

## ZEOLITE AS FEED ADDITIVE TO REDUCE MANURE MINERAL CONTENT

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### ABSTRACT

Two tests were conducted to establish parameters for the use of a zeolite, namely clinoptilolite, as swine feed additive in improving digestion and thus reducing manure mineral content. The first test was conducted in the laboratory to establish the ammonium binding potential of the experimental zeolite and the second test consisted in feeding one of 8 rations to 24 hogs. The experimental zeolite (90%+ clinoptilolite) was subjected to laboratory simulated digestive tract conditions which demonstrated that clinoptilolite is stable even at a pH of 1.5 and that it releases less than 10% of its already low heavy metal content. Furthermore, clinoptilolite lost only 15% of its ammonium adsorption capacity at a pH of 1.5 (120 cmol<sup>(+)</sup>/kg), compared to a pH of 7.0 (140 cmol<sup>(+)</sup>/kg). The second test used a combination of four (4) clinoptilolite levels (0, 2, 4 and 6%), 2 feed qualities (standard energy and protein versus 90% standard energy and protein). The trial used 192 hogs split into 4 groups of 6 (3 females and 3 males) and grown from 23 to 105kg. The results indicated a 5% improvement in feed digestibility using 4% clinoptilolite. Some advantage may be gained by using 2% clinoptilolite for hogs with a body weight of up to 40Kg and 6% for hogs weighing more than 80kg, but for the farm operator, 4% for all body weights is easier to manage while providing insignificant reductions in performance.

### INTRODUCTION

The intensification of farm operations brings challenges in managing manures for the environmental protection of natural resources. Often, transport distances and crop land availability impose serious constraints on the disposal of manures enriched in nutrients from improving diet quality, since most livestock can digest only 30% of feed minerals as opposed to 70% of hydrocarbons. Although manure dewatering techniques can concentrate some nutrients for a more efficient land disposal, the most logical nutrient reducing method for manure is the improvement of mineral digestion. Compared to dewatering techniques, improving nutrient digestion can reduce feed costs and produce leaner carcasses. Use as feed supplement, clinoptilolite is a type of zeolite which can improve feed digestion.

Among the 45 types of zeolites which are clay like minerals mined from sedimentary deposits, clinoptilolite is known for its specific adsorption of ammonium and for its capability in improving feed protein digestion. By definition, clinoptilolite is a species of zeolite that has a relatively 'open' structure with a total pore volume of approximately 35% (Godelitsas and Armbruster 2003) along with a three-dimensional alumino-silicate framework containing narrow four- and five-membered rings constituting intra-micro-pores (channels) capable of hosting exchangeable cations (NH<sub>4</sub><sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>). These channels enhance the selective sorption of clinoptilolite of molecules such as ammonia, dinitrogen, carbon monoxide, and methane which are small enough to enter their channels. The cation-exchange capacity (CEC) of clinoptilolite can theoretically reach 330 meq/100 g and selectively adsorbs cations in the following

order:  $\text{NH}_4^+ > \text{Pb}^{2+} > \text{Na}^+ > \text{Cd}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+}$  (Langella et al. 2000). Barbarick and Pirela (1984) found that clinoptilolite had a high selectivity for  $\text{K}^+$  and  $\text{NH}_4^+$ .

According to Kithome et al. (1999), the amount of  $\text{NH}_4^+$  adsorbed by clinoptilolite increases with pH. At a pH of 4 and 7, the respective  $\text{NH}_4^+$  adsorption was 9,660 mg N  $\text{kg}^{-1}$  at pH 4 and 13,830 mg N  $\text{kg}^{-1}$ . Kesraoui-Ouki and Kavannagh (1997) found that optimum heavy metal removals using clinoptilolite occurred between a pH of 4 and 5. Clinoptilolite also has the highest thermal stability (700°C) in air, while heulandite, a zeolite with similar structure, undergoes structural collapse below 450°C (Çulfaz and Yaşiz 2003; Perraki and Orfanoudaki 2004).

Thus, clinoptilolite is the ideal swine feed additive to improve ammonium retention and protein digestibility. The objective of the research was therefore two fold:

- 1) Measure the ammonium adsorption and macro-mineral desorption capacity of two specific clinoptilolites under laboratory conditions simulating those found in the stomach and intestine of pigs;
- 2) Identify the optimal level of clinoptilolite feed supplementation.

## MATERIALS AND METHODS

### Adsorption and desorption test

The experimental zeolites, supplied by the groups KMI (Nevada, USA) and Steelhead (Idaho, USA), both had a clinoptilolite content exceeding 90%. The clinoptilolite content was determined by comparing the X-Ray Diffraction (XRD) results to that obtained with an almost pure sample. The KMI zeolite was also found to have a Si/Al ratio of 7. Samples of zeolite were mechanically sieved and analyzed according to three different particle sizes, <250  $\mu\text{m}$ , >250  $\mu\text{m}$ , and mixture of the two sizes.

To analyze the absorption capability of the KMI and Steelhead zeolites under conditions of neutral pH, 2.5g samples were placed in a solution of either 100ml of 0.05M  $\text{NH}_4\text{Cl}$  or 0.05M phosphate buffer solution which maintained a neutral pH. The samples were shaken at 150 rpm at room temperature (22°C) for 1 day, 2 days or 3 days. After shaking, the supernatant liquid was separated from the solids centrifugation for 20. The supernatant liquid analyzed for ammonia using a selective probe and for macro-minerals and heavy metals using atomic adsorption spectrophotometer (AAS).

A second test was also carried out to simulate conditions inside a pig's stomach. This experiment was similar in procedure to the previous experiment except that zeolite was immersed in an  $\text{NH}_4\text{Cl}$  solution at a pH of 1.5 at a constant temperature of 40°C. After 4 and 24h, the supernatant liquid was removed by centrifugation, and analyzed for ammonium, macro-minerals and heavy metals, as described above.

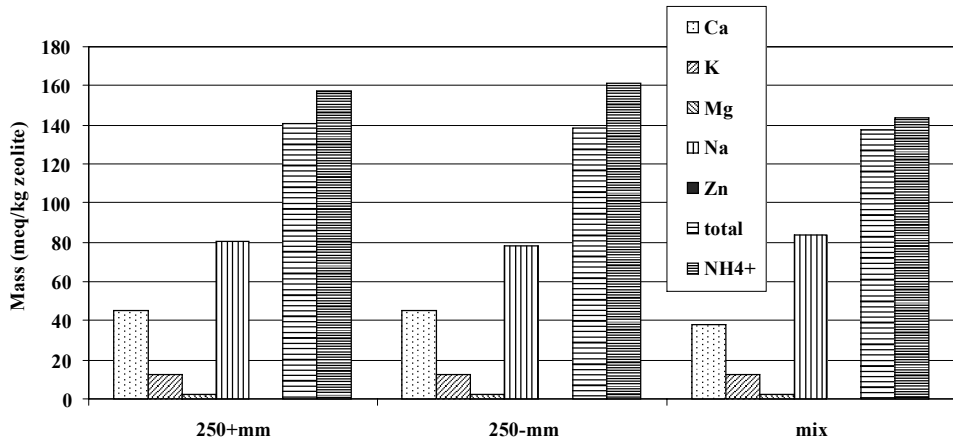
### Feed test

Optimum zeolite dosage in the feed was established using 192 hogs weighing initially 23kg. These hogs were randomly assigned one of eight treatments: 4 levels of zeolite x 2 levels of energy and crude protein. Thus, all treatments were quadrupled with pens of 6 hogs, fed to a market weight of 105kg. The zeolite levels tested were: 0, 1, 2 and 4%. The crude protein and energy level were 100% and 90% of that recommended. Feed consumption was measured daily and hogs were weighed every two weeks along with the feed remaining in the feeders. To compare feed performance level between the 8 treatments, an analysis of variance was used (Steel et Torrie, 1986).

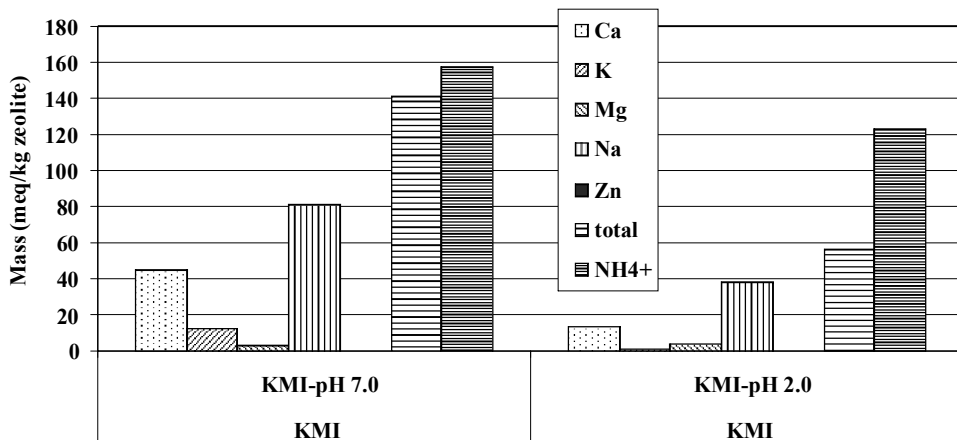
## RESULTS AND DISCUSSION

Figures 1 and 2 illustrate the quantities of ammonium and macro-nutrients adsorbed and desorbed by the KMI clinoptilolites under a pH of 7.0, for the three particle size range selected. In general, the amount of ammonium adsorbed corresponds to that of macro-nutrients desorbed. These macro-nutrients can be beneficial as feed supplements.

Under a pH of 1.5, slightly less ammonium is adsorbed, compared to a pH of 7.0, and less macro-nutrients are released.



**Figure 1.** Ammonium adsorption and mineral desorption with various particle sizes for KMI clinoptilolite.



**Figure 2.** Ammonium adsorption and mineral desorption with KMI clinoptilolite under a pH of 7 and 2.

The feeding trail indicated a 5% improvement in feed digestibility using 4% clinoptilolite. Although the growth rate was not significantly different among all 8 treatments, feed conversion varied with zeolite level (85% confidence level). Some advantage may be gained by using 2% clinoptilolite for hogs with a body weight of up to 40Kg and 6% for hogs weighing more than 80kg, but for the farm operator, 4% for all body weights is easier to manage while providing

insignificant reductions in performance. A proper feed energy to protein ratio with 4% zeolite inclusion can produce leaner carcasses.

## CONCLUSIONS

The KMI clinoptilolite proved to be relatively stable under low pH, still adsorbing 85% of the ammonium adsorbed under a neutral pH. Nevertheless, less macro nutrients are released under a low pH indicating that clinoptilolite releases more of these in the intestine where the pH is closer to neutral. The feed trial indicated that a zeolite level of 4 % (90% clinoptilolite) can improve feed conversion by 5%.

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