

SOIL SCIENCE

Removal of Fixed Ammonium from Clay Minerals by Cation Exchange Resins

AMMONIUM in clay minerals that is not replaceable by K^+ has been defined as fixed NH_4^+ . This fixed NH_4^+ is replaceable to some extent by Na^+ and H^+ , but the amount that can be replaced depends upon the extraction method used. Recent work^{1,2} has shown that small amounts of K^+ or NH_4^+ in the extracting solution block the replacement of fixed NH_4^+ . Thus, the efficiency of an equilibrium extraction of fixed NH_4^+ is decreased by the accumulation of displaced NH_4^+ in the extracting solution². If a clay mineral containing fixed NH_4^+ were equilibrated with a cation exchange resin instead of a soluble salt, there would be less soluble K^+ or NH_4^+ in the system. A comparison of these extraction methods was made, therefore, to determine if there was also less blocking and thus more fixed NH_4^+ removed in a resin extraction.

Samples of Montana vermiculite (0.2 gm.), Wyoming bentonite (0.3 gm.) and Goose Lake Grundite (illite, 0.5 gm.) that had been NH_4^+ -saturated and dried at 110°, 350° and 110° C., respectively, were equilibrated with Na^+ , K^+ and H^+ -saturated samples of 'Amberlite IR-120' in 20 ml. of distilled water. In each case > 32 mesh resin material with an exchange capacity of 4.32 m.equiv. per gm. and a clay mineral:resin ratio of 1:20 (oven dry-weight basis) were used. Samples of the dried, NH_4^+ -saturated clay minerals (0.2 gm. vermiculite, 0.3 gm. bentonite and 0.5 gm. illite) were also equilibrated with 20 ml. of 1 N sodium chloride and with 20 ml. of 1 N potassium chloride. The various systems were equilibrated at room temperature by shaking for periods of 2-8 days. The mixtures were then filtered, the residues were leached with 350 ml. of 1 N potassium chloride, and the NH_4^+ in the leachates was determined by distillation with potassium hydroxide. Before ammonium saturation, the illite was treated with a solution of sodium chloride and $NaB(C_6H_5)_4$ in order to remove K^+ and increase the NH_4^+ fixing capacity³. Illite samples that were not NH_4^+ saturated were included in each experiment, and the results obtained with the NH_4^+ -saturated illite were corrected for nitrogen arising from that originally present in this material.

Table 1 gives the total NH_4^+ contents of the minerals (Kjeldahl analysis), their exchangeable NH_4^+ contents as determined by distilling 1-gm. samples with 400 ml. of 1 N potassium hydroxide, and the amounts of NH_4^+ removed by the resin and soluble salt extractions. In these extractions enough

replacing cation was used to remove at least 80-6, 49.5 and 25.1 m.equiv. of NH_4^+ per 100 gm. from the vermiculite, bentonite and illite samples, respectively, if the distribution coefficient for the exchange of cations was 1.

Comparison of the results obtained by the resin and soluble salt extractions using the same replacing cation shows that although the resin method of extraction was the more effective with all three minerals, it was not markedly so except in the Na^+ treatment of vermiculite. When the NH_4^+ vermiculite was equilibrated with Na^+ (or H^+) resin essentially all of the NH_4^+ was removed, whereas only 76 per cent of the fixed NH_4^+ (that is, NH_4^+ not removed by distillation with potassium hydroxide) was removed by the sodium chloride treatment. It seems safe to assume that with this mineral the efficiency of the resin technique was due to a decrease in the blocking effect of the replaced NH_4^+ , which limited extraction by the sodium chloride technique, since other experiments (to be reported later) indicate that it was not due to a selective adsorption of NH_4^+ by the resin or to a contact effect of the resin.

The influence of the resin on the removal of fixed NH_4^+ from illite and bentonite was very small, and essentially the same, whether Na^+ or K^+ was used. This suggests that with these minerals the effect of the resin was not due to a decrease in the blocking effect of displaced NH_4^+ . More likely it was due to grinding of clay particles by the resin during the prolonged shaking period. This would also explain the observation that potassium resin extracted more NH_4^+ from vermiculite than did potassium chloride. In the vermiculite-resin extractions a distinct decrease in the size of the clay particles was observed.

The results in Table 1 show that the different treatments with K^+ (potassium hydroxide, potassium chloride, potassium resin) did not remove the same amount of NH_4^+ from the clay minerals. To define fixed ammonium, it is necessary, therefore, to specify the method of determination even when K^+ is used as the replacing cation. In the present work NH_4^+ that was not liberated as ammonia by distillation with potassium hydroxide was arbitrarily considered as being fixed.

Previous experiments with vermiculite have shown that the blocking effect of NH_4^+ or K^+ can be reduced by increasing the acidity of the extracting solution². In the case of bentonite and illite, however, hydrogen resin was no more effective than sodium resin (Table 1). Also, instead of the increase observed with vermiculite, there was a decrease in the amount of NH_4^+ removed when the bentonite and illite samples were extracted with potassium chloride instead of potassium hydroxide. These results suggest that factors not encountered with vermiculite are involved in the fixation and release of NH_4^+ in bentonite and illite.

Table 1. AMOUNTS OF NH_4^+ REMOVED FROM NH_4^+ -SATURATED CLAY MINERALS BY VARIOUS TREATMENTS (M.EQUIV. PER 100 GM.)*

Treatment	Ammonium vermiculite	Ammonium bentonite	Ammonium illite
Kjeldahl digestion	81.4	50.4	25.3
Hydrogen resin	80.5	36.7	23.9
Sodium resin	80.5	36.3	23.2
Sodium chloride	68.5	33.0	22.4
Potassium resin	10.7	9.0	22.7
Potassium chloride	8.1	5.7	22.1
Potassium hydroxide distillation	2.8	24.6	22.6

* Mean of two or more determinations. The illite values are corrected for the NH_4^+ removed from similarly treated illite samples that were not NH_4^+ -saturated.

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¹ Hanway, J. J., et al., *Soil Sci. Soc. Amer. Proc.*, **21**, 29 (1957).

² Scott, A. D., et al., *Soil Sci. Soc. Amer. Proc.*, **22**, 388 (1958).

³ Hanway, J. J., *Iowa State Coll. J. Sci.*, **30**, 374 (1956).