it determines its harmful aspect. The results obtained by various workers on this aspect are contradictory. Chamnade (1940) found that clay colloids of soils fixed ammonium which was unavailable to plants and micro-organisms. Bower (1951) reported that 13 to 28 per cent of fixed
ammonium was nitrified and 14 to 25 per cent was available to barley grown by modified Neubauer’s technique in semiarid soils of California. Allison et al. (1951) reported that only 10 per cent of the ammonium fixed by Harpster clay loam soils was nitrified, while the ammonium fixed under moist condition was more available for nitrification than that fixed in soils dried at room temperature or at 100°C. Allison et al. (1953) observed that availability of fixed ammonium by representative U.S.A. soils varied from nil to 14.0 per cent, with an average of 5.24 per cent. Millets grown in a greenhouse assimilated 7 and 12 per cent of ammonium fixed by air-drying and heating respectively. Allison et al. (1953) reported that 5 to 24 per cent of the fixed ammonium was available to nitrifying bacteria, being lowest in vermiculite and highest in montmorillonite soils. Allison et al. (1953) found that ammonium fixed by two vermiculite samples was available to nitrifying bacteria and in the third sample only 11 and 16 per cent was nitrified. Aomine and Higashi (1955) observed that only a part of the fixed ammonium in Japan soils was recovered by rice and wheat crops, its degree of availability depending on the nature of the fixing material. Allison and Roller (1955) reported that 39 and 29 per cent of the fixed ammonium in illite and vermiculite was available to nitrifying bacteria when clays were treated with CaCl₂ and KCl respectively, after ammonium chloride treatment. Nomnik (1957) reported that in the heavy clay soil (pH 6.4), only a fraction of the fixed ammonium was available for nitrification. Walsh (1959) observed that in Wisconsin soils naturally fixed ammonium was unavailable to nitrifying bacteria, but the subsequently fixed ammonium was nitrified.

It may be concluded that fixation and availability of ammonium in soils depends on many factors which yet require a thorough investigation.