

# Evaluation of a South African clinoptilolite for ammonia-nitrogen removal from an underground mine water

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## Abstract

A South African clinoptilolite (Pratley) was evaluated for ammonia-nitrogen ( $\text{NH}_3\text{-N}$ ) removal and compared with Hector clinoptilolite from the USA. Very little difference in performance was experienced between the Pratley and Hector clinoptilolites for  $\text{NH}_3\text{-N}$  removal. Pratley clinoptilolite, however, was found to be less friable and cheaper than Hector clinoptilolite. The operating capacity of Pratley clinoptilolite increased with decreasing flow rate in the range of 15 to 5 bed volumes per hour and decreasing particle size in the range of 0,5 to 1,0 mm and 0,25 to 0,7 mm. The waste regenerant could be renovated and reused at least three times without a serious reduction in output. The  $\text{NH}_3\text{-N}$  stripped from the waste regenerant might be converted into fertilizer to offset some of the costs.  $\text{NH}_3\text{-N}$  can be reduced from about 20 mg/l in the feedwater to less than 1 mg/l. The total costs for  $\text{NH}_3\text{-N}$  removal for a 10 000 m<sup>3</sup>/d plant *with* and *without* regenerant reuse were also estimated.

## Introduction

Some underground waters from mines in South Africa contain high levels (approximately 20 mg/l) of ammonia-nitrogen ( $\text{NH}_3\text{-N}$ ) derived from explosives and possibly also faecal material. This  $\text{NH}_3\text{-N}$  reacts with chlorine during disinfection to impair sterilization, and gives rise to noxious halogenated compounds such as nitrogen trichlorides, as well as chloramines. The ammonia in the water may also cause corrosion of cupronickel heat exchanger tubes used in the refrigeration plants at some of the mines.

Ammonia discharges into the water environment also accelerate eutrophication of dams and dissolved oxygen depletion in receiving waters. (Semmens and Porter, 1979). Ammonia in its undissociated form is also toxic to fish at low levels (<0,5 mg/l) and its removal can be important for fish farming, particularly where a high proportion of the water is recycled (Lewis, 1980).

Ammonia-nitrogen can be removed from waste waters by selective ion exchange using clinoptilolite (clino), biological nitrification and denitrification, liming to pH 11 followed by air (or steam) stripping, breakpoint chlorination followed by treatment using activated carbon, and algae ponds (Jorgenson *et al.*, 1976; Lewis, 1980). Biological nitrification and algae ponds may not be suitable where low temperatures are encountered. Stripping and breakpoint chlorination are considered to be too expensive for the high  $\text{NH}_3\text{-N}$  levels encountered in some underground mine waters. Selective ion exchange of ammonia using the natural zeolite, clinoptilolite, in the sodium form, which is not very sensitive to temperature fluctuations, and which is a locally occurring mineral, will be considered in this paper for  $\text{NH}_3\text{-N}$  removal.

Experimental conditions including laboratory and pilot-scale ammonia removal investigations have been discussed in great detail by many authors (Mercer *et al.*, 1970); Koon and Kaufman, 1971; Hlavay *et al.*, 1982; Marking and Bills, 1982). These investigations, however, have all been performed on foreign clinoptilolites. Recently, a local clinoptilolite supplied by the Pratley Perlite Mining Company (Pty) Limited in South Africa was made available for evaluation.

The objectives of this laboratory-scale study were:

- to compare the local Pratley clinoptilolite with the well-known Hector clinoptilolite from the USA (California) for  $\text{NH}_3\text{-N}$  removal;
- to establish design criteria for  $\text{NH}_3\text{-N}$  removal from laboratory studies for a pilot plant; and
- to determine approximate capital and operating costs for a 10 000 m<sup>3</sup>/d  $\text{NH}_3\text{-N}$  removal plant.

## Genesis of zeolites

Most zeolites in sedimentary deposits formed after burial of the enclosing sediments by the reaction of aluminosilicate materials with the pore water (Munson and Sheppard, 1974). Siliceous volcanic glass is the aluminosilicate material that most commonly served as a precursor for the zeolites, although materials such as clay minerals, feldspars, and gels also reacted locally to form zeolites. The common zeolites generally occur in tuffaceous sedimentary rocks that have not been deeply buried or exposed to hydrothermal solutions. Formation of most of the common zeolites in sedimentary deposits is favoured by a relatively high activity ratio of alkali to hydrogen ions, and a high activity of silica in the pore water. Natural zeolites occur in the USA, Japan, Hungary, South Africa and possibly in other countries.

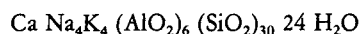
## Structure and chemical composition of clinoptilolite

Clinoptilolite is a natural zeolite. Zeolites are a family of aluminosilicates with an unusual crystalline structure enclosing pores occupied by cation and water molecules, both of which have considerable freedom of movement, permitting, within limits, reversible ion exchange and reversible dehydration (Smith, 1963). About 50 species of natural zeolites have been recognized and an equal number synthesized in the laboratory (Sheppard, 1984).

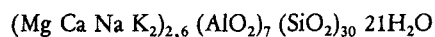
In general, zeolites have an open, infinitely extended three dimensional framework composed of silica and alumina tetrahedrons. All four corner oxygen atoms of each tetrahedron are shared with adjacent tetrahedrons (Mumpton, 1984). However, there is a net negative charge on the framework because of the substitution of aluminium atoms for silicon atoms. Therefore, the higher the silica:alumina ratio the lower its charge

and the lower its cation exchange capacity. This negative charge is balanced by ions found in the interstices of the zeolites, usually alkaline or alkaline-earth cations.

The idealised chemical formula for clinoptilolite is (Pratley Information Sheet, 1977):

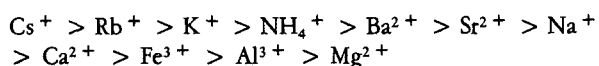


Pratley clinoptilolite has the following formula (Pratley Information Sheet, 1977):



### Selectivity series

The cation selectivity of clinoptilolite is:



(Koon and Kaufman, 1971). Thus, clinoptilolite has a decided preference for larger cations, and its selectivity for  $\text{NH}_4^+$  was exploited by Mercer *et al.* (1970) in the development of an ion exchange process for the removal of ammoniacal nitrogen from municipal sewage effluent.

### Loading and Regeneration

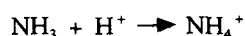
This can be represented as follows (Koon and Kaufman, 1981):

#### Loading

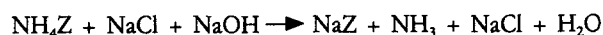


where Z = zeolite

Loading is usually performed under slightly acidic pH conditions to convert any free ammonia to the ammonium ion.



#### Regeneration



Regeneration is usually performed with sodium chloride under alkaline conditions (pH 12 to 12,5) to accelerate the regeneration process. The adsorbed ammonium ions are converted to free ammonia at the high pH and this ammonia diffuses more readily from the tiny pores in the zeolite matrix. Calcium compounds can also be used to regenerate the clinoptilolite.

### Experimental

Clinoptilolite ranging in size from 0,24 to 0,70 mm and 0,5 to 1,0 mm was used in the experiments. Column studies for the establishment of breakthrough curves were carried out using 25,4 mm i.d. x 900 mm columns which were operated in downflow mode.

#### ● Determination of total $\text{NH}_3\text{-N}$ exchange capacity of clinoptilolite

Ten grams of graded clinoptilolite (0,5 to 1,0 mm) that had

been backwashed to remove fines and dried at 105 °C were placed in a small column (16 mm diameter) and equilibrated with 1 M NaCl for one day at a flow rate of 50 ml/h. Excess sodium chloride was removed with deionized water and the clinoptilolite was then saturated with 1 M  $\text{NH}_4\text{Cl}$  for two days at a flow rate of 50 ml/h and washed free of  $\text{NH}_4\text{Cl}$  with deionized water. The ammonium ions were eluted with 0,5 M NaCl for two days at a flow rate of 50 ml/h and the total  $\text{NH}_3\text{-N}$  capacity was expressed as milliequivalents (me)  $\text{NH}_3\text{-N/g}$  dry clinoptilolite.

#### ● Determination of clinoptilolite densities

A 10 g washed and pre-dried sample of clinoptilolite (0,5 to 1,0 mm) was put in a small measuring cylinder containing a convenient amount of water, air bubbles were removed by tapping, and the settled clino (tapped) and displaced water volumes determined. Density was expressed as g/ml.

#### ● Determination of attrition losses

Ten-gram samples of pre-dried clinoptilolite (0,5 to 1,0 mm) were shaken for five days with 30 bed volumes (BV; equal to the gross volume occupied by the exchange material) regenerant solution (5,9 g NaCl/l adjusted to pH 12,5 with NaOH) in polyethylene bottles and the mass loss determined after fines had been removed by washing at 50% bed expansion. Attrition was expressed as the percentage dry mass loss.

#### ● Establishment of breakthrough curves

Clinoptilolite was loaded into columns and backwashed to remove fines. Settled (tapped) volumes of 150 and 220 ml were used. The clinoptilolite was regenerated with 30 BV 0,1 M NaCl solution adjusted to pH 12 or 12,5 with caustic soda (note: a better removal of  $\text{NH}_3$  is obtained at the high pH). Excess NaOH and NaCl were removed by backwashing for 30 min. Loading was performed with approximately 20 mg/l  $\text{NH}_3\text{-N}$  in the feed solution (pH 7) and effluent samples were collected every 20 BV and analyzed for  $\text{NH}_3\text{-N}$  by Nessler's method and breakthrough curves established. The breakthrough point was taken at 2 mg/l  $\text{NH}_3\text{-N}$  in the effluent and the output (volume produced at breakthrough) and the operating capacities at breakthrough (me  $\text{NH}_3\text{-N/ml}$ ) were determined by means of graphical integration.

#### ● Regenerant reuse

The spent regenerant was air-stripped in a small column (60 mm i.d. x 600 mm) packed with Raschig rings to remove  $\text{NH}_3\text{-N}$  to a residue of about 1 mg/l. After pH adjustment with NaOH to 12 or 12,5 this material was reused for regeneration. The cycle was repeated about four times to determine the practicability of regenerant reuse.

### Results and discussion

#### Total $\text{NH}_3\text{-N}$ exchange capacity and density

The total  $\text{NH}_3\text{-N}$  exchange capacities, the bulk densities and

specific gravities of the Pratley and Hector clinoptilolites are given in Table 1.

The total NH<sub>3</sub>-N exchange capacity of Hector clinoptilolite as reported by Koon and Kaufman (1971) is about 1,8 me/g. The total exchange capacity as determined here is slightly less at 1,6 me/g but of the same order.

The total NH<sub>3</sub>-N capacity of Pratley clinoptilolite is about 78% of the capacity of the Hector clinoptilolite on a dry mass basis, but about 29% greater on a wet basis due to a higher density.

#### Attrition losses

The attrition losses of Pratley and Hector clinoptilolites are presented in Table 2.

Pratley clinoptilolite showed a 42% lower mass loss than that of the Hector clinoptilolite which is indicative of a much less friable material.

#### Comparison of breakthrough results of Pratley and Hector clinoptilolites using Pretoria tap water spiked with NH<sub>3</sub>-N

Approximately 40 column runs were performed on Pretoria tap water spiked with NH<sub>3</sub>-N to about 20 mg/l under different regeneration and loading conditions to compare the performance for NH<sub>3</sub>-N removal of the two clinoptilolites. The composition of Pretoria tap water spiked with NH<sub>3</sub>-N is shown in Table 3.

A summary of the loading and regeneration conditions and breakthrough results is presented in Table 4.

The average breakthrough capacities for the first six runs (not all runs are shown) was about 0,16 me/ml which indicated that there was little difference in performance for NH<sub>3</sub>-N removal between the two clinoptilolites. A typical breakthrough curve (run 4) is shown in Figure 1.

An increase in regenerant concentration and pH from 5,9 to 11,8 g/l and 12 to 12,5 respectively had almost no effect on the breakthrough capacity (run 7), while a reduction in the regenerant strength and number of BV used to 5,9 g/l and 15 respectively, resulted in a definite decrease in capacity to about 0,1 me/ml for both clinoptilolites. An increase to 30 BV of regenerant again (run 15) could not increase the breakthrough capacity to its original value. This might indicate fouling or that some of the NH<sub>3</sub>-N was irreversibly adsorbed.

TABLE 1  
TOTAL NH<sub>3</sub>-N EXCHANGE CAPACITIES, BULK DENSITIES  
AND SPECIFIC GRAVITIES OF PRATLEY AND HECTOR  
CLINOPTILOLITES (0,5 TO 1,0 mm)

| Clinoptilolite | Total NH <sub>3</sub> -N capacity |             | Bulk*<br>density<br>g/ml | Particle**<br>density |
|----------------|-----------------------------------|-------------|--------------------------|-----------------------|
|                | me/g (dry)                        | me/ml (wet) |                          |                       |
| Pratley        | 1,21                              | 1,34        | 1,11                     | 2                     |
| Hector         | 1,55                              | 1,04        | 0,67                     | 1,66                  |

\* Dry mass  
Tapped volume

\*\* Dry mass  
Volume of displaced water

TABLE 2  
ATTRITION LOSSES OF PRATLEY AND HECTOR  
CLINOPTILOLITES AFTER SHAKING FOR FIVE DAYS WITH 30  
BV OF REGENERANT AT pH 12,5

| Clinoptilolite<br>type | % mass loss after five days shaking |
|------------------------|-------------------------------------|
| Pratley                | 3,9                                 |
| Hector                 | 9,3                                 |

TABLE 3  
COMPOSITION OF PRETORIA TAP WATER SPIKED WITH  
NH<sub>3</sub>-N

| Constituent                   | Concentration, mg/l |
|-------------------------------|---------------------|
| Na <sup>+</sup>               | 105                 |
| K <sup>+</sup>                | 15                  |
| Ca <sup>2+</sup>              | 32                  |
| Mg <sup>2+</sup>              | 19                  |
| NH <sub>3</sub> -N            | 20                  |
| NO <sub>3</sub> -N            | 0,9                 |
| SO <sub>4</sub> <sup>2-</sup> | 123                 |
| Cl <sup>-</sup>               | 63                  |
| HCO <sub>3</sub> <sup>-</sup> | 225                 |

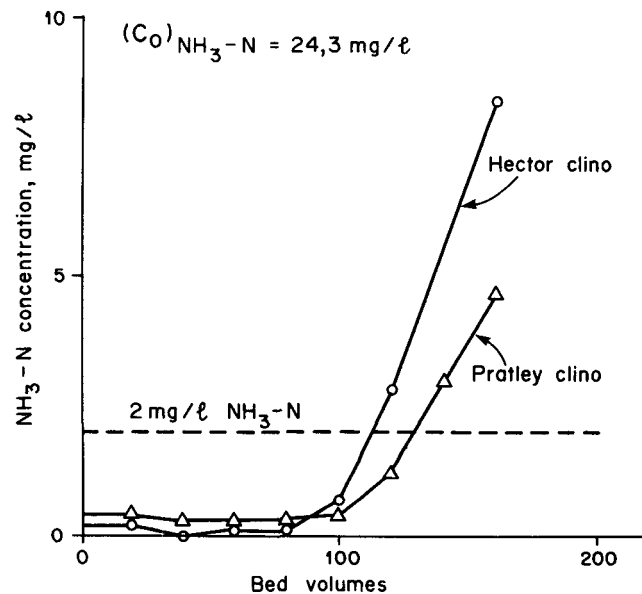


Figure 1  
Comparison of breakthrough curves of Pratley and Hector clinoptilolites.  
Particle size 0,5 to 1,0 mm; loading and regeneration flow rates 15 BV/h;  
1 BV = 150 ml

Run 26 showed the effect of increasing the regenerant strength to 23,6 g/l and of heating the regenerant solution to about 80°C to attempt to restore capacity. An increase in breakthrough capacity to 0,13 and 0,15 me/ml was observed for

**TABLE 4**  
**SUMMARY OF LOADING AND REGENERATION CONDITIONS AND BREAKTHROUGH RESULTS OBTAINED WITH PRATLEY AND HECTOR CLINOPTILOLITES**

| Run No. and type of clinoptilolite | Loading*                     |  |                              | Regeneration                |                                 |                |      |         |
|------------------------------------|------------------------------|--|------------------------------|-----------------------------|---------------------------------|----------------|------|---------|
|                                    | Inf. NH <sub>3</sub> -N mg/l | Av. Eff. NH <sub>3</sub> -N at breakthrough mg/l | % NH <sub>3</sub> -N removal | BV produced at breakthrough | Capacity at break-through me/ml | NaCl conc. g/l | pH   | BV used |
| 1: Pratley                         | 21,5                         | 0,7  | 96,7                         | 118                         | 0,172                           | 5,9            | 12   | 30      |
| Hector                             | 20,5                         | 0,5  | 97,6                         | 111                         | 0,157                           | 5,9            | 12   | 30      |
| 4: Pratley                         | 24,5                         | 0,5  | 97,9                         | 129                         | 0,174                           | 5,9            | 12   | 30      |
| Hector                             | 24,0                         | 0,4  | 98,3                         | 112                         | 0,151                           | 5,9            | 12   | 30      |
| 5: Pratley                         | 20,0                         | 0,6  | 97,0                         | 134                         | 0,146                           | 5,9            | 12   | 30      |
| Hector                             | 20,0                         | 0,4  | 98,0                         | 142                         | 0,159                           | 5,9            | 12   | 30      |
| 7: Pratley                         | 26,0                         | 1,3  | 95,0                         | 124                         | 0,166                           | 11,8           | 12,5 | 30      |
| Hector                             | 28,0                         | 0,5  | 98,0                         | 99                          | 0,147                           | 11,8           | 12,5 | 30      |
| 11: Pratley                        | 22,0                         | 1,4  | 93,6                         | 84                          | 0,101                           | 5,9            | 12,5 | 15      |
| Hector                             | 23,0                         | 1,0  | 95,7                         | 70                          | 0,109                           | 5,9            | 12,5 | 15      |
| 15: Pratley                        | 18,5                         | 1,1  | 94,1                         | 84                          | 0,081                           | 5,9            | 12,5 | 30      |
| Hector                             | 19,8                         | 0,4  | 97,9                         | 86                          | 0,094                           | 5,9            | 12,5 | 30      |
| 26: Pratley                        | 19,6                         | 0,7  | 96,5                         | 93                          | 0,128                           | 23,6           | 12,5 | 30      |
| Hector                             | 15,0                         | 0,3  | 97,7                         | 120                         | 0,147                           | 23,6           | 12,5 | 30      |
| 29: Pratley                        | 21,6                         | 1,7  | 92,1                         | 26                          | 0,039                           | 5,9            | 12,5 | 30      |
| Hector                             | 20,0                         | 0,4  | 98,1                         | 55                          | 0,078                           | 5,9            | 12,5 | 30      |
| 32: Pratley                        | 21,4                         | 0,9  | 95,8                         | 66                          | 0,098                           | 5,9            | 12,5 | 30      |
| Hector                             | 20,0                         | 0,6  | 97,0                         | 72                          | 0,101                           | 5,9            | 12,5 | 30      |
| 35: Pratley                        | 17,8                         | 0,5  | 97,2                         | 68                          | 0,086                           | 58,5           | 12,5 | 30      |
| Hector                             | 17,1                         | 0,4  | 97,7                         | 94                          | 0,115                           | 58,5           | 12,5 | 30      |
| 37: Pratley                        | 21,3                         | 0,9  | 95,8                         | 82                          | 0,121                           | 5,9            | 12,5 | 30      |
| Hector                             | 21,3                         | 0,4  | 98,1                         | 96                          | 0,144                           | 5,9            | 12,5 | 30      |
| 38: Pratley                        | 21,3                         | 1,0  | 95,2                         | 62                          | 0,087                           | 5,9            | 12,5 | 20      |
| Hector                             | 21,3                         | 0,9  | 95,8                         | 77                          | 0,109                           | 5,9            | 12,5 | 20      |
| 39: Pratley                        | 20,6                         | 1,4  | 93,1                         | 51                          | 0,069                           | 5,9            | 12,5 | 10      |
| Hector                             | 20,6                         | 1,5  | 92,7                         | 38                          | 0,052                           | 5,9            | 12,5 | 10      |

\*Loading was carried out at a flow rate of 15 BV/h except for runs 37, 38 and 39 when 7,5 BV/h was used.

Pratley and Hector clinoptilolite, respectively, which demonstrated that foulants or some of the absorbed NH<sub>3</sub>-N that was difficult to remove at room temperature could be removed at elevated temperatures.

On decreasing the regenerant strength to 5,9 g/l (run 29) again and regenerating at room temperature, the breakthrough capacities decreased to 0,04 and 0,08 me/ml for Pratley and Hector clinoptilolite, respectively. Heating the regenerant solution to about 80°C (run 32), again demonstrated that breakthrough capacity could be increased to about 0,1 me/ml for both clinoptilolites. However, even regeneration with 1 M NaCl (run 35) at room temperature could not restore breakthrough capacity to its original levels.

A decrease in the loading flow rate from 15 to 7,5 BV/h resulted in an increase in breakthrough capacity to 0,12 and 0,14 me/ml for Pratley and Hector clinoptilolite, respectively (run 37) while a reduction in capacity was observed with the use of 20 and 10 BV of regenerant (runs 38 and 39).

A significant decrease in breakthrough capacity was experienced with both clinoptilolites after a number of runs. This capacity reduction may be ascribed to fouling, insufficient NH<sub>3</sub>-N removal during regeneration and/or an increase in the cationic strength (Ca, Mg) of the feed solution which is known to affect capacity adversely (Koon and Kaufman, 1971). It was noted during the tests that the conductivity and hardness of the Pretoria tap water had increased as the result of drought conditions. However, on a comparative basis, little difference in performance was observed between the two clinoptilolites except that a

somewhat better quality effluent was produced with the Hector clinoptilolites. Ammonia-nitrogen removals of about 97% were achieved with an average effluent concentration of 1 mg/l and less.

Very little attrition loss was noticed after the 39 runs. According to Koon and Kaufman (1971) a 0,55% attrition loss per regeneration cycle may be expected for Hector clinoptilolite. In this study it has been established that Pratley clinoptilolite was only about half as friable as Hector clinoptilolite so that an attrition loss of about 0,25% per cycle may in practice be expected for Pratley clinoptilolite.

The cost of Hector clinoptilolite is about R700/t (importation costs excluded) compared to a cost of R335/t for the local product. It is expected, therefore, by taking the attrition losses and the capacities of the two clinoptilolites into consideration, that the local product will be more economical in practice.

#### Evaluation of Pratley clinoptilolite for the removal of NH<sub>3</sub>-N from an underground mine water and from Pretoria tap water spiked with NH<sub>3</sub>-N

An underground mine water with the typical composition shown in Table 5 and Pretoria tap water spiked with NH<sub>3</sub>-N (Table 3) were used in the next series of loading experiments.

It is apparent from Table 5 that the cationic strength of the mine water (in particular the hardness) is much higher than that of Pretoria tap water (Table 3) so that shorter runs on the mine water might be expected.

**TABLE 5**  
**TYPICAL COMPOSITION OF THE UNDERGROUND MINE WATER**

| Constituent                   | Concentration, mg/l |
|-------------------------------|---------------------|
| Na <sup>+</sup>               | 225                 |
| K <sup>+</sup>                | 14                  |
| Ca <sup>2+</sup>              | 87                  |
| Mg <sup>2+</sup>              | 34                  |
| NH <sub>3</sub> -N            | 20                  |
| NO <sub>3</sub> -N            | 710                 |
| SO <sub>4</sub> <sup>2-</sup> | 560                 |
| Cl                            | 180                 |

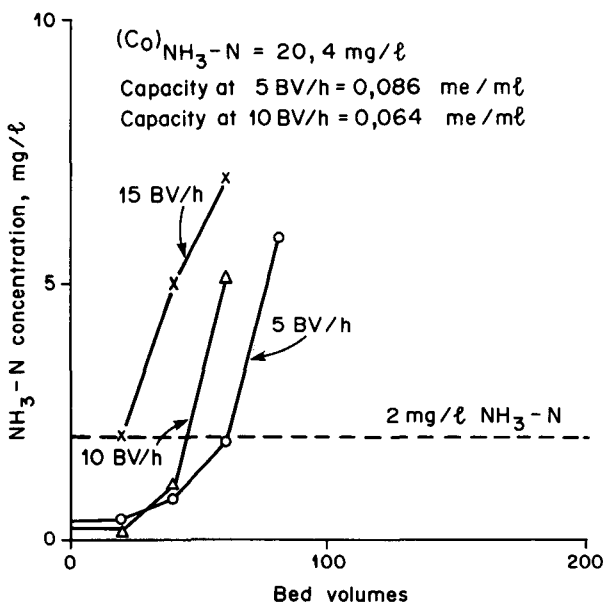
**Effect of loading flow rate on the breakthrough capacity of Pratley clinoptilolite using mine water**

The effect of three different flow rates, i.e. 5, 10 and 15 BV/h on the performance of Pratley clinoptilolite for NH<sub>3</sub>-N removal is shown in Figure 2.

At a flow rate of 15 BV/h it was found that it was not possible to produce an effluent containing less than 2 mg/l of NH<sub>3</sub>-N due to the higher cationic strength of the mine water than of Pretoria tap water. As the flow rate was decreased, output increased, and at 5 BV/h output was about 33% higher than at 10 BV/h. All further work, however, was done at a loading flow rate of 10 BV/h to save time.

**Effect of particle size on the breakthrough capacity of Pratley clinoptilolite using mine water**

The effect of two different particle sizes, i.e. 0,25 to 0,7 mm and 0,5 to 1,0 mm on the performance of the local clinoptilolite for NH<sub>3</sub>-N removal is shown in Figure 3.



**Figure 2**

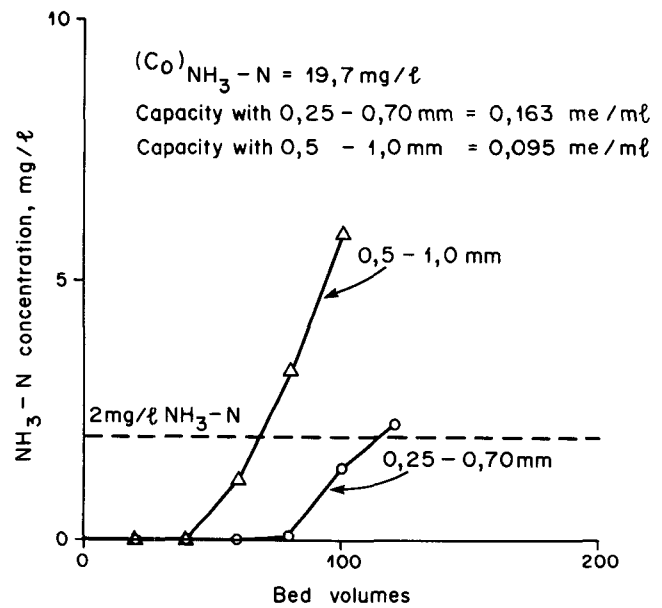
Effect of loading flow rate on the performance of Pratley clinoptilolite using mine water; particle size 0,5 to 1,0 mm; loading and regeneration flow rates 5, 10 and 15 BV/h; regenerant 30 BV 0,1 M NaCl (pH 12,5); 1 BV = 220 ml.

Output was increased by about 69% using the smaller particle size. This is possibly due to the faster adsorption of NH<sub>3</sub>-N on the smaller particles as a result of kinetic effects. However, in practice, a too small particle size is limiting because of excessive pressure drops.

**Effect of loading flow rate on the breakthrough capacity of Pratley clinoptilolite using Pretoria tap water**

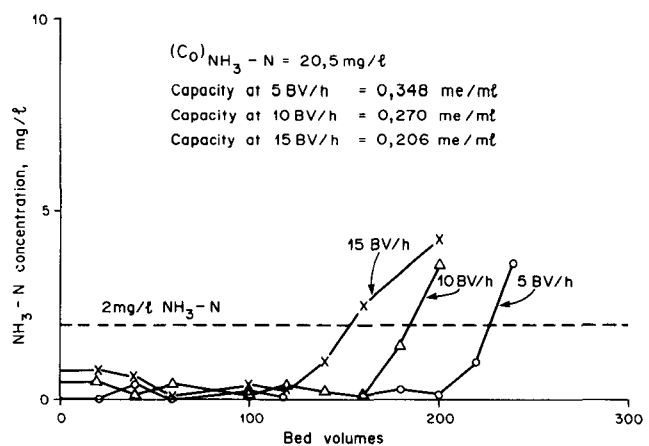
The effect of three different loading flow rates, i.e. 5, 10 and 15 BV/h on the performance of Pratley clinoptilolite for NH<sub>3</sub>-N removal using Pretoria tap water is shown in Figure 4.

Output again increased with decreasing flow rate. However, output and breakthrough capacity are significantly greater in this case than with the mine water because of the lower cationic strength of Pretoria tap water and the smaller particle size used.



**Figure 3**

Effect of particle size on the performance of Pratley clinoptilolite using mine water; loading and regeneration flow rates 10 BV/h; regenerant 30 BV 0,1 M NaCl (pH 12,5); 1 BV = 150 ml



**Figure 4**

Effect of loading flow rate on the performance of Pratley clinoptilolite using Pretoria tap water; loading flow rates 5, 10 and 15 BV/h; regeneration flow rate 10 BV/h; regenerant 30 BV 0,1 M NaCl (pH 12,0); particle size 0,25 to 0,7 mm; 1 BV = 150 ml

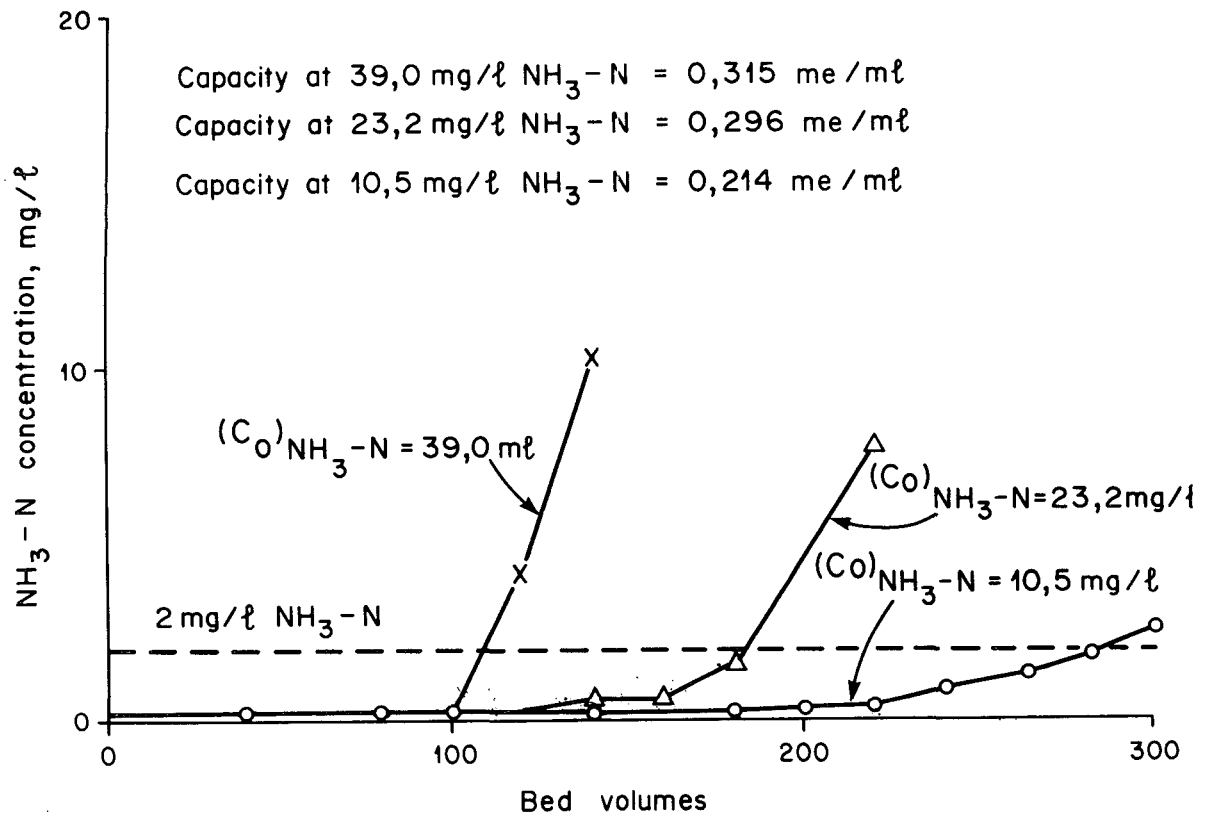


Figure 5  
 Effect of different NH<sub>3</sub>-N feed levels on the performance of Pratley clinoptilolite using Pretoria tap water; loading and regeneration flow rate 10 BV/h; regenerant 30 BV 0,1 M NaCl (pH 12,0); particle size 0,25 to 0,7 mm; 1 BV = 150 ml

**Effect of different concentrations of NH<sub>3</sub>-N in the feedwater on the capacity of Pratley clinoptilolite using Pretoria tap water**

The effect of three different NH<sub>3</sub>-N feed levels of about 10, 23 and 40 mg/l on the performance of Pratley clinoptilolite for NH<sub>3</sub>-N removal is shown in Figure 5.

The NH<sub>3</sub>-N breakthrough capacity of Pratley clinoptilolite increased by about 38% when the NH<sub>3</sub>-N in the feedwater was increased from 10,5 to 23,2 mg/l. Raising the concentration from 23,2 to 39,0 mg/l resulted in only a further 6,4% increase in capacity.

**Comparison of sodium and calcium chloride as regenerants for Pratley clinoptilolite using Pretoria tap water**

The effect of using 30 BV 0,1 M solutions of sodium chloride (pH to 12 with NaOH) and calcium chloride (CaCl<sub>2</sub>·2H<sub>2</sub>O, pH to 12 with lime) as regenerants for Pratley clinoptilolite is shown in Figure 6 (first loading), 7 (second loading) and 8 (elution).

Figure 6 (first loading) shows that, even with the first regeneration-loading cycle, sodium chloride is the better regenerant because output and breakthrough capacity were higher. However, the performance of calcium chloride as regenerant was fairly good. Figure 7, on the other hand, shows that it was not possible to obtain a product water containing less than 2 mg/l NH<sub>3</sub>-N with calcium chloride as regenerant after only the second regeneration-loading cycle. This worsening condition might be ascribed to the fact that very little ammonia was

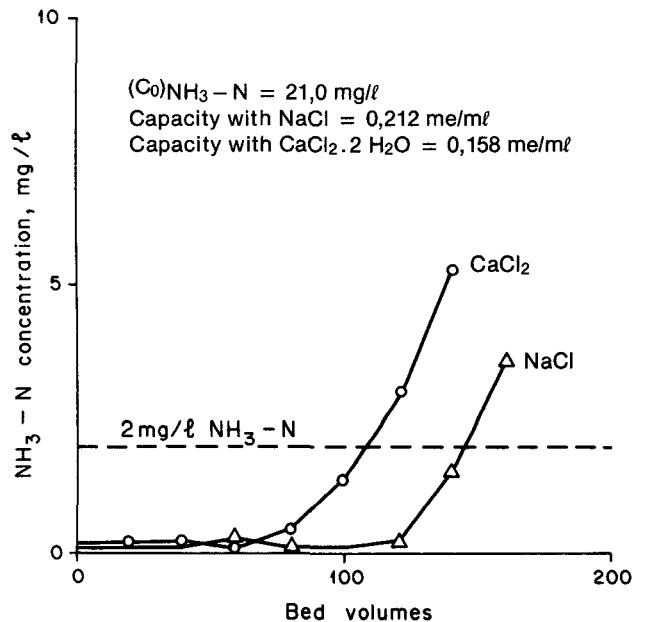


Figure 6  
 Effect of 30 BV 0,1 M NaCl and CaCl<sub>2</sub>·2H<sub>2</sub>O (pH 12) as regenerants on the performance of Pratley clinoptilolite using Pretoria tap water; loading and regeneration flow rate 10 BV/h; particle size 0,25 to 0,7 mm; 1 BV = 150 ml

eluted from the clinoptilolite after the first loading cycle with calcium chloride (Figure 8). The reason for this may have been that the calcium concentration of the regenerant solution had been reduced significantly by precipitation as  $\text{Ca}(\text{OH})_2$  and/or  $\text{CaCO}_3$  at the high pH. These solids could also have precipitated on the clinoptilolite particles causing a physical pore blocking and thereby inhibiting regeneration. The hydrated calcium ion is also substantially larger than the hydrated sodium ion (Koon and Kaufman, 1971) and therefore might find it more difficult than the sodium ion to penetrate the tiny pores in the zeolite matrix, to move freely and displace all the adsorbed ammonia.

#### Effect of regenerant reuse on the breakthrough capacity of Pratley clinoptilolite using mine water

The waste regenerant of which the pH had changed very little during regeneration was air-stripped to remove ammonia, pH adjusted to 12 or 12,5 with NaOH and reused to determine the effect on output because reuse could reduce regenerant and disposal costs significantly. The regeneration reuse results are presented in Figures 9 and 10.

From Figure 9 it can be seen that output decreased from 115 bed volumes after the first use (curves 1 and 2) of the regenerant to 94 bed volumes after the fourth use (curve 5) or third reuse cycle. Curve 3 showed that a lower output resulted when the pH of the regenerant was adjusted to 12 instead of 12,5 prior to regeneration. However, output and effluent quality was still satisfactory after three reuses so that regenerant reuse could be seriously considered to save regeneration and disposal costs.

Figure 10 indicated that most of the ammonia was eluted from the clinoptilolite after 10 BV of regenerant. However, no attempt was made to optimize regenerant requirements. The average  $\text{NH}_3\text{-N}$  content of the waste regenerant (30 BV) was approximately 52 mg/l. This  $\text{NH}_3\text{-N}$  was removed by counter current air-stripping in a small column packed with Raschig rings and it was possible to remove the  $\text{NH}_3\text{-N}$  to a residue of approximately 1 mg/l prior to regeneration. The pH of the solution dropped after air-stripping and it was necessary to adjust the pH of the renovated regenerant to 12 prior to reuse. The stripped  $\text{NH}_3\text{-N}$  may be absorbed in either nitric or sulphuric acid to form ammonium nitrate or ammonium sulphate, respectively, which could possibly be used as fertilizer. It is possible, therefore, that some of a plant's costs could be offset by the benefit of selling a by-product which is derived from the process.

#### Design criteria

Design criteria for a pilot plant were derived from the results obtained after the third reuse of the regenerant (Schoeman *et al.*, 1983). The criteria are presented in Table 6.

#### Process flow sheet

A simplified diagram of a flow sheet for a small pilot plant (approximately  $5\text{ m}^3/\text{d}$ ) to remove  $\text{NH}_3\text{-N}$  from an underground mine water is shown in Figure 11.

#### Estimated budget costs for a 10 000 $\text{m}^3/\text{d}$ plant

Costs were derived from the design criteria (Table 6) and from the conceptual design of a 10 000  $\text{m}^3/\text{d}$   $\text{NH}_3\text{-N}$  removal plant (24 hours operation per day) (Schoeman *et al.*, 1983). A summary of the cost analysis is presented in Table 7.

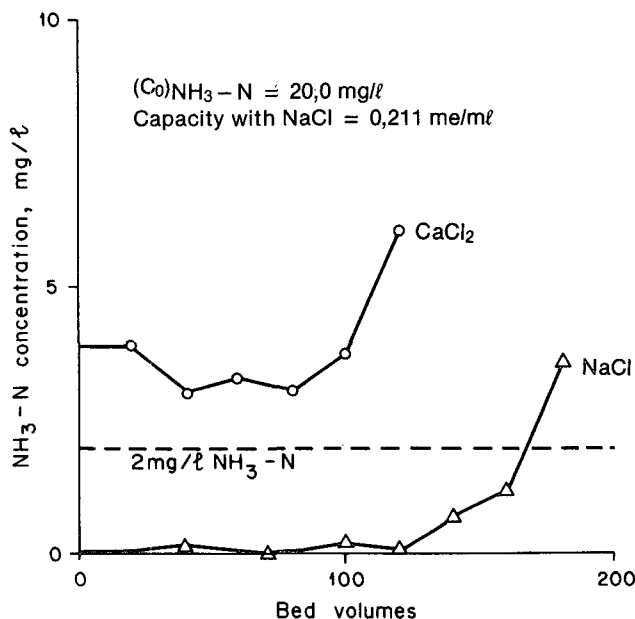


Figure 7  
Effect of 30 BV 0,1 M NaCl and  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  (pH 12) as regenerants on the performance of Pratley clinoptilolite using Pretoria tap water; loading and regeneration flow rate 10 BV/h; particle size 0,25 to 0,7 mm; 1 BV = 150 ml

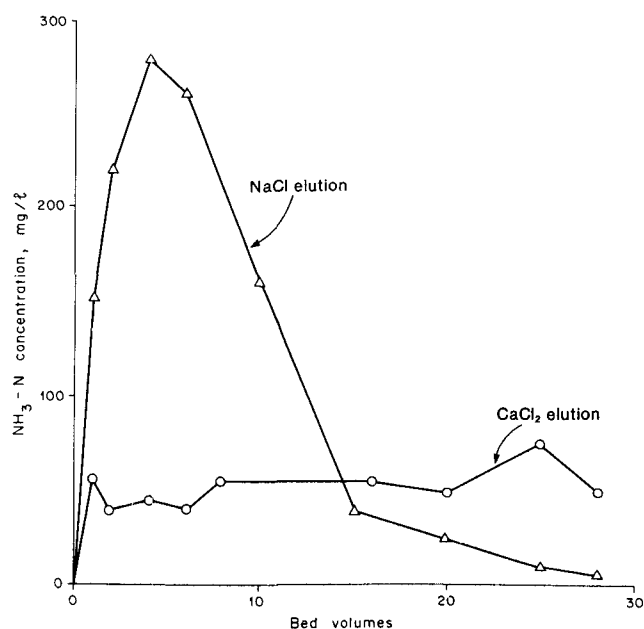


Figure 8  
 $\text{NH}_3\text{-N}$  elution curves of waste regenerant after first loading cycle and regeneration with NaCl and  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$

**TABLE 6  
DESIGN CRITERIA**

|   |  |
|---|--|
| Clinoptilolite particle size  | : 0,25 – 0,7 mm  |
| NH <sub>3</sub> -N exchange capacity  | : 0,13 me/ml or 1,82 kg NH <sub>3</sub> -N/m <sup>3</sup>  |
| Loading flow rate*  | : 10 BV/h  |
| Loading time  | : approximately 9 h  |
| Product water produced  | : 94 BV  |
| Regeneration flow rate  | : 10 BV/h  |
| Regeneration usage  | : 30 BV 0,1 M NaCl adjusted to pH 12 with 0,0178 ge NaOH/l regenerant solution. For regenerant reuse, 0,0067 ge NaOH/l must be added for pH adjustment to 12 after stripping |
| Regeneration time   | : 3 h  |
| Rinsing time  | : 1 h  |
| (NOTE: the rinsing water will contain NaOH and NaCl and may be reused at the mine.) |  |
| NH <sub>3</sub> -N reduction  | : approximately 20 mg/l  |
| Total cycle time  | : 13 h   |
| Cycles per day  | : 1,85   |
| Attrition losses  | : 0,25 % per cycle (assumed)   |
| Water recovery after third reuse of regenerant                                      | : 92,6 %   |
| Waste regenerant produced after third reuse of regenerant**                         | : $\frac{30 \text{ BV}}{2,16 \text{ d}} = \frac{13,9 \text{ BV}}{\text{d}}$  |

\*Laboratory tests showed a higher capacity at a flow rate of 5 BV/h and this flow rate should be used in practice.

$$\frac{13 \text{ h}}{\text{cycle}} \times 4 \text{ cycles (3 regen. reuses)} = 2,16$$

**TABLE 7  
COST SUMMARY – 10 000 m<sup>3</sup>/d NH<sub>3</sub>-N REMOVAL PLANT**

| Item   | Costs*               |                  |                       |                  |
|--|----------------------|------------------|-----------------------|------------------|
|  | No regenerant reuse  |                  | Regenerant reuse      |                  |
|  | R                    |                  | R                     |                  |
| <b>Capital costs</b>   |                      |                  |                       |                  |
| Ion exchange plant including vessels, piping, valves, pumps, instrumentation, installation, etc. | 500 000              |                  | 500 000               |                  |
| NH <sub>3</sub> stripping equipment  |                      |                  | 200 000               |                  |
| Clinoptilolite (66,22 tons at R335/ton)  | 22 184               |                  | 22 184                |                  |
| Contingencies (10%)  | 50 000               |                  | 70 000                |                  |
| Capital investment   | 572 184              |                  | 792 184               |                  |
| Capital cost (20 year life at 10% interest)  | 0,018/m <sup>3</sup> |                  | R0,026/m <sup>3</sup> |                  |
| <b>Operating costs</b>   |                      |                  |                       |                  |
|  |                      | R/m <sup>3</sup> |                       | R/m <sup>3</sup> |
| Labour and supervision   | 0,029                | 0,029            | 0,29                  | 0,029            |
| Power (ion exchange)   | 0,010                | 0,010            | 0,010                 | 0,010            |
| Power (NH <sub>3</sub> stripping)  |                      |                  | 0,030                 | 0,030            |
| Attrition losses (0,25 % per cycle assumed)  | 0,011                | 0,011            | 0,011                 | 0,011            |
| Chemicals for regeneration:  |                      |                  |                       |                  |
| NaCl + caustic soda (NaCl + lime)**  | 0,280                | (0,151)          | 0,114                 | (0,046)          |
| (NaCl at R0,07/kg, NaOH at R0,597/kg and lime at R0,05/kg)                                       |                      |                  |                       |                  |
| <b>Total costs</b>   | 0,348                | (0,219)          | 0,220                 | (0,152)          |

\*1983 prices were used.

\*\*Lime costs were calculated on an equivalent NaOH basis.



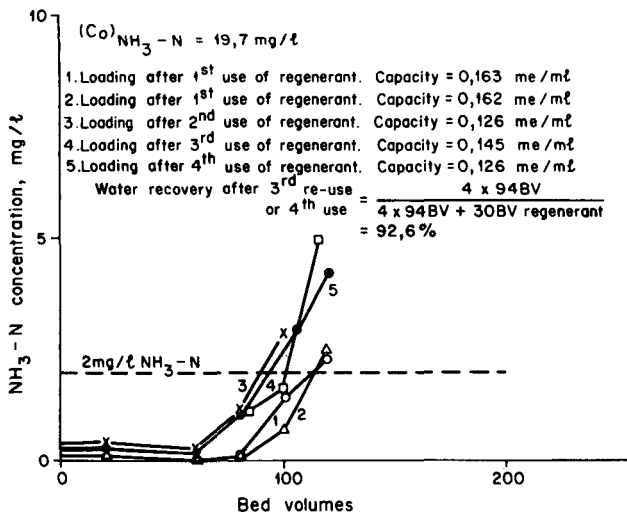


Figure 9  
Effect of regenerant reuse on output. Particle size 0,25 to 0,70 mm; loading and regeneration flow rates 10 BV/h; regenerant 30 BV, 0,1 M NaCl; 1 BV = 150 ml

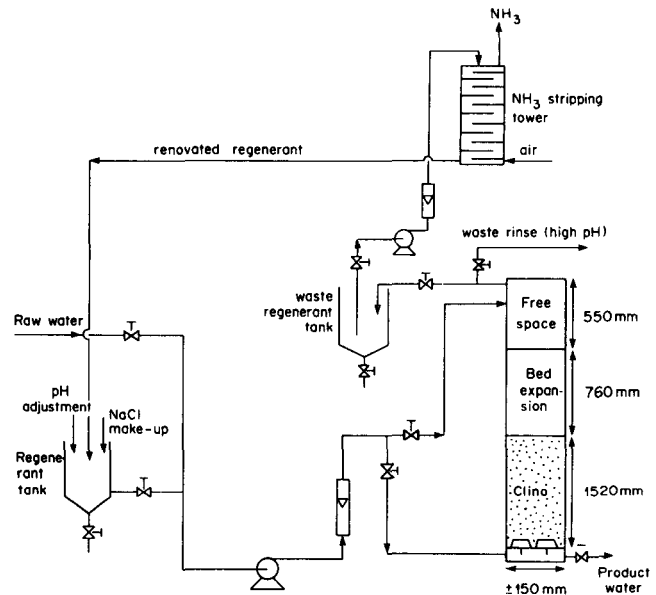


Figure 11  
Diagram of proposed flow sheet for a  $\pm 5 \text{ m}^3/\text{d}$   $\text{NH}_3\text{-N}$  removal pilot plant. 1 BV = 0,027  $\text{m}^3$

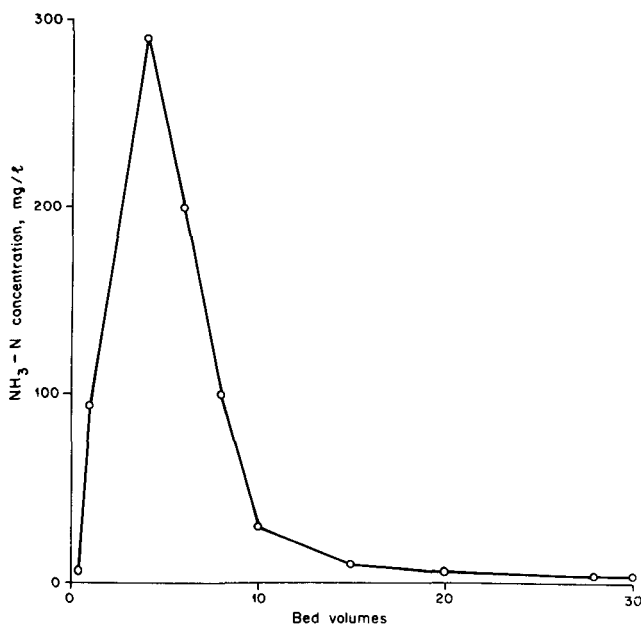


Figure 10  
 $\text{NH}_3\text{-N}$  elution curve; regenerant 30 BV 0,1 M NaCl (pH 12)

## Conclusions

- Very little difference in performance for  $\text{NH}_3\text{-N}$  removal was experienced between Pratley and Hector clinoptilolites. This, and the fact that Pratley clinoptilolite is less friable than Hector clinoptilolite and that the cost of the local pro-

duct is about half that of Hector clinoptilolite (importation costs excluded), indicate that the local product has certain advantages for  $\text{NH}_3\text{-N}$  removal.

- It was found that the capacities of both clinoptilolites deteriorated with use. The magnitude of this problem should be thoroughly investigated by pilot plant trials.
- The operating capacity or output of Pratley clinoptilolite increased with decreasing flow rate in the range of 15 to 5 BV/h and decreasing particle size in the range of 0,5 to 1,0 mm to 0,25 to 0,7 mm.
- Sodium chloride appeared to be a much better regenerant for  $\text{NH}_3\text{-N}$  removal than calcium chloride at a pH of 12.
- The waste regenerant could be renovated and reused at least three times without a serious reduction in output.
- The  $\text{NH}_3\text{-N}$  stripped from the waste regenerant might be converted into  $(\text{NH}_4)_2\text{SO}_4$  or  $\text{NH}_4\text{NO}_3$  and sold as fertilizer to offset some of the costs.
- Ammonia-nitrogen can be reduced from about 40 mg/l to less than 1 mg/l. The total costs for  $\text{NH}_3\text{-N}$  removal for a 10 000  $\text{m}^3/\text{d}$  plant *without* and *with* regenerant reuse were estimated at R0,35/ $\text{m}^3$  (NaCl + NaOH), R0,22/ $\text{m}^3$  (NaCl + lime) and R0,22/ $\text{m}^3$  (NaCl + NaOH), R0,15/ $\text{m}^3$  (NaCl + lime), respectively. These costs are only approximate because regenerant requirements were not optimized and pilot studies should be carried out to verify them and optimize the various process steps.

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