THE EFFECT OF CLINOPTILOLITE PROPERTIES AND SUPPLEMENTATION LEVELS ON SWINE PERFORMANCE

by

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ABSTRACT

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THE EFFECT OF CLINOPTILOLITE PROPERTIES AND SUPPLEMENTATION LEVELS ON SWINE PERFORMANCE

Clinoptilolite is a zeolite and an aluminosilicate that can be fed to swine in order to reduce nutrients being excreted because of their molecular sieving properties, high cation exchange capacities, and a high affinity for the ammonium ion (NH_4^+). Preliminary research has been carried out on utilizing zeolite's unique characteristics for dietary supplementation for livestock, however much of this research is limited and is still in its infancy.

The first objective of the project was to establish the clinoptilolite particle size which would optimize both the feed additive value and the handling of the material. Thus, experiments were performed in order to characterize the chemical and physical properties of zeolite. The NH_4^+ adsorption and macro mineral and heavy metal desorption characteristics of several clinoptilolites were evaluated under conservative conditions and simulating those found inside a pig's stomach, for different particle size distributions and geographic sources of zeolite. Experiments involving physical properties of zeolite looked at the relationship between moisture content and particle size distribution of the zeolite powder to determine the effect on flowability of zeolite under bulk storage conditions.

The effect of zeolite as a feed additive, at inclusion levels of 0, 2, 4 and 6%, in two standard swine diets (high and low protein), was investigated through pig performance, carcass quality and organ and tissue heavy metal concentration measurements. The 192 grower hogs on test initially weighed 23kg, were randomly split into 8 quadruplet groups of 6 (3 females and 3 males) and were fed eight different combinations of zeolite levels (0, 2, 4 and 6%) and two different levels of crude protein (C.P.) and energy. Body weight, body weight gain, feed intake, feed conversion rate, carcass quality and heavy metal uptake by the liver, kidney and muscle tissue were all measured.

The results from this study show that the zeolite with a particle size distribution either > 250 µm or mixed (50% particles greater and smaller than 250 µm) adsorbed the most NH_4^+. Macro mineral and heavy metal release was similar among all particle size distributions tested, but varied between sources of zeolite. Handling properties of zeolite were not affected by moisture content or particle size. The feed trial indicated that zeolite supplementation, combined with a low crude protein and energy diet and at an inclusion level of 4%, showed potential as a feed additive in swine diets for the purposes of nutrient reduction. Nevertheless, zeolite seemed to have a greater impact on energy ingestion, as compared to crude protein. Even at 6% zeolite inclusion in the feed, hog muscle, kidney and liver tissues showed no significant increase in heavy metal contents, as compared to those fed any zeolite.

RESUMÉ

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M. Sc. Génie Bioresouces

THE EFFECT OF CLINOPTILOLITE PROPERTIES AND SUPPLEMENTATION LEVELS ON SWINE PERFORMANCE

La clinoptilolite est une zéolite de la famille des aluminosilicates qui peut être utilisée comme un additif alimentaire dans la ration des porcs afin de réduire les nutriments excrétés. La clinoptilolite possède des propriétés moléculaires qui la font agir comme un tamis, et qui lui donne une forte capacité d'échange cationique (EC) et une affinité spécifique aux ions ammoniums (NH_4^+). Des recherches préliminaires ont démontrée que la clinoptilolite possède des caractéristiques uniques qui en font un additif alimentaire idéal pour les élevages agricoles.

Le premier objectif de ce projet était d'établir la granulométrie de la poudre de zéolite qui optimiserait à la fois sa valeur alimentaire et sa manipulation. Donc, des essais furent réalisés afin de caractériser les propriétés physico-chimiques de la clinoptilolite. Dans un environnement simulant celui de l'estomac des porcs, le pouvoir d'adsorption du NH_4^+ et de désorption des macro minéraux et des métaux lourds furent évalués pour des clinoptilolites de granulométrie et de sources géographiques différentes. Pour évaluer l'écoulement de la zéolite dans les silos d'entreposage, son angle interne de friction fut mesuré sous diverses teneurs en humidité et avec diverse granulométrie.

Afin de déterminer le meilleur taux d'inclusion dans la ration de porcs à l'engraissement, et l'effet du taux de protéine brute (P.B.) et d'énergie dans la ration supplémentée de clinoptilolite, 8 rations furent préparées, en utilisant soit 0, 2, 4 ou 6% de clinoptilolite et soit 100 ou 90% du taux normal de P.B. et d'énergie. Huit quadruples groupes de 6 porcs de 23kg furent alimentés avec chacune des rations et leur gain de poids, et conversion alimentaire furent mesurés pendant 10 semaines. La qualité des carcasses et la teneur en métaux lourds de leur muscle, reins et foie fut évaluée à l'abatage.

Les résultats de cette étude nous montrent qu'une granulométrie de > 250 µm ou mélangée (50% > 250 µm et 50% < 250 µm) optimise l'absorption de l'ammonium dans l'estomac de l'animal et la manutention du produit en poudre. L'angle de friction interne de la clinoptilolite ne fut pas influencé par son taux d'humidité ni sa granulométrie, pour la gamme de valeurs testées.

Les expériences ont aussi démontrées que l'utilisation de la clinoptilolite à un taux de 4%, dans une moulée à faible teneur en P.B. et en énergie (90% de la normale) pourrait améliorer la conversion alimentaire des porcs à l'engraissement. Cependant, la zéolite semble avoir un impact plus important sur l'ingestion de l'énergie comparativement à l'ingestion de la P.B. Même à 6% d'inclusion dans la ration, la clinoptilolite n'a pas eu d'effet significatif sur la teneur en métaux lourds des muscles, reins et foies des porcs à l'essai et en comparaison avec ceux non alimentés de zéolite.

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FORMAT OF THESIS

The following thesis conforms to the manuscript-based thesis format which has been approved by the **Faculty of Graduate Studies and Research, McGill University**. This thesis follows the conditions outlined under "**Thesis preparation and submission guidelines**, section 1, **Thesis preparation**, part C., **Manuscript-based thesis**" which states:

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2. The thesis must be more than a collection of manuscripts. All components must be integrated into a cohesive unit with a logical progression from one chapter to the next. In order to ensure that the thesis has continuity, connecting texts that provide logical bridges preceeding and following each manuscript are mandatory.

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The thesis must include the following:

1. a table of contents;
2. a brief abstract in both English and French;
3. an introduction which clearly states the rational and objectives of the research;
4. a comprehensive review of the literature (in addition to that covered in the introduction to each paper);
5. a final conclusion and summary;
6. a thorough bibliography;
7. Appendix containing an ethics certificate in the case of research involving human or animal subjects, microorganisms, living cells, other biohazards and/or radioactive material.

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CONTRIBUTION OF AUTHORS

The work presented in this thesis was performed by the candidate and supervised by Dr. S. F. Barrington of the Department of Bioresource Engineering, Macdonald Campus of McGill University, Montréal, Québec, Canada. The research project was at the Macdonald Campus of McGill University, Downtown Campus of McGill University, and Macdonald Campus Swine Complex on the Macdonald Campus of McGill University. The authorship for the papers are 1) S. Leung, S. F. Barrington, X. Zhao, and B. El Husseini, 2) S. Leung, S. F. Barrington, X. Zhao, M.-K. Huang, R.I. Cue and S.O. Prasher for the papers in Chapters IV and V, respectively.

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1	Day one (abbreviation for statistical analysis)
2	Day two (abbreviation for statistical analysis)
3	Day three (abbreviation for statistical analysis)
A	Ammonia solution (abbreviation for statistical analysis)
Å	Angstrom
AA	Amino acids
AAS	Atomic adsorption spectrophotometer
AFM	Atomic force microscope
Al	Aluminum
ANOVA	Analysis of variance
As	Arsenic
B	Buffer solution (abbreviation for statistical analysis)
BW	Body weight
BWG	Body weight gain
c	company of dependant observation (KMI, Steel Head, and Commercial Grade Zeolite X)
Ca	Calcium
Cd	Cadmium
CEC	Cation Exchange Capacity
CH_4	Methane
CO	Carbon Monoxide
Co	Cobalt
COD	Chemical oxygen demand
Cr	Chromium
CSTR	Continuously stirred-tank reactors
Cu	Copper
DK	Denmark
e_{ijk}, e_{ijkl}, e_{ijklm}	residual error
e_{ijkl}, e_{ijklm}	residual error

e_{ijklmn}, $e_{ijklmno}$	residual error
$e_{ijklmnop}$	residual error
F	France
FCR	Feed conversion rate
Fe	Iron
FI	Feed intake
G	Greater than 250 µm particle size of zeolite (abbreviation for statistical analysis)
GIT	Gastrointestinal tract
h	hour
H^+	Hydrogen ion
H0	High Protein Diet Supplemented with 0% zeolite
H2	High Protein Diet Supplemented with 2% zeolite
H4	High Protein Diet Supplemented with 4% zeolite
H6	High Protein Diet Supplemented with 6% zeolite
H_2S	Hydrogen Sulfide
ha	hectare
ICP	Inductively coupled plasma
K	KMI zeolite (abbreviation for statistical analysis)
K	Potassium
K^+	Potassium ion
L	Less than 250 µm particle size of zeolite (abbreviation for statistical analysis)
	M Mixed particle size of zeolite (abbreviation for statistical analysis)
L0	Low Protein Diet Supplemented with 0% zeolite
L2	Low Protein Diet Supplemented with 2% zeolite
L4	Low Protein Diet Supplemented with 4% zeolite
L6	Low Protein Diet Supplemented with 6% zeolite
Li^+	Lithium ion
LS Means	Least Square Means (abbreviation for statistical analysis)

m	moisture content of dependant bulk shear test observation (0, 5, and 10%)
M	Any alkali or alkaline Earth cation in chemical formula for zeolite
M	Molarity
meq	Milliequivalence
Mg	Magnesium
Mo	Molybdenum
MSE	Mean square error
N	Nitrogen
n	Valence of M cation in chemical formula for zeolite
N_2	Nitrogen
Na	Sodium
NH_3	Ammonia
NH_4^+	Ammonium ion
NH_4Cl	Sodium Chloride (aqueous solution)
Ni	Nickel
NL	The Netherlands
NS	Not statistically significant (P>0.10)
p	particle size of dependant observation (> 250 µm, < 250 µm, and mixed)
P	Phosphorus
PAM	Polyacrylamide
Pb	Lead
pro_k	the fixed effect of the k^{th} protein level (k = H, L) zeo_l = the fixed effect of the l^{th} zeolite supplementation level (l = 0,2,4,6)
$room_i$	the fixed effect of the i^{th} room (i = 1,2)
row_{ij}	the fixed effect of the i^{th} row in the j^{th} room (i = 1,2; j = 1,2).
RPM	Revolutions per minute
s	solution of dependant observation (ammonia or buffer)
S	Steel Head zeolite (abbreviation for statistical analysis)
SBR	Sequencing batch reactor
Se	Selenium
SE	Standard error (abbreviation for statistical analysis)

sex_m	the fixed effect of pig gender (m = M, F).
Si	Silicon
SO_2	Sulphur Dioxide
St	Strontium
t	time of dependant observation (1, 2, and 3 days; 4 and 24 hours)
TKN	Total kjeldahl nitrogen
TP	Total phosphorus
TS	Total solids
VFA	Volatile fatty acids
VOC	Volatile organic compounds
VS	Volatile solids
$week_n$	the fixed effect of week (n = 0, 2, 4, 6 , 8, 10)
x	a number from 2 to 10 in chemical formula for zeolite
XRD	X-ray diffraction
Y	Dependent observation
y	a number from 2 to 7 in chemical formula for zeolite
Y_{ijk}, Y_{ijkl}	dependant observation
Y_{ijklm}	dependant observation
Zn	Zinc
μ	overall mean

I. GENERAL INTRODUCTION

The pork industry is a very important economic sector for Canada. It has been forecasted that Canadian exports of pork products will reach almost one million metric tons in 2004. In 2002, Canada's pork industry brought in roughly 2.1 billion dollars and exported nearly 800 thousand metric tons of pork products. This placed Canada's pork industry 2nd in the world in net exports of pork products in 2002, only the European Union surpassed Canada in net exports of pork products (USDA FAS 2004). Forecasts and predictions show no signs of the pork industry slowing down in Canada. However, the swine industry has undergone some significant changes in order to get where it is today.

Over the last 25 years the total number of farms producing pigs in Canada has decreased significantly and steadily, from 63,602 in 1976 to an estimated 12,405 in 2001. Saskatchewan is a province which illustrates this trend very well. The Canadian Pork Council (2003) has reported approximately 1,280 pig farms in Saskatchewan in 2001, compared to the 12,246 pig farms that existed in 1976. This translates to approximately only 1/10 of the total number of pig farms remaining in that province, or a 90% reduction in the number of pig farms. The province of Quebec has also seen its fair share of decline, going from 9,067 pig farms in 1976 to an estimated 2,430 in 2001. Thus, in order to keep the Canadian pork industry growing and competitive the number of animals per farm has increased tremendously. The average Canadian farm inventory has increased from 91 pigs per farm in 1976 to an estimated 995 in 2001. Looking at the province of Saskatchewan again, their average inventory increased from 40 pigs per farm in 1976 to an estimated 824 in 2001. This represents a staggering increase in the average number of pigs per farm in this province by a factor of 20 over the last 25 years. The province of Quebec went from an average of 178 pigs per farm in 1976 to approximately 1,567 pigs per farm in 2001.

These changes in the pork industry have generated many environmental concerns coming from both the farming and non-farming rural population, which perceive intensive livestock operations as a major contributor to environmental problems. It is manure which is at the center of the two largest environmental issues facing the swine industry. They are: an unbalanced nutrient cycle due to excess nutrients in swine manure (Nitrogen and Phosphorous in particular) and odour.

Manure produced by animals has been used traditionally as a fertilizer to sustain crop production. This nutrient recycling process, including livestock production and the crop production to feed those animals, is a sustainable way to assure nutrients remain in balance. However, due to the recent trend in intensive livestock housing the volume of manure that is being produced by the livestock is increasing proportionally. Therefore, manure application to fields is putting the nutrient cycle out of balance. In many cases, all over Canada, the application of manure as fertilizer to fields has exceeded the nutrient requirements of the land at the farm level and in some cases, the regional level. Every province in Canada, with the exception of B.C. and Alberta, has had an increase in residual nitrogen levels on over 50% of agricultural land of at least 5 kg/ha between 1981 and 1996 (Figure 1.1).

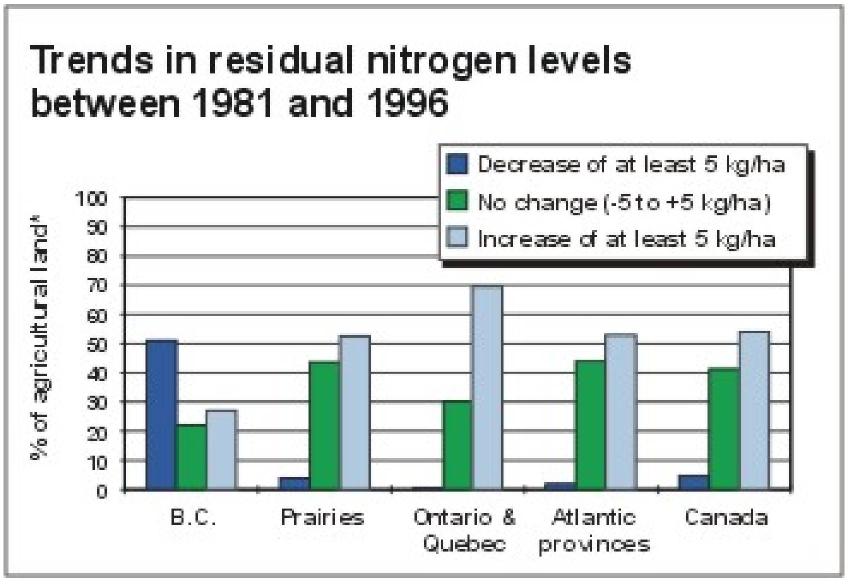

Figure 1.1: Trends in residual nitrogen levels between 1981 and 1996 (Environment Canada, 2004)

Already producers in the L'Assomption, St Hyacinthe and Beauce regions, which market over 50% of all Quebec hogs, have exceeded the nutrient requirements of the land at the regional level. The same problem is observed in the Windsor-Georgian Bay area of Ontario, the Fraser Valley in B.C. and the Lethbridge area in Alberta (Figure 1.2).

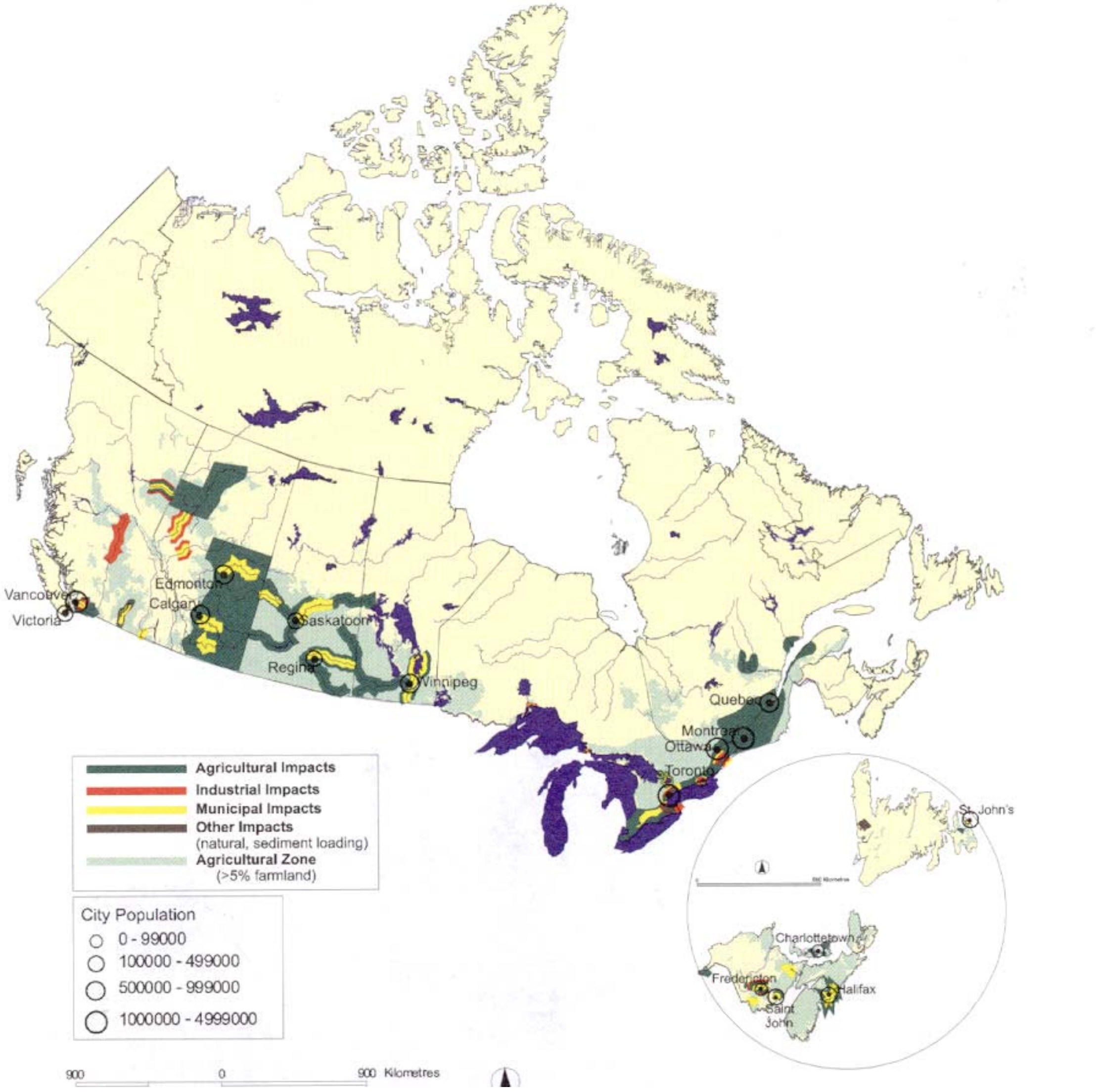

Figure 1.2: Documented sites of nutrient enrichment in Canada in 1998 (Chambers et. al. 2001)

Odours coming from intensive livestock operations may also prove to be as just an important environmental concern as soil nutrient balance, as urbanization expands onto agricultural land. Methane (CH_4), hydrogen sulphide (H_2S) and carbon monoxide (CO) are gases which can build up in confinement housing of livestock and can be life threatening to animals and even humans when they reach a certain critical limit. Ammonia (NH_3) is another gas which can build up in livestock operations, however it is only considered as an irritant and not life threatening (Chénard et al. 1998). Also, odours are one of the main causes of conflicts between livestock producers and their neighbours. In most areas hog producers represent a small minority of the population. Therefore, it is imperative that they maintain a good relationship with their community. If the swine industry wishes to 'clean up' its public perception as polluters, solutions must be developed in order to control odour. Environmental authorities will not allow the swine industry in these regions to expand unless these environmental issues are dealt with.

There are two possible solutions to this manure problem. One possible solution is to treat the manure upon excretion, transport it and distribute the manure to regions where nutrients are in deficit (intense cropping areas). However, this solution would not be economical because of the high costs involved.

The other solution is to improve the nutrient digestibility through diet manipulation to reduce manure nutrient content (Honeyman 1993; Sutton et. al. 1999). Growing Pigs use only 30 to 35% of ingested dietary N (Nitrogen) and P (Phosphorus) (Jongbloed and Lenis, 1998). Diet manipulation has clearly been shown to reduce excess N and P in swine manure and offers the potential to assist in reducing the real or perceived negative effects of odours and other gaseous emissions from swine waste (Cromwell et al., 1998; Sutton et. al., 1999; Jongbloed and Lenis, 1998). Sutton et al. (1999) reviewed the potential for reduction of odorous compounds in swine manure through diet modification and reported that reductions in ammonia emissions by 28 to 79% through diet modifications have been reported.

One form of diet manipulation is the use of feed additives to improve nutrient utilization. Zeolite is a mineral which is beginning to gain some popularity amongst agricultural researchers, because of its Cation Exchange Capacity (CEC), adsorption and related molecular sieving characteristics.

Clinoptilolite, a species of zeolite, has a high affinity for NH_4^+ and K^+ ions which is the basis for many uses that are being developed for this zeolite in agriculture. An unpublished article from the Manitoba Swine Update reported that through the use of clinoptilolite in pig feed, total non-protein nitrogen excretion was reduced by 30-50%. This trend was confirmed by Zimmerman (1996) from experiments carried out on feeding clinoptilolite to swine, it was discovered that nitrogen and phosphorous contents decreased with increasing amounts of clinoptilolite fed to swine. Nakaue et al. (1981) incorporated 10% clinoptilolite in the feed ration of poultry and concluded that ammonia levels were significantly reduced. The addition of zeolites to swine diets have resulted in decreased NH_3 emissions by 9% and H_2S emissions by 7% (Cromwell et al. 1998).

II. GENERAL OBJECTIVES AND SCOPE

2.1 Objectives

The objectives of this research project were to evaluate the feasibility of zeolite as a feed additive in swine diets in order to reduce the environmental impact of their manure. Thus, evaluation was carried out in two main parts:

1. A test of the chemical and physical properties of zeolite

The experiments carried out in the chemical analysis of zeolite involved evaluation of NH_4^+ adsorption as well as the desorption of macro minerals (Ca, Cu, K, Mg, Na, Zn) of KMI zeolite over a three day period under neutral pH. Evaluation of the adsorption properties of NH_4^+ and desorption of heavy metals (Al, As, Cd, Cu, Co, Cr, Fe, Mo, Ni, Pb, Se, St, Zn) of KMI zeolite was also carried out over a 24 hour period under an acidic pH of 1.5, in order to simulate conditions inside of a pig's stomach.

If zeolite is to be used as a feed additive, some design specifications are required regarding the storage of this material. Therefore, experiments were carried out in order to characterize the physical properties of KMI zeolite involving a direct shear apparatus. Zeolite samples were classified according to particle size and moisture content. Three different particle sizes were used (< 250 µm, > 250 µm and mixture) as well as three different moisture contents (0%, 5% and 10%). The amount of shear stress need to cause a failure plane in the samples of zeolite was measured under three different normal loads. From this data angle of internal friction could be calculated, angle of wall friction was also calculated.

2. A feed trial consisting of feeding pigs a standard pig diet supplemented with various concentrations of zeolite to determine the effect on pig performance

During the feed trial growing-finishing pigs were fed a high and low protein/energy diet supplemented with four different levels of KMI zeolite (0, 2, 4 and 6%). Pig performance was determined by measuring the effect of zeolite supplementation on body weight, body weight gain, feed intake, feed conversion rate, carcass quality, and heavy metals released in the liver, kidney and muscle tissue. Therefore the effect of zeolite supplementation level and its interaction with crude protein and energy level could be examined.

2.2 Scope

The zeolite used to supplement the pig diets in the feed trial was supplied by the company KMI, which comes from a mine in Nevada, USA.

Testing the chemical properties of zeolite was limited to ammonia adsorption and mineral desorption.

Testing the adsorption and desorption characteristics of zeolite was also limited to a neutral pH and a pH of 1.5, in order to simulate pH conditions in the stomach of a pig.

The physical properties were limited to testing angle of internal friction and angle of wall friction of the zeolite using only the KMI zeolite. The direct shear test method was employed according to procedures adapted from ASTM D 3080, by Liu and Evett (1997b).

The feed trail was an ad libitum feed trial in which there were 6 pigs, 3 males and 3 females, housed in each pen and there were 32 pens in total. Therefore this feed trial was limited to 24 pigs per treatment (8 different treatments) giving 196 pigs in total. The pigs were growing-finishing pigs and their performance was evaluated over a 10 week period (up to 83.0 ± 5.9 kg).

III. LITERATURE REVIEW

Nutrients such as Nitrogen (N) and Phosphorus (P) are elements that are essential to plant growth and are naturally present in the environment. However, human activities such as agriculture have over loaded the amount of these nutrients (N and P) into the environment, namely our soil, water and air resources. This has left nutrient cycles unbalanced.

Figure 1.2 of the problem statement illustrates that agricultural activities, in Canada, result in soil and water nutrient enrichment. Almost all cases of nutrient enrichment can be associated with the over application of manure as fertilizer to land. This problem results from the specialization trend of agricultural industries. Nutrient over loading has brought about many challenges, such as the manure disposal regulations introduced by environmental authorities. Such regulations limit manure applications based on nutrient content and often prevent livestock operations from expanding until it can be proven that a balanced nutrient cycle can be sustained. This puts livestock producers in a difficult position because their operations have expanded so greatly, producing much more manure relative to the nutrients which their land base can transfer to crops.

Reducing the input of nutrients into the environment is possible by reducing the amount of nutrients in the manure itself, thus balancing the nutrient cycle on individual farms.

This section will discuss the environmental impacts of nutrient overloading on various ecosystems. This literature review will also discuss the methods which can reduce the amount of nutrients excreted in manure.

3.1 Use of Manure in Agriculture

Almost all manure produced on Canadian Farms is applied to agricultural land. Manure is an important additive to agricultural soils because it supplies both nutrients and organic matter. Therefore, it is the most practical and economic method of manure disposal. Depending upon the type of livestock and the rations being fed, fresh manure can contain 65 to 80% of the N and P originally present in the feed. Not all nutrients in manure are immediately available to crops, however. Some are tied up in organic forms and become available over time as the material decomposes, thereby acting as a nutrient source over several years. In addition, the organic matter in manure contributes to improved soil structure, nutrient and water-holding capacity, and drainage. Nutrients are lost from manure between the time it is produced and it is allowed to run off feedlots and from manure storage facilities. A large proportion of manure N is in the form of ammonium (NH_4^+) and, upon exposure to air, can be converted to ammonia gas (NH_3) and lost to the atmosphere (Chambers et. al., 2001).

3.2 Composition of Pig Manure

Pig manure is primarily a mixture of urine and feces, and it contains undigested dietary components, endogenous end products, and indigenous bacteria from the lower gastrointestinal tract (GIT). Manure contains a variety of organic compounds, complex to simple in nature, inorganic compounds, and potentially, feed additives, depending upon the makeup of the diet. Presented below is a table (Table 3.1) of the average values for the nutrient contents reported in 141 swine manure samples (Chénard et al., 1998).

Table 3.1: Nutrient Values in Swine Manure (Livestock waste handbook, 1985).

Swine	Size (kg)	TS[a]	N[a]	P[a]	K[a]
Nursery pig	15.9	8.70	0.70	0.23	0.43
Growing pig	29.5	9.29	0.69	0.23	0.47
Finishing pig	68.0	9.18	0.69	0.22	0.46
	90.7	9.23	0.69	0.23	0.45
Gestating sow	124.7	9.21	0.70	0.24	0.45
Sow and litter	170.1	9.09	0.70	0.23	0.46
Boar	158.8	9.09	0.71	0.24	0.46

[a] = % based on total manure production
TS = Total solids
N = Total nitrogen
P = Total phosphorus
K = Total potassium

Odorous volatile organic compounds (VOC), short-chain volatile fatty acids (VFA), and other volatile carbon-, nitrogen-, and sulfur-containing compounds from microbial fermentation in the GIT of pigs can be emitted immediately after feces are excreted

(Sutton et al., 1999). Odorous compounds are generally grouped as alcohols, carbonyls, disulfides, mercaptans, organic acids, phenols, sulfides, and volatile amines. Fifteen volatile organic compounds (acetic, propanoic, butanoic, 3-methyl butanoic and pentanoic acids, phenol, 4-methyl phenol, indole, 3-methyl indole, methanithiol, dimethyl sulfide, dimethyl disulfide, dimethyl trisulfide, and hydrogen sulfide) extracted from swine manure have been identified as the primary compounds causing odours (Adeola, 1999).

3.3 Environmental Concerns

Environmental concerns relating to the over application of animal manure (Figure 1.2 in Problem Statement for affected regions in Canada) can be divided into three categories (Jongbloed and Lenis, 1998; Jongbloed et al., 1999). Concerns related to the soil (accumulation of nutrients), the water (eutrophication), and the air (odours and global warming). Eutrophication refers to the process of over fertilization of a body of water by nutrients that produce more organic matter than self-purification reactions can overcome (Chambers et al., 2001).

3.4 Environmental Impacts of Increased Nutrients

In 1996, The N surplus in Canada was 7.3 kg/ha for the total area of agricultural land (68 million hectares), similarly the P surplus in Canada in 1996 was 0.8 kg/ha for all agricultural land (Chambers et al., 2001). The primary consequence of nutrient addition is similar for all ecosystems, namely increased plant growth. However the secondary consequences (e.g. changes in faunal diversity, effects on nutrient cycling, impacts on adjacent ecosystems) differ. Outlined below are three selected types of ecosystems which react differently to an increase in, and type of nutrient loading.

3.4.1 Forest ecosystems

Fertilization studies involving single N applications have confirmed that N is the major limiting element for tree growth in many Canadian forest ecosystems (Weetman et al., 1987). Increased N deposition can lead to increases in forest growth and can also change species dominance and diversity by favouring the growth of plants better adapted to high concentrations of N. Forrest ecosystem N saturation occurs when a point is reached where N supply, as a result of N deposition, is in excess of the total plant and microbial demand for N. It is further characterized by the conversion of excess N to nitrate, which is then leached to surface or ground waters. Nitrate leaching can affect downstream waters, cause changes in soil chemistry, and an increase in soil acidity (Aber et al., 1995). In Canada, an analysis of nitrate concentrations in runoff water to Turkey Lake in central Ontario, and Lac Laflamme in southern Québec, identified the forests surrounding these lakes as being in the early stage of N saturation (Jeffries, 1995). Leaching of nitrate associated cations can also cause nutrient imbalances in trees, in particular changes in calcium:aluminum and magnesium:nitrogen ratios. These imbalances have been linked to reduction in net photosynthesis, photosynthetic N-use efficiency, forest growth, and tree mortality (Schulze, 1989; McNulty et al., 1996; Aber et al., 1995; Cronan and Grigal, 1995; Chambers et al., 2001).

3.4.2 Lake ecosystems

Nutrients are essential to lakes because they provide the raw material for the growth of algae, the food source of zooplankton, which in turn are eaten by fish. Surplus growth of algae and other effects occur when the inflow of nutrients exceeds the lake's capacity to absorb these nutrients (Chambers et al., 2001).

Phosphorus in lakes is highly reactive, binding with soil particles and minerals in the water column. Once this binding has occurred the P is largely unavailable to bacteria and algae for growth. It is the amount and rate of turnover of the remaining dissolved phosphorus that dictates the extent of algal growth. The ability of a lake to retain P depends on net sedimentation, which depends on the flushing rate and depth in the lake. Rapidly flushed lakes reflect the concentration of the inflowing waters. Lakes that flush very slowly are largely determined by its sedimentation characteristics. Nutrient supply strongly affects the growth of aquatic plants in lakes, particularly algae. In the majority of north temperate lakes, P is the nutrient most in demand, and algal growth and biomass is P-limited (Vollenweider, 1976 as cited by Chambers et al., 2001). Thus, in many lakes, algal growth is a function of P concentration (Watson et al., 1997).

Algal blooms can affect lakes in several ways: increased water turbidity, reduced aesthetic appeal and even decreased recreational use. As enrichment continues, erratic and sometimes severe outbreaks of different algal taxa (e.g. Chrysophyta, Haptophyta, Dinophyta) can negatively affect water quality, the aquatic food web and can even cause fish kills (Leeper and Porter, 1995 as cited by Chambers et al., 2001). Highly eutrophic systems (lakes very rich in nutrients) tend to be predominated by blue-green algae that form dense, foul-smelling and noxious blooms, often as surface scums, because many of these algae are buoyant. Many species of blue-green algae produce potent toxins, which can poison zooplankton, fish, avian, waterfowl, terrestrial wildlife, livestock and even humans (Carmichael, 1992; Kotak et al., 1993, 1996). Also, in highly eutrophic lakes zooplankton can also undergo boom and bust cycles and diversity may be reduced and production limited. So called "coarse" fish species, such as carp, may come to dominate the fish population while success of spawning and survival of more desirable species, such as trout or bass, becomes more and more tenuous due to the overwhelming organic detritus and periodic de-oxygenation as algal blooms decompose. This results in a simplified aquatic food web. In addition, the overabundance of organic matter caused by excessive algal populations can smother the lake bottom resulting in reduced biodiversity of benthic organisms. Organic matter also accumulates in crevices between rocks where decay can consume enough oxygen to damage the survival of fish eggs (Chambers et al., 2001).

3.4.3 Ground water

Nitrate contamination of ground water is usually associated with over-application of manure to agricultural lands however, under fertilization can also result in the leaching losses of nitrate. These loses can be as large as those observed for over fertilized crops because crop growth is impaired leaving a sizeable amount of moisture in the soil. This extra moisture fosters microbial activity resulting in larger net N mineralization (Campbell et al., 1993). Nitrate is soluble in water and if it is not assimilated by plants, it is free to move with percolating water beyond the root zone and into ground water (Miner et al., 2000a). In contrast to nitrate, ammonium concentration is adsorbed onto clay minerals and is not as prone to leaching; however under aerobic conditions it is subject to bacterial oxidation to nitrate and may be readily mobilized. Normally ammonium concentration in soils is very low. Phosphorus movement into ground water is retarded through soil adsorption and mineral precipitation reactions in the unsaturated zone (Wilhelm et al., 1994; Harman et al., 1996 as cited by Chambers et al., 2001).

Approximately 26% of Canadians rely on ground water for their domestic water supply. This translates to approximately 8 million Canadians using groundwater for their drinking water supply. It is also expected that ground water supplies a significant percentage of livestock drinking-water supplies in Canada (Chambers et al., 2001). Certain N forms have been known to cause adverse health effects (Figure 4). Ingestion of high quantities of nitrate or nitrite may result in methaemoglobinaemia ("blue baby syndrome"), a condition resulting from the oxidation (by nitrite) of ferrous (Fe^{2+}) to ferric (Fe^{3+}) iron in haemoglobin, the oxygen carrier of mammalian blood. The resulting mathaemoglobin has no oxygen carrying capacity. Symptoms are cyanosis, asphyxia, and death. The most sensitive subpopulation is infants less than three months of age (Chambers et al., 2001; Morse, 1995). Water-borne nitrate or nitrite can also cause methaemoglobinaemia problems for terrestrial animals. However, nitrogen toxicity in terrestrial animals is mostly associated either with air pollution (nitrogen dioxide, ammonia or nitrate) or the consumption of vegetation with high nitrate levels (Chambers et al., 2001).

Figure 3.1: Canadian aquifers vulnerable to nitrate contamination (Chambers et al., 2001)

3.5 Methods to Reduce Nutrient Excretion in Swine

The Netherlands was the first country to initiate a large research program to reduce the environmental impact of livestock production. Three main solutions were proposed by Jongbloed and Lenis (1998).

1. The first one was a reduction of mineral input via the feed (diet manipulation).
2. The second one was a stimulation of practical solutions at the farm level, such as distribution and application of manure.
3. The third solution was to upgrade manure by processing on a large scale for export purposes

4. Another solution not proposed by Jongloed and Lenis (1998) is the use of genetically modified pigs.

3.5.1 Diet manipulation

3.5.1a Phosphorus (Phytase)

Much work on improving nutrient digestibility in pigs has been carried out in France, Denmark, and The Netherlands. Phosphorus losses in growing pigs in the three countries averaged 63% (Dourmad et al., 1999a; Fernández et al., 1999 ; van der Peet-Schwering et al., 1999). It was concluded from the research conducted in the three countries, that the major cause of low P utilization in pigs is that dietary P digestibility is very low (Figure 3.2). The main reason for that is that up to about 75% of the P in feedstuffs is of plant origin and is present as phytate, the salt of phytic acid, which is almost indigestible for pigs (Poulsen et al., 1999). Since dietary phytate is not hydrolyzed efficiently into inorganic phosphate, large amounts of phosphorus are excreted in feces, leading to phosphorus wastage, and environmental pollution (Li et al., 1997). An experiment conducted by Veum et al. (2001) illustrates the indigestibility of phytate P well. In this experiment the use of a low-phytate hybrid corn resulted in as much as a 50% P reduction in swine waste as compared with a normal corn diet. Low-phytate corn was used in another study (Spencer et al., 2000) and was found to reduce P excretion by 37%. It was concluded from this study that low-phytate corn contains at least five times as much available P as normal corn.

As a result of the indigestibility of phytate P traditionally what was done to meet the pig's P requirement was that feed manufacturers and farmers added inorganic P to pig feeds in excess amounts. However, in the presence of supplementary or intrinsic phytase, phytic acid can be hydrolyzed to liberate free orthophosphates and inositol for absorption (Jongbloed and Lenis, 1998). Harper et al. (1997) conducted two experiments in which phytase was used to supplement corn-soybean meal diets in growing-finishing pigs. It was found that overall P digestibility was improved by 33% and 44% in the two experiments conducted. It was also concluded in a study carried out by Traylor et al. (2001) that the use of supplemental phytase was an effective means of improving Ca and P utilization by growing swine fed soybean meal-based diets. Through the use of phytase as a dietary supplement to pig diets farmers and feed manufacturers could stop feeding inorganic P in excess amounts since improved phosphorus utilization in pigs would be realized. This would result in an improved N:P ratio which makes swine manure more environmentally and economically suitable as a source of fertilizer (Spencer et al., 2000).

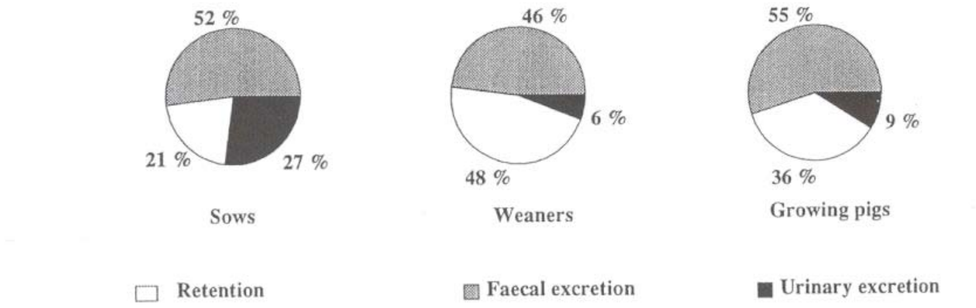

Figure 3.2: Mean phosphorus retention, urinary and faecal excretion for sows, weaners and growing pigs in France, The Netherlands, and Denmark (Poulsen et al., 1999)

3.5.1b Nitrogen

From the nutrient digestibility research carried out in France, Denmark, and The Netherlands by Fernández et al. (1999), Dourmad et al. (1999a), and van der Peet-Schwering et al. (1999) nitrogen losses in the three countries averaged 66% in growing pigs. Two complementary approaches have been proposed according to Dourmad et al. (1999b) for improving the efficiency of utilization of N by pigs and, consequently, reducing N excretion. The first approach is to ensure adequate protein and amino acid supplies at all times according to the growth potential of the animal or its physiological status (phase feeding). This requires making supplies of energy and protein (amino acids) appropriate to the pig's potential and its stage of production, and to production objectives. The second approach is to improve dietary amino acid balance and consequently reduce the protein content of the diet (ideal protein concept). This can be achieved through the combination of different protein sources and the utilization of industrial amino acids. With these cumulative beneficial effects, it is expected that N output in the slurry and in the atmosphere can be reduced by 20 to 30%, through better feeding management, without any significant increase in feeding costs. The production of a standard pig required 7.9, 8.7 and 8.4 kg in Denmark, France and The Netherlands, respectively (Table 3.2).

Table 3.2: Nitrogen consumption, retention and losses in the production of a standard pig (kg/pig produced) in Denmark (DK), France (F) and The Netherlands (NL) (Dourmad et al., 1999b)

	Consumption			Retention			Losses		
	DK	F	NL	DK	F	NL	DK	F	NL
Piglet[a]	1.4	1.4	1.2	0.3	0.4	0.3	1.2	1.1	0.9
Weaner	1.3	1.1	0.8	0.6	0.5	0.4	0.7	0.6	0.4
Growing pig	5.4	6.1	6.4	2	2	2.1	3.4	4.1	4.3
Total									
Kg N/pig	8	8.6	8.4	2.8	2.9	2.9	5.2	5.8	5.5
g N/pig	80	80	74	28	27	25	52	53	49
Relative	100	100	100	35	33	34	65	67	66

[a]Including the contriubution of the sow.

3.5.1b.i Ideal protein concept

The ideal protein concept is the concept of studying dietary amino acids in a pattern to match the animal's amino acid needs (Honeyman, 1993), an example of this concept is given in Table 3.3.

Table 3.3: Ideal Amino Acid Patterns for Pigs in Three Weight Categories[a] (Baker, 1996)

	Ideal patterns (% of lysine)		
Amino acid	5-20 kg	20-50 kg	50-110 kg
Lysine	100	100	100
Threonine	65	67	70
Tryptophan	17	18	19
Methionine	30	30	30
Cystine	30	32	35
Methionine + cystine	60	62	65
Isoleucine	60	60	60
Valine	68	68	68
Leucine	100	100	100
Phenylalanine + tyrosine	95	95	95
Arginine	42	36	30
Histidine	32	32	32

[a]ratios are expressed on a true digestible basis.

An important benefit of the ideal protein concept is that the requirements for all dispensable amino acids (AA) and total crude protein can be quickly derived after the requirements for one amino acid are established. This concept may also be used to reduce amino acid excesses that occur in practical swine diets, without affecting animal performance. For an effective use of the ideal protein concept in pig diet formulation, ideal protein should be expressed based on available, rather than total amino acid levels in the diet (Tuitoek et al., 1997a). Research carried out by Tuitoek et al. (1997a, b), shows that the N excretion could be reduced by close to 40% by varying the AA balance in a corn-soybean diet fed to growing pigs. Dropping crude protein levels along with supplementation of amino acids in an ideal protein ratio shows significant reductions in Nitrogen excretion. Sutton et al. (1999) reported a reduction in total N in manure by 42% by reducing crude protein levels from 18 to 10% crude protein with synthetic amino acids. Reducing the crude protein in practical diets from 21 to 14% crude protein plus synthetic amino acids in growing diets (pigs between 35 and 65 kg) and from 19 to 13% crude protein plus synthetic amino acids in finishing diets (pigs between 65 and 95 kg) reduced N excretion by 40% (Hobbs et al., 1996).

3.5.1b.ii Phase feeding

Phase feeding refers to feeding programs that match the animal's nutrient requirement as the animal's age/size changes. In the U.S., the common practice is to feed a grower diet (20-60kg) and a finisher diet (60-110 kg). In calculations using distinct grower (30-60 kg) and finisher (60-100 kg) diets, total N excretion was reduced by 10-14% (Table 3.4) (Koch, 1990 as cited by Honeyman, 1993). Sutton et al. (1999) cite an experiment carried out by Boisen et al. (1991) in which N excretion was reduced by 4.4% through the use of phase feeding. This concept can be applied more thoroughly by using a variety of diets to match closely the nutrient requirements of each growth phase.

Table 3.4: The effect of phase feeding on nitrogen excretion (Honeyman, 1993)

		Two phase		
	Single phase	Grower	Finisher	Two phase overall
Crude Protein, %	16	16.5	14	14.9
Feed conversion (intake/gain)	3	2.5	3.3	3.6
Feed intake/period (kg)	210	75	132	207
N intake (kg)	5.38	1.98	2.95	4.93
N excretion (kg)	3.48	1.16	1.86	3.02

3.5.1c Zeolite

According to Mumpton and Fishman (1977) zeolites are crystalline, hydrated aluminosilicates of alkali and alkaline earth cations that possess infinite, three-dimensional crystal structures. The oxide empirical formula of zeolite is $M_{2/n}O \cdot Al_2O_3 \cdot xSiO_2 \cdot yH_2O$, where M is any alkali or alkaline earth cation, n is the valence of that cation, x is a number from 2 to 10, and y is a number from 2 to 7. They are further characterized by an ability to lose and gain water reversibly and to exchange some of their constituent cations without major change of structure (Figure 3.3).

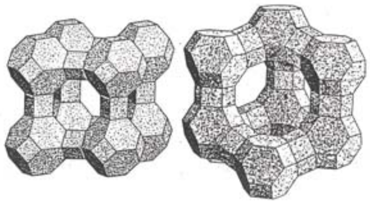

Figure 3.3: Arrangements of truncated cubo-octahedron (sodalite) units to enclose large central cavities (cages). Left = sodalite unit connected by double 4-rings of oxygen in the structure of synthetic zeolite A. Right = sodalite units connected by double 6-ring of oxygen in structure of faujasite and synthetic zeolites X and Y (Mumpton and Fishman, 1977)

The large cavities and entry channels of zeolites are generally filled with water molecules so that hydration spheres form around the exchangeable cations. If the water is removed (heating zeolite for several hours or overnight at 350 to 400°C) molecules having effective cross-sectional diameters small enough to fit through the entry channels are readily adsorbed on the inner surfaces of the dehydrated central cavities. Molecules too large to fit through the entry channels are excluded and pass around the outside of the zeolite particle, giving rise to the well-known “molecular sieving” property of most crystalline zeolites (Figure 3.4) (Mumpton and Fishman, 1977).

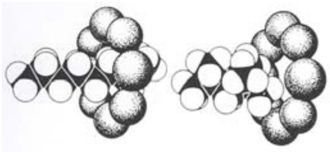

Figure 3.4: Illustration of molecular sieving properties of zeolite (Mumpton and Fishman, 1977)

An important characteristic of zeolites is cation-exchange capacity (CEC), which is a measure of the number of counterions present per unit weight or volume of the zeolite and represents the number of cations available for exchange. Crystalline zeolites are some of the most effective cation exchangers known, commonly having capacities of 2 to 3 meq/g, twice that of bentonite clays. This high cation-exchange capacity is the most important property in agricultural processes (Mumpton, 1984). Clinoptilolite, a species of zeolite, is probably the most abundant zeolite in nature and has found many applications in agriculture because of its attractive properties, its wide geographic distribution, its wide geographic distribution, and the high-grade and large-size nature of many of its deposits (Sheppard, 1984). The chemical formula of clinoptilolite is $(Na_4K_4)(Al_8Si_4O_{96})\cdot 24H_2O$ and the total cation exchange capacity has been reported to be about 2.3 meq/g (Mumpton and Fishman, 1977). Semmens (1984) reported values between 1.75 and 2 meq/g. The cation selectivity for clinoptilolite is K^+, $NH_4^+ > H^+ > Na^+ > Sr^{2+} > Ca^{2+} > Mg^{2+} > Li^+$ (Huang and Petrovic, 1994). It can be seen that clinoptilolite has a high selectivity for the ammonium ion. The addition of clinoptilolite to feed is assumed to have a similar effect to that of antibiotics, as the clay mineral is able to bind 135 meq ammonium equivalent to 1.89 g nitrogen per 100 g clinoptilolite (Poulsen and Oksbjerg, 1995). This selectivity may result in a more gradual release of ammonia (Huang and Petrovic, 1994) following the breakdown of ingested protein and hence lead to more efficient utilization of this nutrient (Mumpton and Fishman, 1977).

The slow release properties of zeolite have been taken advantage of in horticultural applications. It was reported by Hershey et al. (1980) that potassium released from a K-clinoptilolite-amended potting medium indicated that this zeolite behaved like a slow-release K fertilizer (and probably NH_4^+ as well). This slow release property could be advantageous when feeding zeolite to animals since it could allow more time for the animals to more efficiently utilize ingested nutrients for growth.

Research involving agricultural applications of zeolite is still in its infancy. Most of the initial research fist took place in Japan in 1960's, therefore information is limited. Zimerman (1996) found that both nitrogen and phosphorus concentrations in the feces of clinoptilolite fed pigs (at the 0, 2, 4 and 8% level) decreased with increasing supplementation concentrations. It was also noticed from this experiment that the ratio of nitrogen to phosphorus increased with increasing dietary clinoptilolite concentrations. The relationship was found to be highly significant and linear suggesting that clinoptilolite sequestered nitrogen within the feces but had no effect on phosphorus. Cool and Willard (1982) conducted an experiment feeding clinoptilolite of 95% purity as a dietary supplement for swine. They found a 34% increase in weight gain-to-feed ratio. Shurson et al. (1984) fed zeolite A (a type of synthetic zeolite) and clinoptilolite of 85 ± 5% purity to growing pigs and found that daily N retained increased as increasing amounts of zeolite A were fed, and net protein utilization increased with increasing levels of zeolite A and clinoptilolite in the feed (Table 3.4). In an experiment carried out by Pond et al. (1988) it was concluded that the addition of 2% clinoptilolite of 90 ± 5% purity to the diets of growing swine improved weight gain. Smaller relative liver and kidney weights of animals fed supplemented diets may have been a response to decreased quantities of NH_4^+ ion and other metabolites absorbed from the gastrointestinal tract for processing, which allowed utilization of a greater percentage of ingested nutrients for growth of non-visceral tissues. Poulsen and Oksbjerg (1995) fed Klinofeed (70% clinoptilolite content) to growing pigs (30-50 kg) and found that Klinofeed elevated nitrogen excretion in faeces and lowered nitrogen excretion in urine. However, the total N excreted was reduced by 6.5% and 2%, respectively, when feeding the pigs basal diet A and B supplemented with Klinofeed.

Table 3.5: Effects of Adding 0, 1, 2, 3% Zeolite A (trial 3) or 0, 2.5, 5.0, 7.5% clinoptilolite of 85 ± 5% purity (Trial 4) to starter diets on nitrogen balance[a] (Shurson et al., 1984)

	Trial 3					Trial 4				
Nitrogen	Level of zeolite A, %					Level of Clinoptilolite, %				
Variable	0	1	2	3	MSE[b]	0	2.5	5	7.5	MSE[b]
Daily N retained, g	4.71	5.77	5.84	6.02	1.64	5.35	5.03	5.25	4.77	0.26
Net protein util.[de], %	58.7	63.3	63	62.7	20.5	66.3	65.7	65.8	61.2	6.4

[a] All values presented are mean values from four pigs assigned to each treatment group

[b] MSE = mean square error.

[d] Net protein utilization, % = 100(N balance ÷ N intake).

[e] Significant linear reduction (P<.05) in trial 4.

Mumpton and Fishman (1977) refer to an experiment done by Kondo and Wagai (1968) were the use of zeolites were evaluated using young and mature Yorkshire pigs in 60-day and 79-day experiments, respectively. They found a 25 to 29% increase in weight gain in animals of both ages receiving diets containing 5% clinoptilolite versus animals receiving normal diets. Feed efficiencies were also about 35% greater in animals receiving zeolite than those of normal rations when fed to young pigs, but only about 6% greater when given to older animals. In addition, the digestive process was more thorough when zeolites were added to the diet because the particle size of the feces of the control group was noticeably coarser than that of the experiment group. The feces of the animals in the control group were also richer in all forms of nitrogen than zeolite-fed animals, indicating that zeolite contributed towards a more efficient conversion of feedstuff nitrogen to animal protein.

In the experiment conducted by Shurson et al. (1984) in general as increasing levels of zeolite A and clinoptilolite were fed to the pigs mineral retention was decreased as increasing amounts of zeolite A or clinoptilolite were fed. However in the clinoptilolite group, phosphorus mineral retention was greatest in pigs supplemented with 2.5% clinoptilolite. Also, Potassium mineral retention was greatest in pigs supplemented with 5.0% clinoptilolite, within the clinoptilolite group (Table 3.6).

Table 3. 6: Percentage mineral retention[a] in pigs supplemented 0, 1, 2, 3% Zeolite A (Trial 3) or 0, 2.5, 5.0, 7.5% clinoptilolite of 85 ± 5% purity (Trial 4) in starter diets (Shurson et al., 1984)

	Trial 3						Trial 4					
	Level of zeolite A, %				Significance[bc]		Level of Clinoptilolite, %				Significance[bc]	
Mineral	0	1	2	3	MSE[d]	P value	0	2.5	5	7.5	MSE[d]	P value
Phosphorus	61.7	55.3	55.2	44	24.6	0.01	55.7	59.3	50.4	47.8	26.1	0.05
Potassium	54.4	52.3	47.7	45	9.6	0.01	47.4	44	48.3	42.7	29.1	NS

[a] All values presented are mean values from four pigs assigned to each treatment group

[b] Probability values indicate significant linear reductions at the level shown

[c] NS = not significant (P>.10).

[d] MSE = mean square error.

3.5.2 Stimulation of practical solutions at the farm level

All of the recommendations for stimulation of practical solutions at the farm level were concerned with odour reduction. Sources of odour have been identified as the animal facilities, manure storage facilities, and land application procedures. According to Miner (1999) one of the more frequent sources of odour complaints is the manure storage/treatment system (particularly anaerobic storage systems). Another major odour emission source is the sprinkler or nozzle that is used to distribute liquid manure as part of land spreading operations. Also, liquid manure on the surface of the ground continues to emit odour until it dries or it is absorbed by the soil. Practical solutions are given by Miner (1999) and are as follows:

There are several options available to producers in order to control anaerobic lagoon odour. For example, enclosed anaerobic digesters can reduce organic content by 90% while producing a biogas that can be converted to electricity. Permeable covers for lagoons are also available which greatly decrease odours.

Field application of manure by injecting manure directly into the soil is another possibility for producers to reduce odours. This can be done instead of pumping dilute liquid manure through a high-pressure sprinkler which causes significant escape of manure odorants to the air due to the spraying surface area created.

Building odour control can be achieved through the use of slotted floors, flushed gutters and fill and dump tanks are among the possibilities. Flushed buildings and the fill and dump under-floor storage tanks (pit recharge system) are a special concern if recirculated water is being used for flushing. When water is recycled from a lagoon, the water may have a sufficient concentration of odourous gasses itself. Under these conditions, it may be necessary to aerate or otherwise deodorize the lagoon water (Miner, 1999).

3.5.3 Physical treatment of animal manure to reduce nutrient losses

3.5.3a Solid-liquid separation

The most common way to physically treat animal manure is to separate the solid fraction from the liquid fraction. According to Zhang and Westerman (1997) effective solid-liquid separation that is capable of removing a substantial amount of organic solids from fresh liquid or slurry manure will potentially offer the benefits of production of nutrient-rich organic solids (reducing the amount of nutrients in the liquid fraction of the manure), odour reduction in anaerobic lagoons, and improvement in the economics of subsequent liquid manure treatment processes due to reduced organic loading rates on an annual basis. The separated solids can be utilized on nearby intensive crop farms.

3.5.3b Mechanical separation

Screening and centrifugation are the primary means of mechanical separation. The maximum total solids separation efficiency for the liquid or slurry manure by physical separation is in the range of 48 to 70% (Table 3.7).

Table 3.7: Performance of Mechanical Separators on Swine Manure (Zhang and Westerman, 1997)

Separation technique	Screen opening (mm)	TS in raw manure (%)	Separation Efficiency (%)					TS in solids (%)	Liquid flow rate (L/min)
			TS	VS	COD	TKN	TP		
Stationary Screen	1.5	0.2-0.7	9	-	24	-	-	6	235
	1	0.2-0.7	35	-	69	-	-	9	123
	1	1.0-4.5	6-31	5-38	0-32	3-6	2-12	5	-
Vibrating Screen	1.7	1.5	3	-	6	-	-	17	37-103
	0.841	1.5-2.9	10	-	1-14	-	-	18-19	15-103
	0.516	1.8	27	-	24	-	-	20	37-57
	0.516	3.6	21-52	25-55	17-49	5-32	17-34	9-17	38-150
	0.39	0.2-0.7	22	28	16	-	-	16	67
	0.44	1-4.5	15-25	18-38	13-26	2-5	1-15	13	-
	0.104	3.6	50-67	54-70	48-59	33-51	34-59	2-8	38-150
Rotating Screen	0.75	2.5-4.12	4-8	-	4	-	-	16-17	80-307
	0.8	1-4.5	5-24	9-31	2-19	5-11	3-9	12	-
Belt Press	0.1	3-8	47-59	-	39-40	32-35	18-21	14-18	-
Centrifuge	-	1-7.5	15-61	18-65	7.8-44	3.4-32	58-68	16-27	-

TS = Total Solids
VS = Volatile Solids
COD = Chemical Oxygen Demand
TKN = Total Kjeldahl Nitrogen
TP = Total Phosphorus

3.5.3b.i Sloping stationary screen

The sloping stationary screen (Figure 3.5) has an inclined screen mounted where manure (liquid/slurry) is delivered to the top edge. The solid fraction (not large enough to pass through the screen) rolls down the incline and is collected. The liquid fraction passes through the screen and is collected as well (Zhang and Westerman, 1997). Chastain et al. (2001a) found that an inclined stationary screen removed 61% of the total solids (TS), 63% of the volatile solids (VS), 67% of the chemical oxygen demand (COD), 49.2% of the total kjeldahl nitrogen (TKN), 52% of the organic-N, 53% of the total phosphorous, and 51% of the total potassium from flushed dairy manure. More performance characteristics of the sloping stationary screen are given in Table 3.7.

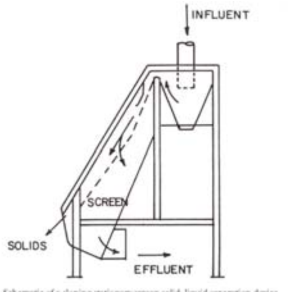

Figure 3.5: Sloping Stationary Screen (Miner et al., 2000b)

5.3.3b.ii Vibrating screen

The liquid/slurry manure is brought to the center of the vibrating screen (Figure 3.6). The vibrating motion moves particles across the screen that are not large enough to pass through. These particles eventually get moved off to the side where they are collected. The liquid portion flows through and is collected (Zhang and Westerman, 1997). Performance characteristics of the vibrating screen are shown in Table 3.7.

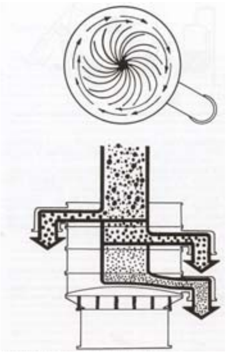

Figure 3.6: Vibrating Screen Solid-Liquid Separator (Miner et al., 2000b)

3.5.3b.iii Centrifuges/hydro-cyclones

The sloping stationary screen and vibrating screen are out-dated pieces of equipment, but may still be found on farms. Today, centrifuges/hydro-cyclones are used more frequently as a means of mechanical separation. Centrifuges and hydro-cyclones cause separation between liquid from solid using centrifugal force. There are horizontal and vertical centrifuges.

A horizontal decanter centrifuge (Figure 3.7) uses a closed cylinder of continuous turning motion. The centrifugal force separates liquids and solids on the wall in two layers. An auger, turning at a slightly higher speed than the cylinder moves the solids to the conic part where they are discharged. Liquids leave at the other end of the cylinder (Zhang and Westerman, 1997). Performance characteristics of the vibrating screen are shown in Table 3.7.

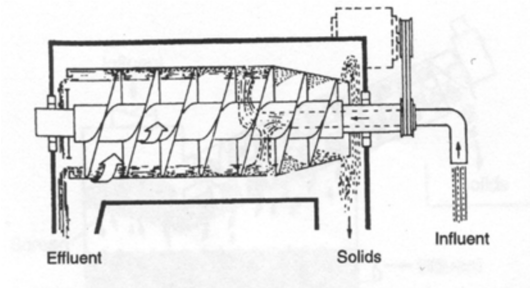

Figure 3.7: Horizontal decanter centrifuge (Zhang and Westerman, 1997)

In a hydro-cyclone (Figure 3.8), manure slurry is pumped tangentially through the inlet near the top and a strong swirling motion of the liquid, developed as a result, will accelerate the gravity settling of solid particles to the bottom/apex of the cone. The liquid is discharged through a cylindrical tube fixed in the center of the top (Zhang and Westerman, 1997).

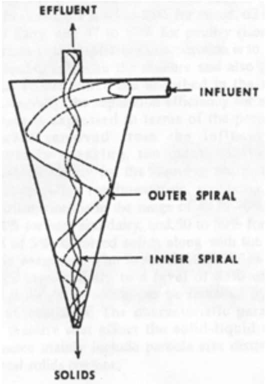

Figure 3.8: Hydro-cyclone (Zhang and Westerman, 1997)

3.5.3b.iv Presses

The separated solids, solid cakes, generated from the above methods usually have a moisture content too high (85-95%) to be piled for composting purposes. Therefore presses are used to further dewater solid cakes.

Presses use the principle of pressurizing solids with rollers or screws against an opposing screen or a perforated belt, through which the liquid is removed. There are three basic types of presses. The roller press uses two concave screens and a series of brushes and rollers (Figure 3.9).

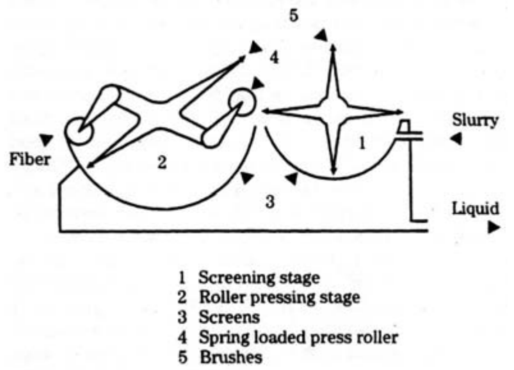

Figure 3.9: Roller press (Zhang and Westerman, 1997)

The slurry is brought to the first concave screen where it is delivered by the brushes to the second screen where rollers squeeze the slurry against the screen. The belt press uses a flat, woven fabric belt that runs horizontally between two rollers. The liquid is squeezed through the belt and collected, the solids continue along the belt where they are dropped off and collected. The screw press (Figure 3.10) uses a central screw conveyor housed in a cylindrical screen. The screen is used to retain the solids in the manure slurry which is pumped into the screen chamber and the screw is used to convey the solids to the discharge chute (Zhang and Westerman, 1997).

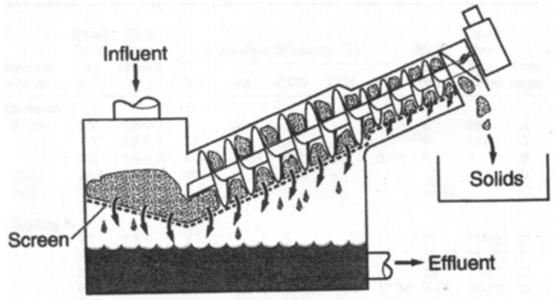

Figure 3.10: Screw press separator (Zhang and Westerman, 1997)

During the transport, the solids are compacted and dewatered. Chastain et al. (2001b) conducted research on the removal of solids and major plant nutrients from swine manure using a screw press separator and concluded that a screw press would be expected to remove 14.9% of the TS, 19.6% of the VS, 9.2% of the TKN, 16.0% of the organic-N, and 14.8% of the TP added to a typical pit-recharge swine building. More performance characteristics of presses are given in Table 3.7.

3.5.3c Chemical treatment

The purpose of chemical treatments to manure is to increase the particle size through flocculation so that separation efficiency can be increased. Separation efficiency can be improved significantly (from between 48 to 70% to a level of 85% or higher) by pre-treating manure using chemical treatments. Chemical treatment of wastewater involves the addition of chemicals to alter the physical state of dissolved and suspended solids to facilitate removal by physical separation processes (Zhang and Westerman, 1997). The chemical treatment can be performed either as a continuous process in manure transport pipelines where the chemicals are added and mixed into the manure continuously or as a batch process in a mixing tank where the chemicals are added and mixed into the manure in batches. Processes involved in chemical treatment are chemical precipitation, particle coagulation, and flocculation.

Chemical precipitation is the formation of insoluble precipitate through the chemical reactions between the dissolved ions in the wastewater, and is mostly used for removal of dissolved phosphorus. The most commonly used chemicals include chloride or sulfate salts of these metals. Besides forming precipitates with dissolved phosphorus, these chemicals also induce coagulation of suspended particles.

Coagulation is the destabilization of colloidal particles by neutralizing their surface charges to form small visible flocs.

Flocculation is the further agglomeration of coagulated particles upon addition of a polyelectrolyte which absorbs the particles in the liquid and bridges the particles to allow them to form large flocs. Natural polymers, such as modified starches and chitoson and synthetic polymers, such as the polymers derived from polyacrylamide (PAM) are available as flocculants.

When combined with a settling basin and the addition of 300 mg/L PAM with 60 min of settling, Chastain et al. (2001a) found total solids separation improved from 61% to 92% and phosphorus removal increased from 53% to 86%. Several experiments have also been carried out using limestone dust to precipitate solids from swine manure. Worley and Das (2000) observed that adding alum (aluminum phosphate) resulted in 75% phosphorus, 20% nitrogen, and 8% potassium removal from a settling basin with a solution of recirculated lagoon effluent and fresh swine waste. Barrington et al. (2004) concluded that fine limestone dust had the potential to effectively precipitate up to 96 and 90% of the total phosphorus (TP) and total solids (TS) of high TS swine manure (7.4%), without significantly altering pH. In another experiment conducted by Barrington et al. (2002) the incorporation of limestone dust to swine manure concentrated 90% of the TS and TP into a sludge representing 45% of the initial mass.

3.5.3d Anaerobic treatment

Anaerobic treatment is one of the most common processes in wastewater treatment and has found applications to the treatment of livestock manure. According to McLean (1995), anaerobic digestion is the breakdown of organic matter by the coordinated activity of a number of microbial populations, in the absence of oxygen, to methane and carbon dioxide.

The anaerobic process functions optimally over two temperature ranges, the mesophilic (30-38^{o}C) and the thermophilic (55-60^{o}C). According to Miner et al. (2000c) Thermophilic digestion is more rapid than mesophilic digestion and can therefore be conducted in a smaller tank (Table 3.8). Anaerobic digestion can also occur at low temperatures, below 35^{o}C, and is called psychrophilic.

Table 3.8: Hydraulic retention time (days) for well mixed –anaerobic digesters operated at various temperatures (Miner et al., 2000c)

Temperature (^{o}C)	Hydraulic retention time (days)
55-60	10-15
35-38	30
20-25	60-90

Most anaerobic conversion processes operate optimally at a pH close to neutrality (6-8). When the rate of acid generation exceeds the rate of breakdown to methane, a process imbalance results in which pH, gas production rate and methane concentration fall. Therefore controlling pH ensures methane generation and it is desirable to have sufficient alkalinity in the influent to buffer anaerobic systems. If the buffer capacity is inadequate lime, sodium hydroxide or sodium bicarbonate must be supplied.

Sufficient macro-nutrients are required for bacterial growth. Nitrogen and Phosphorus are especially important macro-nutrients, and a chemical oxygen demand:nitrogen:phosphorus ratio of 100:10-1:5-1 is recommended. According to Miner et al. (2000c) livestock manure is a plentiful source of these macro-nutrients. Other trace elements such as nickel, cobalt, iron and manganese are also important.

Anaerobic treatment usually occurs in an anaerobic digester, which is an enclosed tank that excludes oxygen through which manure is passed and is subjected to anaerobic digestion. Conventional digesters used for animal wastewater treatment include continuously stirred-tank reactors (CSTR) and plug-flow reactors (Zhang et al. 2000). Anaerobic lagoons are also extensively used on farms for animal wastewater treatment.

3.5.3d.i Continuously Stirred Tank Reactor (CSTR)

The completely mixed or continuously stirred tank reactor (CSTR) consists of a stirred tank into which there is a feed of reacting material entering (collected from a flush system for swine manure) and from which there is a discharge of partially reacted material. Upon entering the reactor, the feed fluid is almost instantaneously mixed with the fluid already present, and the reactor contents are uniform throughout the entire reactor volume. As a result of the mixing, the composition of the discharge stream is the same as that of the contents in the reactor. The mixing in the CSTR is extremely important, and it is assumed that the fluid in the reactor is perfectly mixed. In practice, perfect mixing can be obtained if the mixing is sufficient and the liquid is not too viscous. If the mixing is inadequate, there will be bulk streaming between the inlet and the outlet, and the composition of the reactor contents will not be uniform (Reynolds and Richards, 1996).

These types of digesters work best with a manure solids content of 3-10% solids. Manure is processed in a heated tank above or below ground. A mechanical gas mixer is necessary to keep the solids in suspension.

3.5.3d.ii Plug flow digester

The plug flow reactor is non-mixed and the influent passes through a set of baffles or trenches (Chynoweth et al., 1999). New influent is added to the digester, which pushes older material through to the discharge end (Figure 3.11) and a cover is generally employed in order to trap biogas which accumulates. Plug flow digesters are typically rectangular in cross section and have length-to-width ratios of approximately 10:1 and are generally used to handle influent with a solids content of 8 to 12% (Miner et al., 2000c). They are generally built to serve smaller operations in which mixing and heating equipment would add significant additional costs to the digester.

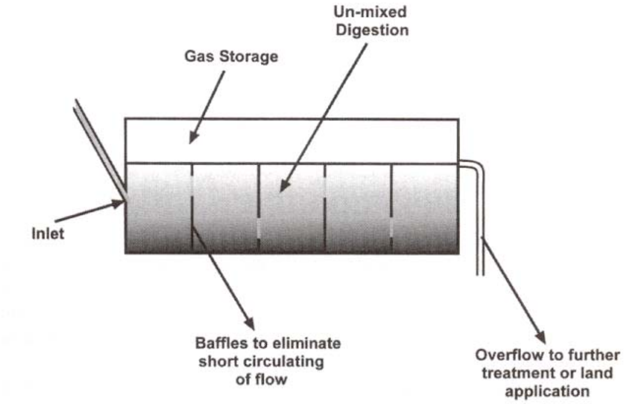

Figure 3.11: Plug flow anaerobic digester (Miner et al., 2000c)

3.5.3d.iii Anaerobic lagoons

Anaerobic lagoons (Figure 3.12) were fist built to receive the liquid manure flushed or scraped from livestock confinement buildings and to retain that manure until the manager of the operation could apply it to crop-or pastureland. However it was discovered that when it was time to apply the manure to crop-or pastureland, the manure changed in quality over time (solids decreased significantly and a decrease in nitrogen and phosphorus quantities were also noticed). According to Miner et al. (2000c), the anaerobic digestion process in a lagoon is essentially the same as what happens in

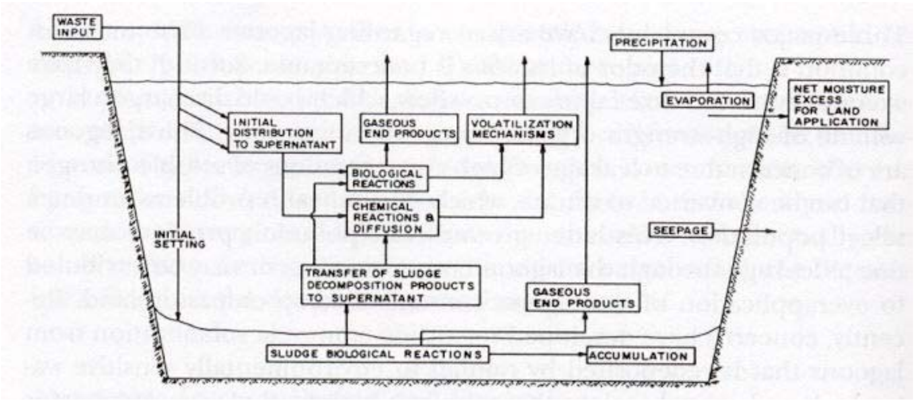

Figure 3.12: Anaerobic Lagoon Storage (Miner et al., 2000c)

digesters, except there is no temperature control. The rate depends upon the climate of the lagoon location. Thus, in colder climates (<5°C), anaerobic digestion essentially ceases. This means that organic material that flows into the lagoon during this time is stored but very little treatment other than sedimentation occurs. Both soluble and particulate organic material accumulates. As the temperature increases (>5°C), activity becomes more intense until the backlog of accumulated organic material is processed. It is during this warming period that anaerobic lagoons are most likely to evidence odor problems because there is a more heavily loaded situation since the routine waste load is augmented by the material that was stored during the cold period. Impermeable covers can be placed on top of lagoons which traps gas produced during decomposition of the manure.

3.5.3e Aerobic treatment

Aerobic treatment is a process whereby aerobic bacteria use dissolved and suspended organic matter as a source of energy to produce additional bacterial mass and to conduct normal biological functions (Miner et al., 2000d). Aerobic bacteria require the presence of dissolved free oxygen to sustain their metabolic processes. This type of treatment is common in the municipal wastewater field, and has been applied to livestock waste treatment. The costs involved in maintaining an adequate oxygen supply have turned most livestock producers away from this treatment option. However due to the environmental issues facing livestock producers today aerobic treatment is viewed as a potential supplement to anaerobic digestion for reducing odour, ammonia volatilization, and as a component in the process to achieve an effluent suitable for discharge. From an experiment carried out by Luo et al. (2001) it was found that when the treatment of swine manure consisted of an anaerobic phase followed by an aerobic treatment phase 76% of the total phosphorus (TP) was removed while increasing the pH of the manure from 7.5 to 8.5. Aerobic treatment is also used to reduce nitrogen concentration by denitrification in anaerobic reactors that have alternating aerobic and anaerobic conditions (Miner et al. 2000d). Burton (1994) reported that when aerobic treatment to pig slurry was applied, treatment was inhibited at temperatures greater than 47^{o}C and at temperatures lower than 10^{o}C. N removal by aerobic treatment happens through the dentirification process however, the P and K in the manure would remain. According to Miner et al. (2000d) there are two basic types of anaerobic treatment: fixed film processes and suspended growth processes (activated sludge).

3.5.3e.i Aeration process

An outside source of oxygen is essential for aerobic treatment processes since oxygen is only slightly soluble in water (7 to10 mg/L) and organic matter content in liquid animal manure is very high. Miner et al. (2000d) reviews two types of aeration systems: diffused aeration in which air is blow in small bubbles into the wastewater, and mechanical aeration in which an aerator is installed that beats, pumps, throws, or otherwise creates a large surface area of wastewater in contact with the air so that oxygen can be absorbed to replace that consumed by aerobic bacteria as they metabolize the soluble organic wastes. In addition to supplying the necessary oxygen to maintain the aerobic process, aeration equipment provides mixing of the material.

3.5.3e.ii Trickling filter

The trickling filter (Figure 3.13) is an example of a fixed film process commonly used in agriculture. In this treatment system stones are contained in a cylindrical tank (reactor) with air vents along the outside which provide aeration. Wastewater with dissolved organic matter is passed over the stones. The stones develop a covering layer of bacteria that feed on the organic matter contained in subsequent wastewater waves that come along in cycles. Since the air vents along the outside of the reactor provide aeration, the bacteria have the oxygen they require as well as food from the organic matter contained in the wastewater. Eventually, the bacteria die and the layer developed on the stones is sheared off by waste wastewater waves and the process begins over again. The treated wastewater discharges to a settling basin where the solids settle and are removed for alternate treatment, usually aerobic (Miner et al. 2000d). There is debate over the applicability of this technology for nutrient removal. Barnes (1995) states that this technique is not applicable to the achievement of nutrient removal while Miner et al. (2000d) states that 75 to 90% of the applied organic matter can be removed by the trickling filter.

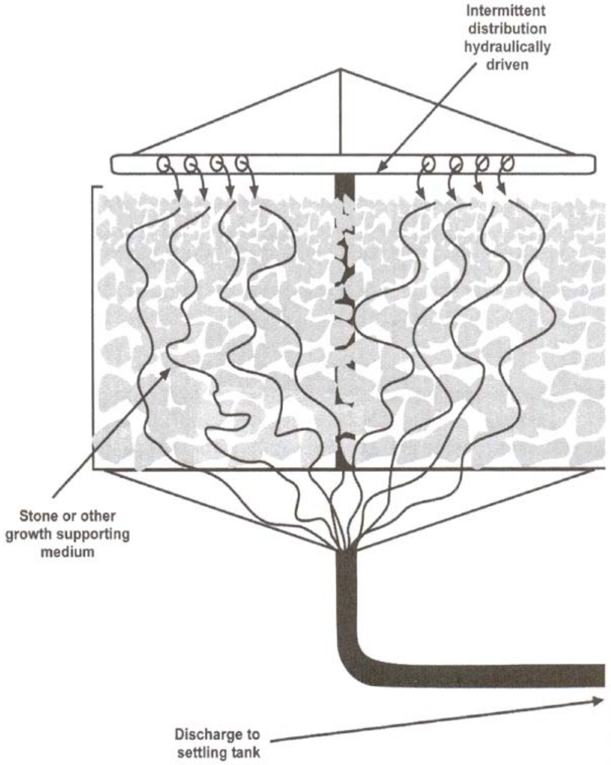

Figure 3.13: Schematic of a fixed film aerobic treatment process (Miner et al., 2000d)

3.5.3e.iii Activated sludge (suspended growth)

Activated sludge systems differ from tickling filters in that the aerobic bacteria, which decomposes organic matter, is not fixed to any surface but is rather suspended in the wastewater that it is treating. Biomass, containing aerobic bacteria, is added to incoming wastewater which is sent to an aeration tank where it is held for a certain amount of time to ensure suitable contact time with the wastewater. After the mixture has spent a sufficient amount of time in the aeration tank it goes to a sedimentation tank where the biomass (activated sludge) is separated from the effluent and is returned to the beginning of the aeration tank to continue the process. Each time the activated sludge goes through the process, a build of biomass occurs. Therefore, to avoid overloading the system with activated sludge, an amount equal to each day's net growth must be drawn off, treated and disposed of to maintain an optimal concentration of aerobic bacteria (Barnes, 1995; Miner et al., 2000d). This process has a continuous influent and effluent flow.

3.5.3f Sequencing Batch Reactors (Combined Aerobic/Anaerobic Processes)

For the purposes of nutrient removal most of the treatment of agricultural wastes and wastewater treatment technologies involve combined anaerobic/aerobic phases. Chynoweth et al. (1999) describe the nutrient removal process as follows: for nitrogen removal, ammonia nitrogen resulting from metabolism of nitrogenous organic compounds must be oxidized aerobically after which nitrogen may be removed anaerobically by denitrification. This is accomplished by recycle of aerobic effluent back through an anaerobic denitrification process. Biological removal of phosphorus is sometimes accomplished by the use of anaerobic pre-fermenters which produce volatile acids which then enhance uptake of phosphorus by bacteria in subsequent aerobic operations. This may be accomplished in a sequencing batch reactor (SBR) which has the capability to alternate between aerobic and anaerobic conditions. Since SBRs have this ability to alternate in a cyclic fashion, oxidation of ammonia nitrogen is enhanced and a reduction of nitrates is achieved (Fernandes at al., 1991). According to the Environmental Protection Agency (1999) the SBR works in the following manner: wastewater enters a partially filled reactor (tank), containing biomas. Once the reactor is full it behaves like a conventional activated sludge system (described in the previous section, 3.5.3) but without a continuous influent or effluent flow. The aeration and mixing is discontinued (anaerobic phase) after the biological reactions are complete, the biomass settles, and the treated supernatant is removed. SBRs have gained wide acceptance for removing biochemical oxygen demand and nutrients from wastewaters and is also gaining popularity in the treatment of swine wastes (Lee et al., 1997).

Fernandes at al. (1991), conducted laboratory experiments with screened liquid manure on a sequencing batch reactor having aerobic/anaerobic cycles and concluded that 99% of the ammonia nitrogen, 93% of the total Kjeldahl nitrogen (TKN), 97% of the chemical oxygen demand (COD) and 97% of the Suspended Solids (SS) removal were achieved during the treatment. Obaja et al. (2004) also found exceptional nutrient removal rates using an SBR and found 99.8% of N and 97.8% P removal of piggery wastewater. A total nitrogen and phosphorus removal of 90% and 89%, respectively on swine wastewater, were achieved by Lee et al. (1997) when supplementing acetate and fermented swine waste were supplemented as organic matter. A control reactor receiving no supplementation achieved total nitrogen and phosphorus removals of 76% and 15%, respectively.

3.5.4 Transgenic pig

A transgenic (or genetically modified) animal is one whose genome contains DNA of exogenous origin that has been introduced through experimental manipulation (Jacenko, 1997 as cited by Van Reenen et al. 2001). Most of the work on environmentally friendly transgenic pigs has been carried out by the University of Guelph, conducting studies on the phosphorus utilization capabilities of transgenic pigs (called Enviropigs^{TM}) that synthesize phytase in their salivary glands.

Forsberg et al. (2003) cite work done by Golovan et al. (2001) on the true digestibility of dietary P in soybean meal as the source of P for weanling and growing-finishing pigs from the G1 generation of one line (WA line) of transgenic pigs. It was found that the transgenic pigs were able to digest 88 and 99% of the dietary P, respectively, compared with non-transgenic pigs that only digested 49 and 52% respectively. Fecal material from the weanling and growing-finishing transgenic pigs contained a maximum of 75 and 56% less P, respectively, than that of non-transgenic pigs fed the same diet. Unpublished data from the University of Guelph (2004), supports these findings. Upon studing several lines of Enviropigs^{TM} in more detail it was found that they produce sufficient phytase to digest practically all of the phytate in a cereal grain diet. Also, phosphorus in feces from young grower pigs not supplemented with phosphate was reduced by 75% while that in finisher pigs was reduced by 56 to 67% when fed diets not supplemented with phosphate.

CONNECTING TEXT

The use of dietary supplements is a nutrient reduction option available to hog producers with large operations and limited land base to apply their manure. Very little research has been done on characterizing zeolite to determine its suitability as a feed additive for swine. In order for zeolite to be considered feasible as a dietary supplement for reducing nutrients in swine manure it must have a high affinity for NH_4^+ and must desorb other minerals while inside the stomach of the pig, namely heavy metals in toxic amounts. Furthermore, if producers are going to use zeolite, it is desirable to use a product which has favourable handling characteristics. Therefore, the following paper investigates chemical and physical properties of different types of zeolite to determine which zeolite posses the most favourable adsorption, desorption and handling characteristics in terms of a dietary supplementation for swine.

IV. EFFECT OF PHYSIO-CHEMICAL PROPERTIES OF CLINOPTILOLITE ON ITS PERFORMANCE AS A FEED ADDITIVE FOR SWINE

4.1 Introduction

The agriculture industry, particularly the swine industry, is facing stricter regulations due to increasing concern over the adverse environment impacts of its manures, such as the build up of nitrogen and phosphorus in soil and water. Zeolite is a natural feed additive which, recently has been proven to improve nutrient digestion in animals, thus reducing manure nutrient content and therefore reducing these impacts. Clinoptilolite is the most appropriate zeolite for this purpose because of its specific physical and chemical properties and abundance around the world, ensuring availability at low costs (Torracca et al., 1998).

Zeolites are aluminosilicates with a three dimensional framework structure bearing AlO_4 and SiO_4 tetrahedra. The tetrahedra are linked together by oxygen molecules, forming interconnecting cages and channels (Englert and Rubio, 2004). Zeolites are mostly found in specific types of sedimentary rocks (tuffs) in the form of small crystals (0.1-100 μm) associated with clays, other silicate and aluminosilicate phases of similar density.

Clinoptilolite is a species of zeolite that has a relatively ‘open’ structure with a total pore volume of approximately 35% (Godelitsas and Armbruster, 2003) and its chemical formula according to Mumpton and Fishman (1977) is $(Na_4K_4)(Al_8Si_4O_{96})\cdot 24H_2O$. Their three-dimensional aluminosilicate framework contains narrow four- and five- membered rings constituting intra-framework micro pores or channels capable of hosting extra-framework/exchangeable cations (e.g. Na^+, K^+, Ca^{2+}) in association with mobile H_2O molecules (Godelitsas and Armbruster, 2003). The crystals of clinoptilolite accommodate two different systems of micro pores interconnected within the lattice, the first has both eight- and ten-membered rings forming A- and B- type channels (3.3X4.6 and 3.0X7.6 Å, respectively), and the second forms eight-membered rings forming C-type channels (2.6X4.7 Å). Clinoptilolites are also further characterized by having a Si/Al ratio of greater than 4 (Perraki and Orfanoudaki, 2004). Çulfaz and Yağiz (2003) reported a Si/Al ratio of between 4 and 5.5 for clinoptilolite.

These channels give rise to the well-known "molecular sieving" property of zeolites. Molecules having effective cross-sectional diameters small enough to fit through the channels are readily adsorbed on the inner surfaces. Molecules which are too large to fit through the channels are excluded and pass around the outside of the zeolite particle (Mumpton and Fishman, 1977). Contained within the channels are mobile water molecules and exchangeable cations such as NH_4^+, Na^+, K^+, and Ca^{2+}.

The physical structure of clinoptilolite allows for enhanced sorption properties towards gases and cations. Clinoptilolite has the ability to adsorb molecules such as ammonia, dinitrogen, carbon monoxide, and methane which are small enough to enter their channels. Clinoptilolite is also currently being used to adsorb H_2S, SO_2, CO, N_2 and CH_4 (Cincotti et al., 2003). The cation-exchange capacity (CEC) of clinoptilolite can theoretically reach 330 meq/100 g. Due to this high CEC, clinoptilolites are excellent binding agents for cations dissolved in aqueous solutions. Langella et al. (2000) tested the adsorption capability of clinoptilolite for environmental contaminants and found its cation selectivity to be $NH_4^+ > Pb^{2+} > Na^+ > Cd^{2+} > Cu^{2+} \approx Zn^{2+}$. Barbarick and Pirela (1984) found that clinoptilolite had a high selectivity for K^+ and $NH4^+$.

Two important factors which affect ion exchange are temperature and pH (Rodríguez-Iznaga et al., 2002; Godelitsas and Armbruster, 2003). Ion-exchange is normally enhanced by elevated temperatures (Godelitsas and Armbruster, 2003). According to Kithome et al. (1999) the adsorption capability of clinoptilolite for NH_4^+ increased with pH increasing from 4 to 7. Some 9.66g NH_4^+/kg of zeolite was adsorbed at pH 4 while 13.83g NH_4^+/kg was adsorbed at a pH of 7. Kesraoui-Ouki and Kavannagh (1997) found that optimum heavy metal adsorption with clinoptilolite occurs between a pH of 4 and 5. Clinoptilolite is very stable under low pH, compared to other zeolites (Shurson et al., 1984) and also has the highest thermal stability (700^oC) in air, while heulandite, a zeolite with similar structure undergoes structural collapse below 450^oC (Çulfaz and Yağiz, 2003; Perraki and Orfanoudaki, 2004).

Because of its high and selective NH_4^+ adsorption capacity, and its stability under high temperatures and low pHs, clinoptilolite has been used as a feed additive (Shurson et al., 1984). Nevertheless, clinoptilolite must be fed in the form of a powder, which implies that its flowability properties must be known to design proper handling and storage systems.

Limited research pertains to the flowability of zeolites, in powder form. Studying the inter-particle forces of cohesive powders using an Atomic Force Microscope (AFM), Jones et al. (2003) found that zeolite showed adhesion increasing strongly with relative humidity and reported an average roughness value of 150 nm. This roughness value pertains to the height of irregularities on the surface of zeolite particles, as the surface of zeolite particles is not smooth, leading to particle interlocking. Generally, the flowability of powders increases with greater particle size, and there appears to be a critical size range above which flowability does not show any improvement (Abdullah and Geldart 1999).

4.2 Objective

The objective of this study was to characterize the physico-chemical properties of KMI clinoptilolite (Nevada, USA), to compare KMI clinoptiloite's properties to Steel Head (Idaho, USA) and a commercial zeolite (Zeolite X), and to determine the optimal powder particle size distribution for clinoptilolite to be used as a feed additive for hogs. A fine clinoptilolite powder is expected to yield better ammonia adsorption characteristics because of greater particle surface exposure, and to be better suited as a feed supplement. On the other hand, a powder of coarse particle size distribution is expected to demonstrate better flowability and ease of handling. Thus, this paper also investigates particle size distribution which optimizes both feed efficiency and flowability.

4.3 Materials and Methods

4.3.1 Experimental zeolites

The main experimental zeolite was rich (90% +) in clinoptilolite and was supplied by KMI, operating a mine in Nevada, USA. The characteristics of this clinoptilolite were compared to that of another zeolite (90%+ clinotilolite) supplied by Steel Head, operating a mine in Idaho, USA, and a commercial grade zeolite (35% clinoptilolite). The clinoptilolite content of all zeolite samples was determined by X-Ray Diffraction (XRD). The KMI zeolite was found to have an Si/Al ratio of 7. Samples of KMI zeolite were mechanically sieved into three different particle size distributions, <250 μm, >250 μm, and a 1:1 mixture of the two particle sizes. Such fractions where used to determine both the chemical absorption and the bulk shear properties.

4.3.2 Mineral desorption and ammonium adsorption methodology

Two tests were conducted which provided data on the adsorption of ammonium and the release of macro minerals and heavy metals with time, under neutral conditions using three particle size distributions (<250 μm, >250 μm, and a 1:1 mixture of the two particle sizes) of the KMI and Steel Head zeolite. These tests were repeated for KMI and the commercial grade zeolite, under conditions simulating the digestive track of a hog using the 1:1 mixture of particle sizes. The release of heavy metals is important in predicting the possible contamination of the meat. The first test was conducted at room temperature and under a neutral pH to simulate the intestine environment. Room temperature instead of body (39°C) temperature was used to measure minimal amounts of ammonium adsorption and mineral release. The second test was conducted under acidic conditions (pH = 1.5) and 39°C to better simulate the stomach environment. All tests were conducted using either duplicate or triplicate samples.

The mineral adsorption and desorption capability of the KMI and Steel Head clinoptilolites, in the intestine of hogs, was simulated by exposing samples to an ammonia solution under neutral pH. Rather than the body temperature of the animals of 39°C, room temperature of 22°C was used to conduct the test to measure the minimal amounts of adsorption and desorption, as higher temperatures enhance this effect. Using all three particle size distributions, duplicate 2.5g samples of both KMI and Steel Head zeolites were placed in a 100ml solution of 0.05M NH_4Cl and 0.05M sodium phosphate buffer solution, where the buffer solution maintained a neutral pH. The samples were shaken at 120rpm and held at a constant temperature of 22^{o}C for 1, 2 or 3 days. Then, the supernatant liquid was removed and its solids were precipitated by centrifugation for 20 min at 9000 RPM. The ammonia content of the supernatant liquid was then determined using a, selective ammonia probe (Orion 95-12) to measure the NH_4^+ adsorbed by the zeolite. The supernatant liquid was also analyzed for its content in macro minerals and heavy metals, using an atomic adsorption spectrophotometer (GBC Scientific Equipment Pty Ltd, 22 Brooklyn Ave., Dandenong, Victoria, Australia), to quantify their level of release by the zeolite.

An adsorption and desorption experiment was carried out to simulate conditions inside a pig's stomach, where the pH is 2.0 (Shurson et al. 1984) and the temperature is 39°C, in order to compare the structural stability of KMI zeolite to a commercial grade zeolite with much less clinoptilolite content. This time, triplicate 2.5g samples of both the KMI and commercial grade zeolite (Zeolite X) were immersed in an NH_4Cl solution at a pH of 1.5, achieved by adding HCl. Samples were then shaken at 120rpm for 4 and 24 h, at a constant temperature of 39°C+/- 1°C. Feed spends less than one day inside the pig's stomach. The 4 and 24h test periods allowed some measure of the effect of time on the ammonium adsorption behavior of the zeolites, and its release of heavy metals. The supernatant liquid was separated from the zeolite by centrifugation for 20 min at 9000 RPM, and analyzed for ammonium using a selective probe, for macro minerals, Al and Fe, and heavy metals using AAS (GBC Scientific Equipment Pty Ltd, 22 Brooklyn Ave., Dandenong, Victoria, Australia). Quantifying the Al and Fe provided data on the stability of the zeolites under acidic conditions.

4.3.3 Bulk shear test methodology

Since zeolites must be stored and handled when using them as a feed additive, the design of such facilities requires some knowledge of their flowability. This can be estimated from their shear properties. Samples of the KMI zeolite were prepared by sieving into three particle size distribution sets, as explained above and by adding water to obtain three different moisture contents. Before adding water, zeolite samples were oven dried at 105°C for 24 hours and then rewetted with distilled water to obtain 5 and 10% moisture contents. Dry samples (0% moisture content) were also kept for testing. Moisture content of the zeolite was confirmed using the microwave oven method (Liu and Evett 1997a).

Samples were placed inside the shear box of a direct shear tester (Wykeham and Farrance, Inc., Weston Road, Slough, England). The test procedure was carried out as described in Liu and Evett (1997b), along with a calibration of the proving ring. Two types of tests were carried out. The first test involved filling both halves of the shear box with zeolite, exposing this sample to three different pressures and measuring its resistance to shear, thus yielding its angle of internal friction. The second test repeated the first procedure, but involved placing a piece of galvanized sheet metal (a common construction material for storage bins) in the bottom half of the shear box, flush with its top border. This produced the angle of wall friction between zeolite and galvanized steel sheeting.

For both tests, three different normal stresses were applied (22.6, 33.6, 66.8 kN/m^2). Triplicate samples were sheared at a rate of 1.09mm/min and the shear box displacement and proving ring dial readings were taken every 30 seconds. Proving ring dial readings were converted into shear stresses and plotted against shear box displacement readings, to find the shear stress at which the specimen failed. The failure shear stresses were then plotted against the normal stresses for given particle size distributions and moisture contents, to give the force required to cause particles to slide against each other or against the wall material of the storage or auger. The y-axis intercept gave the cohesion value representing a measure of particle to particle bonding strength.

4.3.4 Statistical analysis

All data were analyzed by ANOVA with the mixed model procedure in SAS (1999). Adjustments were made to account for all multiple comparisons. The statistical models are described as follows:

4.3.4a NH_4^+ adsorption

$$Y_{ijklm} = \mu + p_i + s_j + t_k + c_l + p{\cdot}s_{ij} + p{\cdot}t_{ik} + p{\cdot}c_{il} + s{\cdot}t_{jk} + s{\cdot}c_{jl} + t{\cdot}c_{kl} + p{\cdot}s{\cdot}t_{ijk} + p{\cdot}s{\cdot}c_{ijl} + p{\cdot}t{\cdot}c_{ikl} + s{\cdot}t{\cdot}c_{jkl} + p{\cdot}s{\cdot}t{\cdot}c_{ijkl} + e_{ijklm}$$

4.3.4b Minerals released versus NH_4^+ adsorbed

$$Y_{ijkl} = \mu + p_i + s_j + c_k + p{\cdot}s_{ij} + p{\cdot}c_{ik} + s{\cdot}c_{jk} + p{\cdot}s{\cdot}c_{ijk} + e_{ijkl}$$

4.3.4c Heavy metal release

$Y_{ijk} = \mu + t_i + c_j + t{\cdot}c_{ij} + e_{ijk}$

4.3.4d Shear test

$Y_{ijk} = \mu + p_i + m_j + p{\cdot}m_{ij} + e_{ijk}$

4.3.4e Parameters of the models

Y_{ijk}, Y_{ijkl}, Y_{ijklm} = dependant observation
μ = overall mean
p = particle size of dependant observation (> 250 µm, < 250 µm, and mixed)
s = solution of dependant observation (ammonia or buffer)
t = time of dependant observation (1, 2, and 3 days; 4 and 24 hours)
c = company of dependant observation (KMI, SteelHead, and Commercial Grade Zeolite X)
m = moisture content of dependant observation (0, 5, and 10%)
e_{ijk}, e_{ijkl}, e_{ijklm} = residual error

4.4 Results and Discussion

4.4.1 NH_4^+ adsorption and minerals released under neutral pH

The adsorption and desorption of minerals for both KMI and Steelhead clinoptilolites under a neutral pH and at room temperature (to measure desorption under minimal temperatures) in the ammonia solution are shown in Figures 4.1 to 4.7. A statistical analysis was performed on the results obtained for the ammonia adsorption characteristics (Table 4.2 to 4.4). A significant interaction was found between the particle size distribution of the zeolite, the type of solution used (ammonia or buffer) and length of exposure time of the zeolite to the solution (days) ($P < 0.0001$). Significant interactions were also found between time and company (KMI or Steel Head) ($P < 0.01$) and solution and company ($P < 0.001$). The statistical analysis shows that KMI zeolite adsorbed more NH_4^+ than Steel Head zeolite ($P < 0.0001$) when placed in the same solution (ammonia or buffer) (Table 4.2). KMI zeolite also adsorbed significantly more

NH_4^+ than Steel Head zeolite ($P < 0.0001$) on days one, two and three (Table 4.3). It can also be seen that when exposed to the same solution (ammonia or buffer) for the same duration of time, the > 250 µm particle size adsorbed significantly more NH_4^+ than < 250 µm particle size and the mixed particle size on day one (Table 4.4). On days two and three the > 250 µm and < 250 µm particle size zeolites did not differ significantly ($P > 0.05$) however, both of them significantly adsorbed more NH_4^+ than the mixed particle size ($P < 0.05$). The mechanism behind this is still unclear. The >250 µm and mixed particle size distributions of both the KMI and Steel Head zeolites samples performed consistently, reaching almost maximum adsorption of ammonia after one day, and peaking after two days. For both KMI and Steel Head, the < 250 µm particle size distribution adsorbed ammonium more slowly, reaching only half and then the full value of that adsorbed by the other particle size distributions after one and three days, respectively.

Since feed does not stay in the stomach of a pig for more than one day, it is most beneficial to use a zeolite which peaks quickly in terms of NH_4^+ adsorption. The statistical analysis shows that the particle size distribution of > 250 µm significantly adsorbed more NH_4^+ than the < 250 µm or mixed particle size ($P < 0.05$). Furthermore it was found that KMI zeolite with a particle size distribution of > 250 µm was more desirable, in terms of adsorptive capabilities as a feed additive. The NH_4^+ adsorption capabilities after one day for KMI zeolite with a particle size distribution of > 250 µm was found to be 1.58 ± 0.02 meq and 1.49 ± 0.02 meq of NH_4^+/g of zeolite in the ammonia and buffer solution, respectively. The KMI zeolite with a mixed particle size distribution also performed comparably, though statistically not as well ($P < 0.05$), as the > 250 µm particle size after one day and would also be suitable, in terms of adsorptive capabilities as a feed additive, adsorbing 1.43 ± 0.01 meq of NH_4^+/g of zeolite in the ammonia solution and 1.31 ± 0.05 meq of NH_4^+/g of zeolite in the buffer solution.

An analysis of the macro minerals (Ca, Cu, K, Mg, Na, and Zn) released over a three day period by each particle size distribution, for both the KMI and Steel Head zeolites was also carried out and compared to the amount of ammonia adsorbed. Since the buffer solution that was used in this experiment was a sodium phosphate buffer, the sodium values obtained for the minerals released from the zeolite were skewed by the sodium in the buffer solution, thus the total minerals released analysis excluded buffer solution values. Figures 4.1 to 4.7 for NH_4^+ adsorbed vs. total amount of minerals released suggest that the total amount of minerals desorbed corresponded to the amount of NH_4^+ adsorbed in nearly a 1:1 ratio, with the exception of the first day for the particle size distribution of < 250 µm for both KMI and Steel Head zeolites. This indicates that the ammonium adsorbed displaced minerals which become available in the hog's stomach.

The differences in NH_4^+ adsorbed and the total amount of minerals released (Ca, Cu, K, Mg, Na, and Zn) were analyzed using SAS. From the analysis, it was found that the effect of the two different companies (KMI and Steel Head) was not significant ($P > 0.05$). A significant interaction was found between particle size and time ($P < 0.0001$) on the NH_4^+ adsorbed vs minerals released. Table 4.5 shows that with the exception of the $<$ 250 µm particle size, there were no significant differences ($P > 0.05$) between any of the NH_4^+ adsorbed vs minerals released within any of the days. For the particle size distribution of < 250 µm for both KMI and Steel Head zeolites, there was a significant difference ($P<0.05$) between NH_4^+ adsorbed vs Minerals released on day 1 vs day 2 or 3. The values obtained for NH_4^+ adsorbed and total minerals released, indicate that significantly more (approximately twice as many) minerals were released compared to NH_4^+ adsorbed.

The reason for this low NH_4^+ adsorption in relation to the other samples tested is still uncertain. Likely, the particle size played a significant role. Although > 250 µm particle size distribution has a lower surface area for the same amount of total weight, allowing for less NH_4^+ adsorption, its inter particle flow channels may allow for a faster diffusion of ions. For the finer particle size distribution, the surface of the clinoptilolite particles and the openings of the pores within their crystalline structure could have been blocked by dust produced during the grinding process, leading to slower ion exchange rates (Inglezakis et al. 1999; Zorpas et al. 2002). To increase ion exchange rates, rigorous washing of clinoptilolite powders has shown to be effective (Inglezakis et al. 1999). The clinoptilolite regains part of its natural porosity, leading to higher uptake rates. Increasing the agitation speed has also been proven to increase ion exchange rates. Inglezakis et al. (1999) found that increasing agitation from 210 to 650 rpm helped to unclog the pores of the clinoptilolite. The release of minerals (Ca, Cu, K, Mg, Na, and Zn) was not affected by this clogging phenomenon because their release does not depend on diffusion.

4.4.2 NH_4^+ adsorption and minerals released under acidic pH

A pH of 1.5 and a temperature of 39°C simulated the conditions inside a hog's stomach. Under such conditions, samples of the KMI zeolite and the commercial grade zeolite released limited amounts of heavy metals (Table 4.6). In terms of minerals released versus ammonium adsorbed, there were no significant differences between the 4 and 24h results ($P < 0.05$) (Figure 4.7). Overall, KMI zeolite was more acid resistant, releasing a lower percentage for 4 out of 6 minerals (Al, Cu, Fe, and Pb) compared to the commercial grade zeolite (Table 4.6). With the exception of 3 heavy metals, Al, Fe and Pb, based on the total content released and Al released after 24hrs, the KMI clinoptilolite was lower than the level of heavy metals considered toxic to swine (Table 4.7). If the KMI zeolite was to be fed to hogs at a level as high as 6%, it is expected that the amounts of heavy metals released after even 24h would not be high enough to exceed the toxicity threshold (Table 4.7).

According to Tomazovic et al. (1996), a greater Si/Al ratio makes the zeolite more stable and more resistant to acids. The relative percentage of Al release under acidic conditions indicates that the KMI zeolite was more stable than the commercial grade zeolite. Effectively, the commercial zeolite had a greater Al content, compared to the KMI zeolite.

In terms of ammonia adsorption capabilities under these specific conditions, KMI zeolite was found to adsorb 1.23 ± 0.01 meq of NH_4^+/g of zeolite and the commercial grade zeolite was found to adsorb 0.77 ± 0.02 meq of NH_4^+/g of zeolite, only about half as much as the KMI zeolite. Under acidic conditions (Figure 4.7) the KMI zeolite is capable of significantly adsorbing more NH_4^+ ($P< 0.05$) while releasing less total minerals per NH_4^+ adsorbed. The KMI zeolite adsorbed 47 meq of NH_4^+/100g more ammonium and desorbed 12 meq/100g of zeolite more macro-minerals (total of Ca, K, Mg, and Na) compared to the commercial zeolite (Figure 4.7). Therefore, KMI zeolite is quite adequate as feed supplement when used as a powder with a mixed particle size distribution. It is resistant to acidic conditions as shown in Figure 4.7 by its limited release of Al and Fe thus allowing ammonium adsorption in the stomach of hogs without structural break down.

4.4.3 Angle of internal and wall friction of KMI zeolite

The values for the angle of internal friction were found to be smaller for the > 250 μm particle size, as compared to that of the < 250 μm particle size (Figures 4.8, 4.9 and 4.10), though not statistically significant ($P < 0.05$). This finding is consistent with those of Abdullah and Geldart (1999) who reported that in general, the flowability of powders increases with particle size. Nevertheless, neither particle size, moisture content, nor the interaction of the two factors was found to have a significant effect on the angles of internal friction, under consolidation pressures of 23, 34 and 67 kPa. The average internal angle of friction for KMI zeolite was calculated as 78.25 ± 0.65^{o}. Cohesion values were all assumed to be zero. This was possible since bulk solids such as zeolite can be considered cohesionless by soil mechanics terminology (Jenike 1994), and a direct shear apparatus originally designed for soil mechanics was used.

From Figures 4.8, 4.9 and 4.10, the angle of internal friction is observed to increase with load, implying that zeolite is compressible and that a greater storage depth can lead to a higher angle of internal friction. Since there was no significant effect ($P > 0.05$) of treatment (particle size and moisture content) on angle of internal friction, only the mixed particle size KMI zeolite at 5% moisture content was used to measure the angle of wall friction with galvanized steel. This angle was found to be 78.40 ± 0.34^{o} (Figure 4.11) and under consolidation pressures of 23, 34 and 67 kPa, is compressible.

4.4.4 Storage bin flow pattern of KMI zeolite

Regarding flow of bulk materials within storage bins, there are two hopper flow patterns which are recognized (Jenike, 1987). Mass flow, which occurs when the solid flows throughout the hopper whenever any of it is withdrawn (Jenike, 1987) and funnel flow which occurs when a solid drawn through an outlet of a bin forms a channel within the stored mass, and flows toward the outlet within that channel while the mass around it and against the walls remains stationary (Jenike, 1994).

Drescher (1992) graphically related the wall friction angle and the angle of internal friction to the maximum slope angle of a hopper wall (against the vertical) which ensures mass flow for a conical hopper. The larger the wall friction angle, the steeper the hopper has to be in order to achieve mass flow. The results obtained from the present experiment showed that when storing zeolite in a conical silo, no matter how steep the hopper angle, mass flow is not achievable and funnel flow should be expected. Rat-holes are the most common flow problem associated with funnel flow bins. A rathole is a stable pipe or vertical cavity that empties above the bin outlet. The material is left stranded in stagnant zones that usually remain in place until an external force is applied to dislodge it (Prescott and Barnum, 2000). Finally, the depth of storage of zeolite, affecting the angle of internal friction of this compressible material, becomes irrelevant, as it would not affect funnel flow conditions.

4.5 Conclusions

From the chemical characteristics observed, it can be concluded that the KMI zeolite with a > 250 µm particle size distribution provided the most favorable characteristics, adsorbing the most NH_4^+ (1.58 ± 0.02 meq of NH_4^+/g of zeolite under neutral pH and a temperature of 22°C). Though not performing statistically as well ($P < 0.05$), the mixed particle size was comparable to that of the > 250 µm particle size distribution adsorbing 1.43 ± 0.01 meq of NH_4^+/g of zeolite under neutral pH and a temperature of 22°C. Grinding zeolite to a fine dust powder (< 250 µm) is not recommended, as ammonium adsorption is significantly lower ($P < 0.05$), after one day, the time which feed generally spends in the stomach of hogs. As ammonium is being adsorbed, the zeolite releases an almost equivalent amount of minerals, thus providing added nutrition to the animal. The KMI zeolite demonstrated excellent stability under high acidic conditions simulating that existing inside a hog's stomach, as it released limited amounts of Al and Fe and was found to adsorb 1.23 ± 0.01 meq of NH_4^+/of zeolite.

The angle of internal friction of the KMI zeolite does not vary significantly for the range of particle size distribution (> 250 µm, < 250 µm, and mixed) and moisture content (between 0 and 10%) tested. The angle of internal friction was observed to increase with load, indicating that the KMI zeolite is a compressible material. Furthermore, the angle of wall friction measured indicates that storing zeolite in a silo, irregardless of particle size, load or moisture content, will lead to funnel flow.

The results of this study indicates that the KMI zeolite with a particle size distribution of > 250 μm and mixed particle size are appropriate zeolites, in terms of adsorptive capabilities, quality, and handling characteristics, for use as a dietary supplement in pig feed.

4.6 Acknowledgements

This project was financially supported by the Fédération des producteurs de porcs du Québec and the Natural Science and Engineering Research Council of Canada.

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Table 4.1: Bulk composition of all three experimental zeolites carried out by XR Defraction (weight%) (Core Laboratories Canada Ltd., AB)

	KMI Zeolite	Steel Head	Zeolite X
Quartz (SiO_2)	Trace-1	0	12
Plagioclase ($NaAlSi_3O_8$ - $CaAl_2Si_2O_8$)	Trace-1	2	41
Calcite ($CaCO_3$)	1	1	1
Dolomite ($[CaMg]CO_3$)	Trace-1	1	0
Clinoptilolite ($KNa_2Ca_2(Si_{28}Al_7)O_{72}\cdot 24H_2O$)	97-98	94	37
Opal (SiO_2 .nH_20)	0	2	0
Muscovite/Illite ($KAl_2[AlSi_3O_{10}][OH]_2$)	0	0	9

Table 4.2: Statistical analysis (solution•company interaction) of NH4+ adsorption (meq/g of zeolite)

sol·company	LS Means	SE
$A\cdot K^{a}$	1.4599	0.006184
$A\cdot S^{b}$	1.31	0.006184
$B\cdot K^{c}$	1.3409	0.006184
$B\cdot S^{d}$	1.2381	0.006184

^{abcd} = interactions with different letters differ significantly from one another ($P < 0.05$)
A = Ammonia Solution
B = Buffer Solution
K = KMI zeolite
S = Steel Head zeolite
LS Means = least square means
SE = standard error

Table 4.3: Statistical analysis (company•time interaction) of NH4+ adsorption (meq/g of zeolite)

company·time	LS Means	SE
$K\cdot 1^{a}$	1.184	0.00757
$S\cdot 1^{b}$	1.0267	0.00757
$K\cdot 2^{c}$	1.5156	0.00757
$S\cdot 2^{d}$	1.411	0.00757
$K\cdot 3^{c}$	1.5016	0.00757
$S\cdot 3^{d}$	1.3845	0.00757

^{abcd} = interactions with different letters differ significantly from one another ($P < 0.05$)
K = KMI zeolite
S = Steel Head zeolite
1 = Day one
2 = Day two
3 = Day three
LS Means = least square means
SE = standard error

Table 4.4: Statistical analysis (particle size•solution•time interation) of NH_4^+ adsorption (meq/g of zeolite)

ps·sol·time	LS Means	SE
G·A·1^{abcd}	1.5028	0.01312
G·A·2^{a}	1.5462	0.01312
G·A·3^{abcd}	1.4902	0.01312
G·B·1^{cdef}	1.4136	0.01312
G·B·2^{abcd}	1.4953	0.01312
G·B·3^{bcde}	1.4287	0.01312
L·A·1^{i}	0.7111	0.01312
L·A·2$^{a(b)}$	1.5349	0.01312
L·A·3^{a}	1.5745	0.01312
L·B·1^{j}	0.4142	0.01312
L·B·2^{abcd}	1.4964	0.01312
L·B·3^{abc}	1.5136	0.01312
M·A·1^{efg}	1.3569	0.01312
M·A·2$^{(d)efg}$	1.3939	0.01312
M·A·3^{efg}	1.354	0.01312
M·B·1^{h}	1.2335	0.01312
M·B·2^{fgh}	1.313	0.01312
M·B·3^{gh}	1.2973	0.01312

$^{(b)}$ =should be omitted when considering the comparison between GB3 and LA2

$^{(d)}$ = should be omitted when considering the comparison between GA1 and MA2

^{abcdefgh} = interactions with different letters differ significantly from one another ($P < 0.05$)

G = > 250 µm particle size zeolite
L = < 250 µm particle size zeolite
M = Mixed particle size zeolite
A = Ammonia Solution
B = Buffer Solution
1 = Day one
2 = Day two
3 = Day three
LS Means = least square means
SE = standard error

Table 4.5: Statistical analysis of NH_4^+ adsorption (particle size•time interaction) - minerals released (meq/g of zeolite)

ps·time	LS Means	SE
G·1^{abc}	0.2122	0.02933
G·2^{abc}	0.2098	0.02933
G·3^{abc}	0.153	0.02933
L·1^{d}	-0.6095	0.02933
L·2^{a}	0.2837	0.02933
L·3^{ab}	0.2375	0.02933
M·1^{c}	0.03938	0.02933
M·2^{bc}	0.07746	0.02933
M·3^{c}	0.03468	0.02933

^{abc} = interactions with different letters differ significantly from one another ($P < 0.05$)
G = > 250 µm particle size zeolite
L = < 250 µm particle size zeolite
M = Mixed particle size zeolite
1 = Day one
2 = Day two
3 = Day three
LS Means = least square means
SE = standard error

Table 4.6: Total heavy metals released at temperature = 40^{o}C and pH = 1.5 (mg/kg of zeolite)

	KMI					Zeolite X				
		LS Means		LS Means			LS Means		LS Means	
Element	Total	4h	SE	24h	SE	Total	4h	SE	24h	SE
As	34	42.972	11.539	38.997	11.539	-	54.707	11.539	35.723	11.539
Al	650	707.150	71.848	765.580	71.848	17 000	760.010	71.848	784.220	71.848
Cd	1	0.1015^{a}	0.014	0.1499^{a}	0.017	1.0	0.06826^{b}	0.014	0.06233^{b}	0.014
Cu	28	0.9881^{a}	0.255	1.3057^{a}	0.255	12	2.0451^{b}	0.255	1.6619^{b}	0.255
Co*	3.8	-	-	-	-	3.0	-	-	-	-
Cr*	<2.0	-	-	-	-	6.0	-	-	-	-
Fe	3 800	7.4278^{a}	5.631	8.4477^{a}	5.631	8 600	105.14^{b}	5.631	97.0186^{b}	5.631
Mo*	8	-	-	-	-	<2.0	-	-	-	-
Ni	1.4	-	-	-	-	6.0	-	-	-	-
Pb	50	2.812	0.226	2.693	0.226	12	3.212	0.226	2.862	0.226
Se	0.64	-	-	-	-	41	-	-	-	-
St	151	-	-	-	-	-	-	-	-	-
Zn	231	92.4594^{a}	5.511	76.1609^{a}	5.511	-	6.0608^{b}	5.511	5.5963^{b}	5.511

* = release of this heavy metal was below the detection limit.

^{a,b} = different letters differ signficantly ($P < 0.05$) from one another within element group

LS Means = least square means

SE = standard error

NOTE: total heavy metal release was carried out by Body Cote Laboratories (Pointe Claire, PQ)

Table 4.7: Heavy metal concentrations considered toxic to swine (mg/kg of zeolite)

Element	Tolerable Level[1]	Tolerable Level[2,3]
As	50	50
Al	-	200
Cd	0.5	0.5
Cu	250	100-250
Co	-	150
Cr	3 000	1 000 - 3 000**
Fe	500-3000	600
Mo	100	20
Ni	100	100
Pb	30	30
Se	-	2
St	-	3000
Zn	1 000	1000

[1] = Agriculture Canada et al. (1985)

[2] = National Academy of Science (1980)

[3] = National Academy of Science (1998)

** = dependant on type of salt

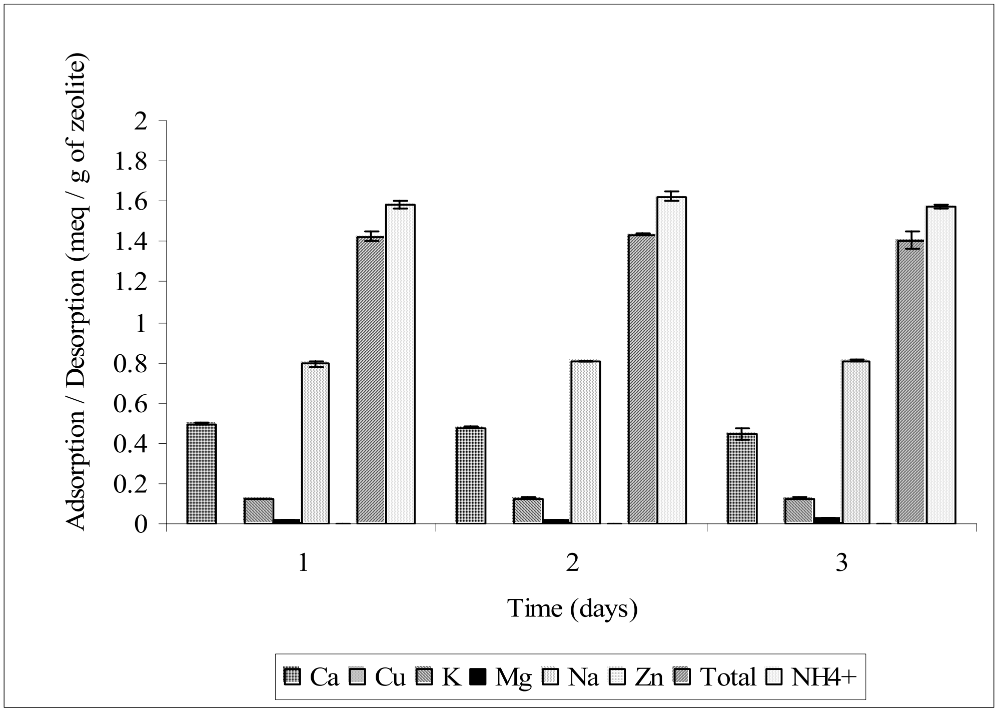

Figure 4.1: Mineral desorption (Ca, Cu, Mg, Na, Zn, and Total) versus NH_4^+ adsorption under a neutral pH at 22°C for > 250 µm KMI zeolite in a 0.05M NH_4Cl solution (meq/g of zeolite). Total refers to summation of Ca, Cu, Mg, Na and Zn mineral desorption

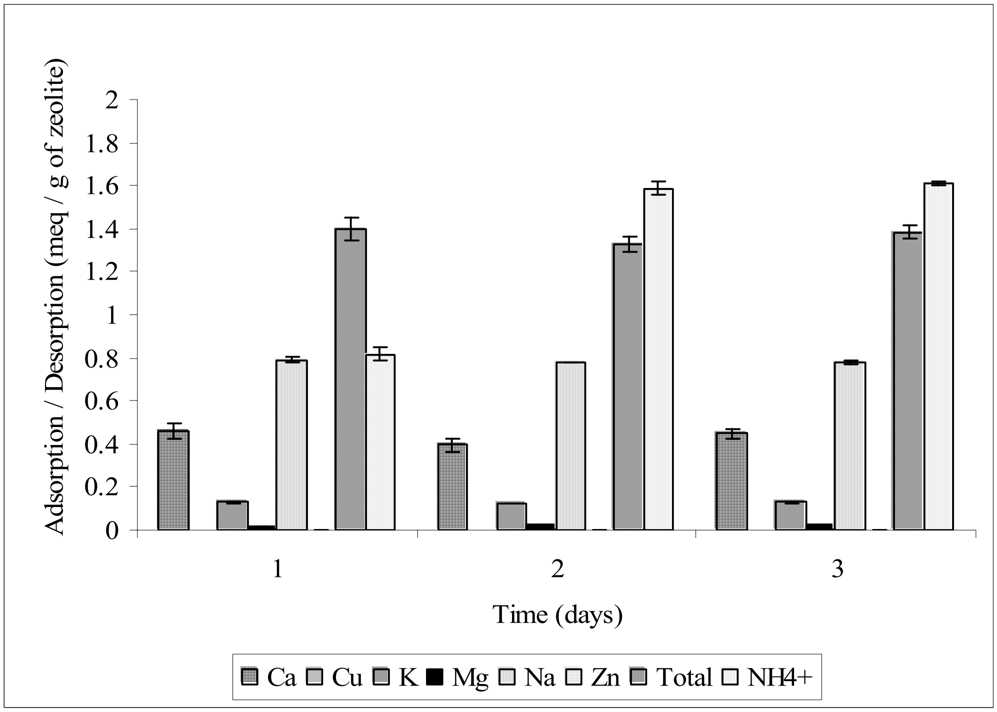

Figure 4.2: Mineral desorption (Ca, Cu, Mg, Na, Zn, and Total) versus NH_4^+ adsorption under a neutral pH at 22°C for < 250 µm KMI zeolite in a 0.05M NH_4Cl solution (meq/g of zeolite). Total refers to summation of Ca, Cu, Mg, Na and Zn mineral desorption

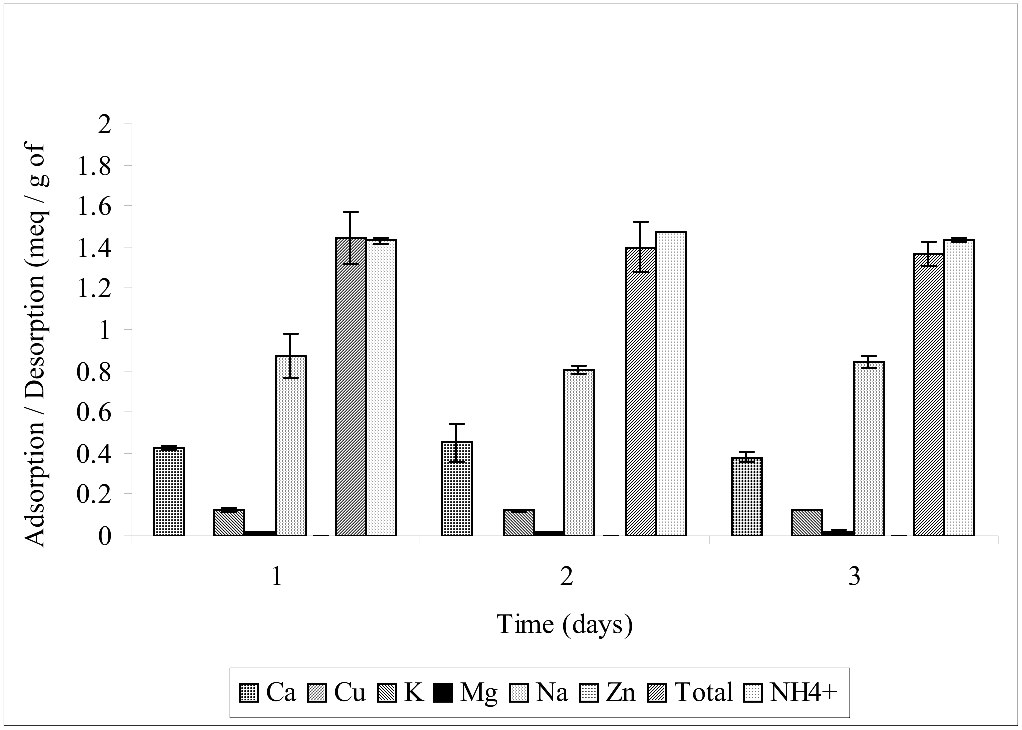

Figure 4.3: Mineral desorption (Ca, Cu, Mg, Na, Zn, and Total) versus NH_4^+ adsorption under a neutral pH at 22°C for mixed KMI zeolite in a 0.05M NH_4Cl solution (meq/g of zeolite). Total refers to summation of Ca, Cu, Mg, Na and Zn mineral desorption

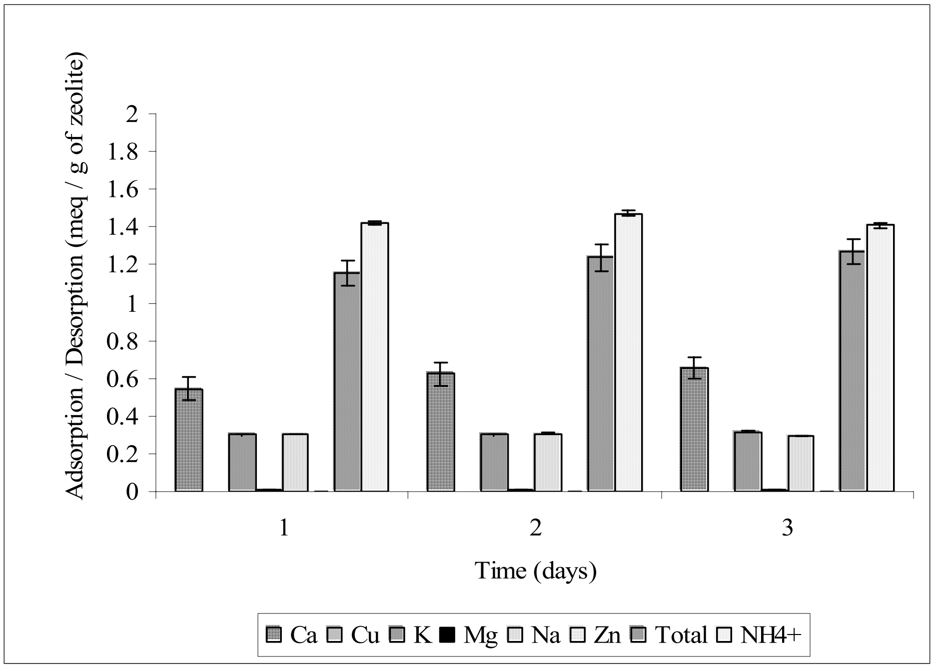

Figure 4.4: Mineral desorption (Ca, Cu, Mg, Na, Zn, and Total) versus NH_4^+ adsorption under a neutral pH at 22°C for > 250 μm Steel Head zeolite in a 0.05M NH_4Cl solution (meq/g of zeolite). Total refers to summation of Ca, Cu, Mg, Na and Zn mineral desorption

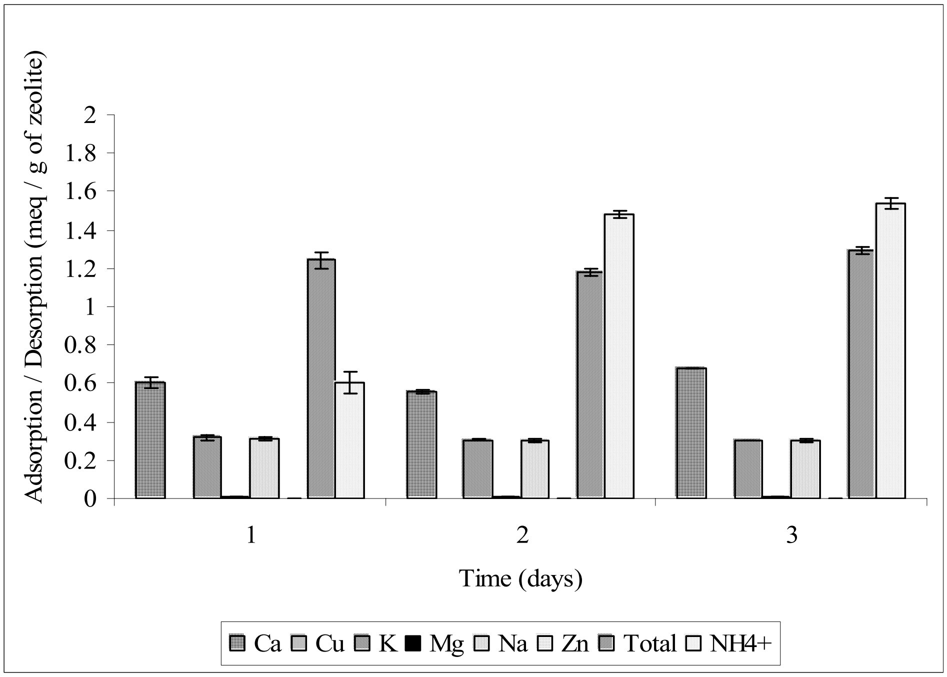

Figure 4.5: Mineral desorption (Ca, Cu, Mg, Na, Zn, and Total) versus NH_4^+ adsorption under a neutral pH at 22°C for < 250 µm Steel Head zeolite in a 0.05M NH_4Cl solution (meq/g of zeolite). Total refers to summation of Ca, Cu, Mg, Na and Zn mineral desporption

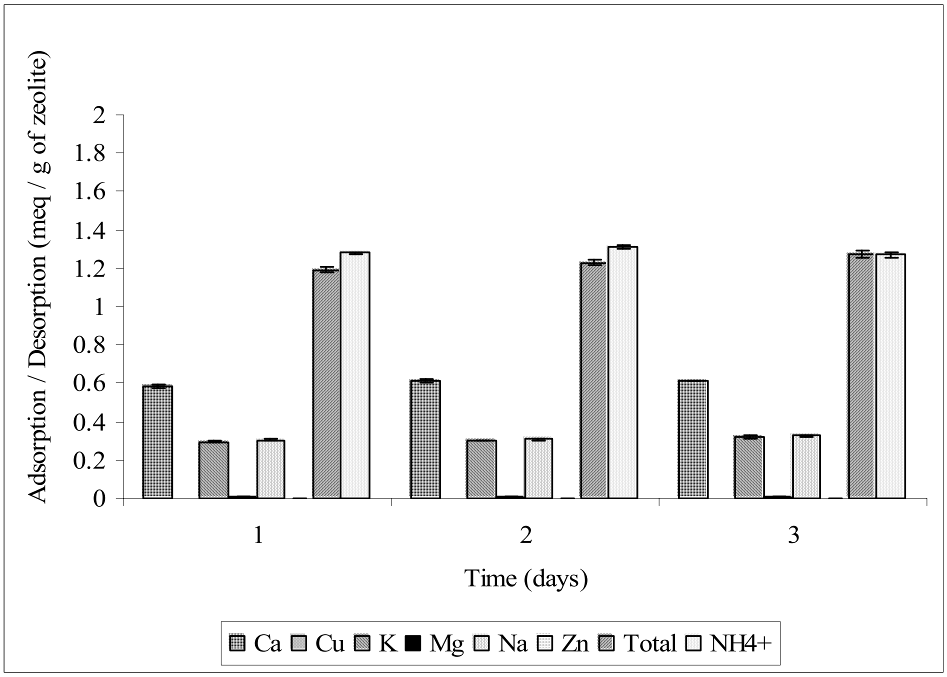

Figure 4.6: Mineral desorption (Ca, Cu, Mg, Na, Zn, and Total) versus NH_4^+ adsorption under a neutral pH at 22°C for mixed Steel Head zeolite in a 0.05M NH_4Cl solution (meq/g of zeolite). Total refers to summation of Ca, Cu, Mg, Na and Zn mineral desporption

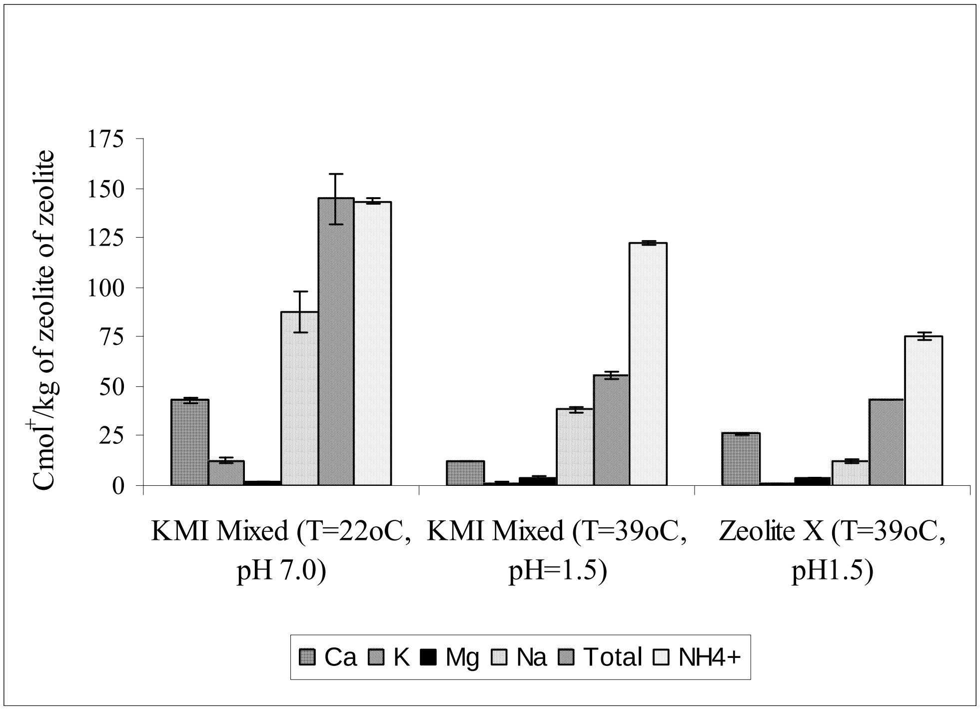

Figure 4.7: Mineral (Ca, K, Mg, Na and Total) desorption and NH_4^+ adsorption of mixed KMI zeolite under a neutral pH at 22°C and pH of 1.5 at 39°C versus a mixed particle size commercial grade zeolite under a pH of 1.5 at 39°C (meq/g of zeolite). Total refers to summation of Ca, K, Mg and Na mineral desporption

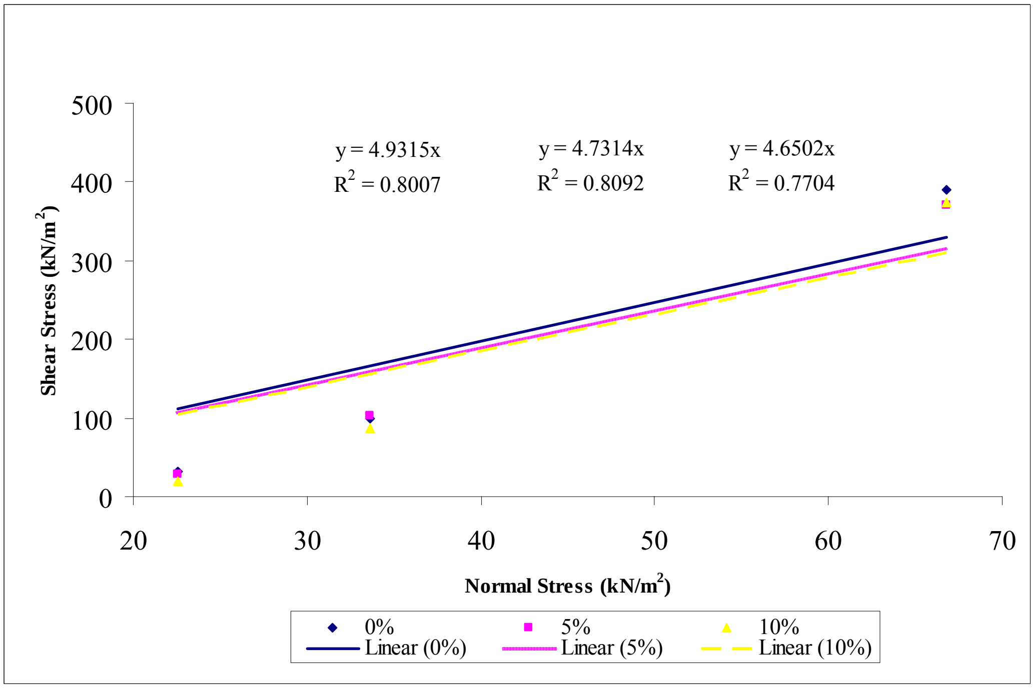

Figure 4.8: Shear Stress (kN/m^2) versus Normal Stress (kN/m^2) for mixed KMI zeolite at 0%, 5%, and 10% moisture content under normal loads of 22.6, 33.6, 66.8 kN/m^2 to determine angle of internal friction

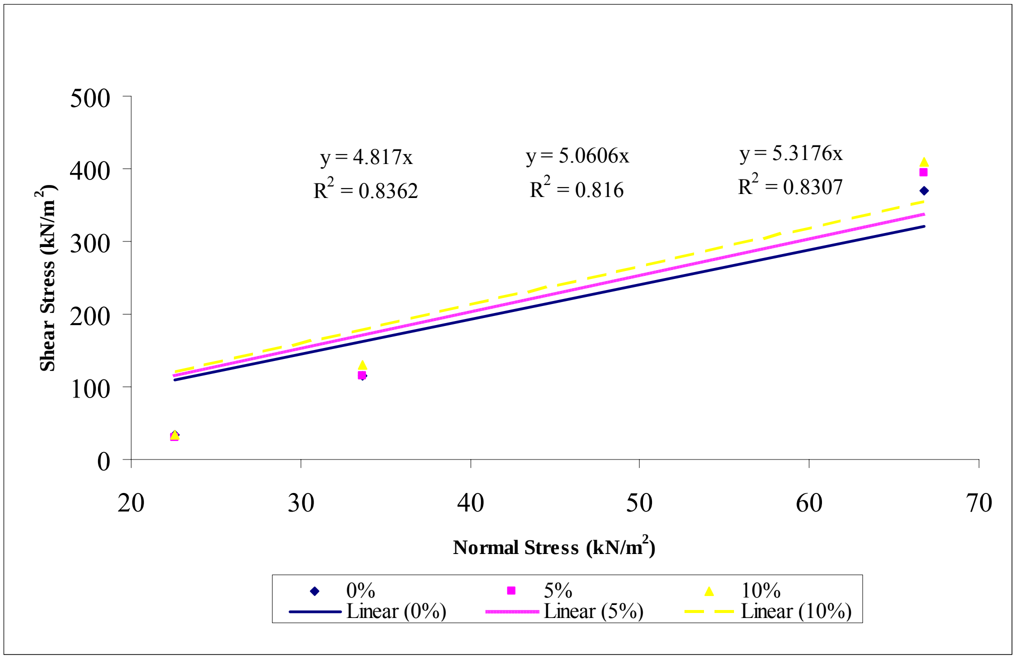

Figure 4.9: Shear Stress (kN/m^2) versus Normal Stress (kN/m^2) for <250 µm KMI zeolite at 0%, 5%, and 10% moisture content under normal loads of 22.6, 33.6, 66.8 kN/m^2 to determine angle of internal friction

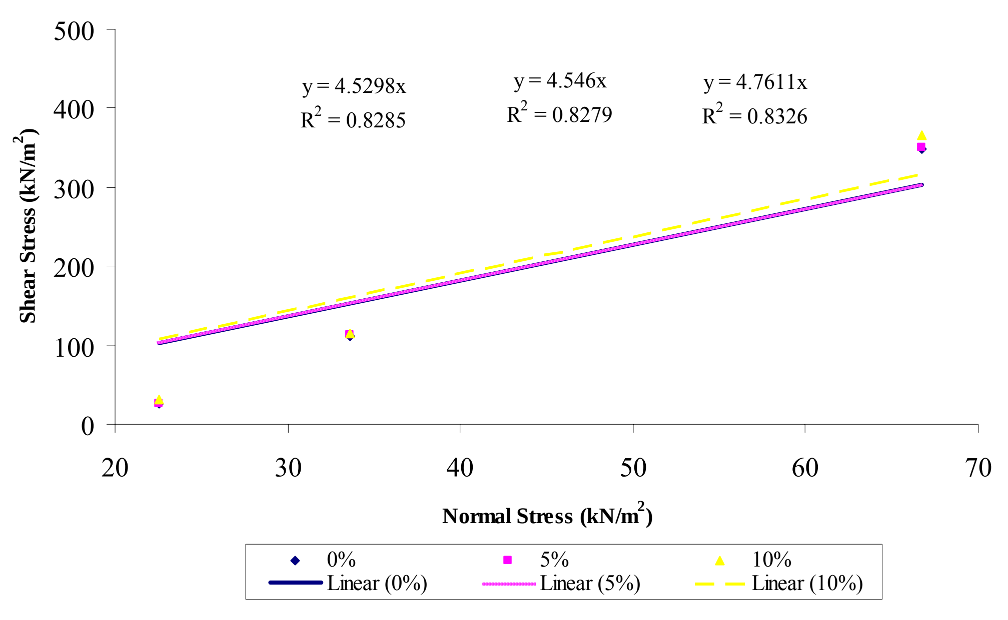

Figure 4.10: Shear Stress (kN/m^2) versus Normal Stress (kN/m^2) for >250 µm KMI zeolite at 0%, 5%, and 10% moisture content under normal loads of 22.6, 33.6, 66.8 kN/m^2 to determine angle of internal friction

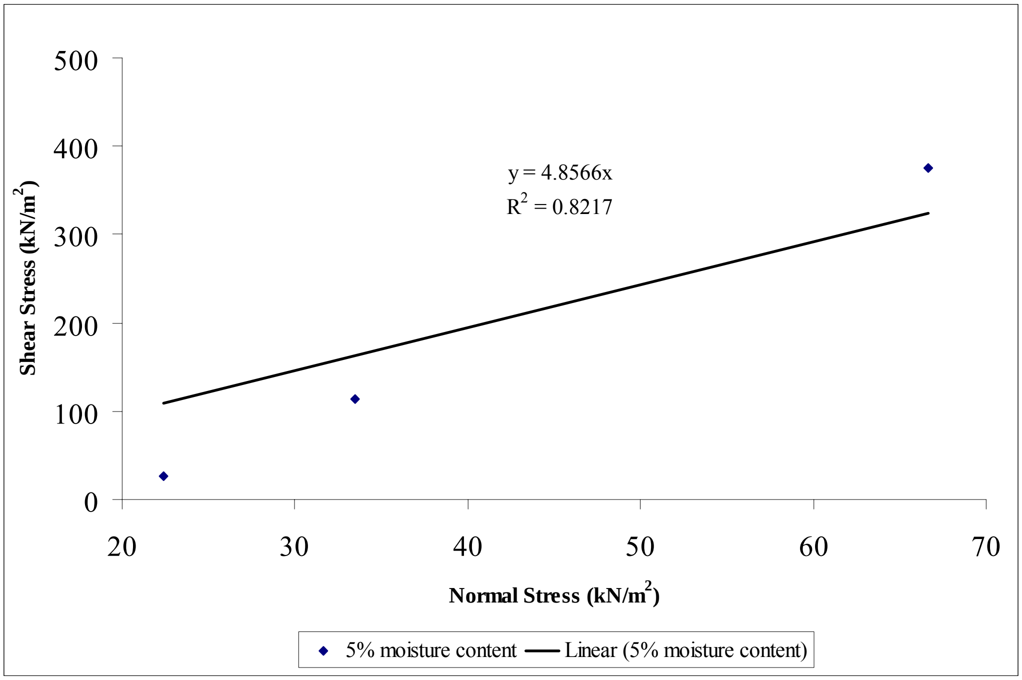

Figure 4.11: Shear Stress (kN/m^2) versus Normal Stress (kN/m^2) for mixed KMI zeolite at 5%, and 10% moisture content under normal loads of 22.6, 33.6, 66.8 kN/m^2 to determine angle of wall friction

CONNECTING TEXT

The characterization of the chemical and physical properties of zeoltie has shown that this mineral possesses great potential for nutrient reduction. However, hog producers will not likely supplement their feed with zeolite unless this mineral can enhance or benefit their product. Therefore, the following paper investigates the effect of zeolite supplementation to standard pig diets on pig performance, carcass quality and heavy metal concentrations in the liver, kidney and muscle tissue.

V. THE EFFECT OF CLINOPTILOLITE ON PIG PERFORMANCE, CARCASS QAULITY, AND HEAVY METAL CONCENTRTATIONS IN THE LIVER, KIDNEY AND MUSCLE TISSUE

5.1 Introduction

The specialization trend of the livestock industry, particularly the swine industry, has lead to fewer but more intensive operations. Swine manure is a valued source of fertilizer for crop production, yet many of the large swine production units do not have an adequate land base to apply the manure they produce at sustainable rates (Grandhi, 2001). Nevertheless, producers continue to apply their manure at normal rates which has lead to nutrient overloading, particularly nitrogen (N) and phosphorus (P). In Canada, the application of manure as fertilizer to fields has exceeded the nutrient requirements of the land at the farm level and in some cases, the regional level. Already producers in the L'Assomption, St Hyacinthe and Beauce regions, which market over 50% of all Quebec hogs, have exceeded the nutrient requirements of the land at the regional level. The same problem is observed in the Windsor-Georgian Bay area of Ontario, the Fraser Valley in B.C. and the Lethbridge area in Alberta (Chambers et al., 2001). Deterioration of air and water quality which can lead to reduced biodiversity in ecosystems and can even threaten human health are some of the consequences of nutrient overloading that have been well documented (Chambers et al., 2001; Jongbloed and Lenis, 1998; Morse, 1995). The three main concerns about animal manure is air quality (odours), eutrophication (nitrates leaching into ground water) and accumulation of nutrients in the soil (Jongbloed and Lenis, 1998).

There are two possible solutions to this problem. One solution would involve farmers applying the manure they produce according to the nutrient requirements of the land. The excess manure would then be distributed to areas that are experiencing a nutrient deficit (intensely cropped areas). However, this is costly and uneconomical. The other solution is to improve the nutrient digestibility through diet manipulation to reduce manure nutrient content (Honeyman, 1993; Sutton et. al., 1999).

Only until recently have zeolites been exploited in the agricultural and environmental industry for their physical and chemical properties. Zeolites are, by definition, crystalline, hydrated aluminosilicates of alkali and alkaline earth cations that possess an infinite, three-dimensional crystal structure (Mumpton and Fishman, 1977). Clinoptilolite is a species of zeolite which contains a ten-member ring channel pore system with eight-member ring cross-channels (Zhao et al., 1998). These channels give rise to the well-known "molecular sieving" property of zeolites. Molecules having effective cross-sectional diameters small enough to fit through the channels are readily adsorbed on the inner surfaces. Molecules which are too large to fit through the channels are excluded and pass around the outside of zeolite particle (Mumpton and Fishman, 1977). Clinoptilolite is further characterized by having an Si/Al ratio greater than 4 and being thermally stable in excess of 500^{o}C (Zhao et al., 1998). Their high cation exchange capacities (2 to 3 meq/g as reported by Mumpton (1984)), affinity for NH_4^+ ions (Barbarick and Pirela, 1984; Langella et al., 2000), and abundance all over the world (Torracca et al., 1998) make clinoptilolite an ideal feed additive for the purposes of improving nutrient digestibility, hence reducing manure nutrient content in livestock.

Although still in its infancy, as a feed additive, zeolites have been shown to improve weight gain in growing swine (Pond et al., 1988; Coffey and Pilkington, 1989), broilers (Fethiere et al., 1994), beef cattle and sheep (Tsitsishvili et al., 1984), and lead to a better feed efficiency and egg productivity in laying hens (Olver ,1997). However some researchers have observed either no effect (Pearson et al., 1985) or an adverse effect (Poulsen and Oksbjerg, 1995) when using zeolite as feed supplement. Zeolite purity, geographic source, particle size, supplemental levels used in diets, health status and weight range of the treated animals are all factors which can contribute to variations in observed results (Mumpton and Fishman, 1977; Pond and Yen, 1982; Pond et al., 1988).

5.2 Objective

The objective of this study was to ivestigate the effect of zeolite supplementation at the 0, 2, 4 and 6% inclusion level in both a high or low crude protein and energy level pig diet on body weight, body weight gain, feed intake, feed conversion rate and carcass quality of swine. The optimal zeolite supplementation level was also determined. The effect of feeding zeolite, up to a feed supplementation level of 6%, on the heavy metal concentration in the liver, kidney and the muscle tissues of the pigs from the starter to finishing phase was carried out as well.

5.3 Materials and Methods

5.3.1 Materials

One hundred and ninety two crossbred pigs (½ Duroc, ¼ Landrace and ¼ Yorkshire) with an average weight of 23.9 ± 1.0 kg (standard deviation) at the start of the experiment, participated in this ad libitum feed trial at the Macdonald Campus Swine Unit (Ste-Anne-de-Bellevue, PQ). Six pigs (3 male and 3 female) were randomly assigned to a 3m x 1.8m concrete slatted floor pen inside one of two rooms having two rows each. There were 8 pens per row in each room, with 2 rows per room and 2 rooms, resulting in a total of 32 pens (Figure 5.1).

5.3.2 Experimental diets

Before the feed trial started, each pen within each row and room was randomly allocated one of the 8 different types of feed (rations), from Lyrco Nutrition, Inc. (St-Valérien de Milton, PQ) which primarily consisted of corn and soybean meal (described in Table 5.1 and 5.2). The first four rations had a regular crude protein (C.P.) and energy level while the last four rations had a low C.P. (92%) and energy level. The zeolite used as a dietary supplement in this experiment was supplied from the KMI mine in Nevada, USA. An analysis of the bulk composition of the zeolite used to supplement the diets is provided in Table 5.3. The ammonium adsorption capacity of this zeolite was assayed in Chapter IV (Leung et al. 2004). The pigs were fed the starter ration for the first six weeks, then the grower ration was fed between weeks six and ten, the finisher ration was then used throughout the remainder of the experiment (Table 5.1).

Each pen had its own individual feeder and even though it was an ad libitum feed trial, the number of 25 kg feed bags put into the feeders to ensure that the animals could eat as desired, was recorded everyday. Hence, the weight of feed put into each feeder was recorded so that feed intake could be recorded.

5.3.3 Data collection (growth measurements)

Initially the pigs had an average body weight of 23.9 ± 1.0 kg and were weighed every two weeks along with the weight of the feeders (with feed inside) in order to calculate feed intake. The pigs remained on their respective diets until they were of appropriate weight for slaughter. At week 14 the pigs reached a market weight of 110.9 ± 9.0 kg, and were sent to the Olymel slaughter house in Princeville, PQ where carcass quality evaluation was carried out.

Twenty samples of the muscle, twenty samples of the liver and twenty four samples of the kidney were taken at the Olymel Slaughter house and brought back to the laboratories of McGill University where they were digested at 500^{o}C, using sulphuric acid and hydrogen peroxide and analyzed for heavy metals using Inductively Coupled Plasma (ICP) analysis (Varian, VISTA-MPX, CCD Simultaneous: ICP-OES, Australia Pty. Ltd.) .

5.3.4 Statistical analysis

Body weight, body weight gain, feed intake, feed conversion ratio, carcass quality and heavy metal concentration released in the liver, kidney, and muscle were analyzed by ANOVA with the mixed model procedure in SAS (1999) using a factorial models. Bodyweight, body weight gain, and carcass quality were measurements taken on individual pigs. Feed intake, feed conversion ratio, protein intake, and protein conversion ratio were measurements taken on the pens. The statistical models are described as follows:

5.3.4a Final statistical models for overall analysis

1. Body weight and body weight gain models

$Y_{ijklmnop} = \mu + room_i + row_{ij} + pro_k + zeo_l + sex_m + week_n + pro\cdot zeo_{kl} + pro\cdot sex_{km} + pro\cdot week_{kn} + zeo\cdot sex_{lm} + zeo\cdot week_{ln} + sex\cdot week_{mn} + pro\cdot zeo\cdot sex_{klm} + pro\cdot zeo\cdot week_{kln} + pro\cdot sex\cdot week_{kmn} + zeo\cdot sex\cdot week_{lmn} + pro\cdot zeo\cdot sex\cdot week_{klmn} + pig_{ijklmno} + e_{ijklmnop}$

2. Feed intake, feed conversion rate

$Y_{ijklmn} = \mu + room_i + row_{ij} + pro_k + zeo_l + week_m + pro\cdot zeo_{kl} + pro\cdot week_{km} + zeo\cdot week_{lm} + pro\cdot zeo\cdot week_{klm} + e_{ijklmn}$

5.3.4b Final statistical models for weekly analysis

1. Body weight and body weight gain models

$Y_{ijklmno} = \mu + room_i + row_{ij} + pro_k + zeo_l + sex_m + pro\cdot zeo_{kl} + pro\cdot sex_{km} + zeo\cdot sex_{lm} + pro\cdot zeo\cdot sex_{klm} + pen_{ijkln} + e_{ijklmno}$

5.3.4c Feed intake, feed conversion rate models

$Y_{ijklm} = \mu + room_i + row_{ij} + pro_k + zeo_l + pro\cdot zeo_{kl} + e_{ijklm}$

5.3.4d Carcass quality model (fat percentage, muscle percentage, and carcass index)

$Y_{ijklmno} = \mu + room_i + row_{ij} + pro_k + zeo_l + sex_m + pro\cdot zeo_{kl} + pro\cdot sex_{km} + zeo\cdot sex_{lm} + pro\cdot zeo\cdot sex_{klm} + pen_{ijkln} + e_{ijklmno}$

5.3.4e Heavy metal concentration in liver, kidney, and muscle

$Y_{ijkl} = \mu + pro_i + zeo_j + sex_k + e_{ijkl}$

NOTE: insufficient samples to conduct a factorial analysis

5.3.4f Parameters of the models

Y = Dependent observation

μ = overall mean

$room_i$ = the fixed effect of the i^{th} room (i = 1,2)
row_{ij} = the fixed effect of the i^{th} row in the j^{th} room (i = 1,2; j = 1,2).
pro_k = the fixed effect of the k^{th} protein level (k = H, L) zeo_l = the fixed effect of the l^{th} zeolite supplementation level (l = 0,2,4,6)
sex_m = the fixed effect of pig gender (m = M, F).
$week_n$ = the fixed effect of week (n = 0, 2, 4, 6 , 8, 10)
e_{ijkl}, e_{ijklm}, e_{ijklmn}, $e_{ijklmno}$, $e_{ijklmnop}$ = residual error

5.3.5 Animal care

The study was approved by the Macdonald Campus Animal Care Committee (Appendix A) and animals were cared for in accordance with the guidelines of the Canadian Council on Animal Care (1993).

5.4 Results and Discussion

5.4.1 Pig Performance

The pigs appeared to be healthy and readily consumed their feed allocation throughout the entire data collection period which lasted 10 weeks. The effect of the room was analyzed for body weight, body weight gain, feed conversion rate and feed intake. Tables 5.4 to 5.7 show that placing the pigs in two different rooms with identical environmental conditions had a significant impact on the final body weight of the pigs, overall body weight gain, and feed intake. The fact that the pigs in room 2 performed significantly better ($P < 0.05$) than pigs in room 1 can be attributed to the use of room 1 to ship out various pigs from the barn (pigs not in this experiment), every Tuesday. This was standard practice at the Macdonald Campus Swine Unit. This caused a mixing type of effect to take place, between pigs being transported and pigs participating in this feed trail and undoubtedly caused undue stress on the pigs being housed in the first room. Pigs under stress have been reported by researchers as having significantly lower average daily gains, live body weights and altered feed patterns than pigs under stress free conditions (Hyun et al. 1998; Ekkel et al. 1995).

The effect of the different rows within the rooms and zeolite and on body weight, body weight gain, feed conversion rate and feed intake was analyzed and found to have no significant effect on any of the pig performance parameters. The effect of sex, week and protein all had a significant effect on body weight, body weight gain, feed intake, and feed conversion rate. These results were expected since it is a well known fact that sex, protein and time (week) all have a significant impact on the growth of living organisms such as pigs.

5.4.2 Effect of Zeolite on Pig Performance

On a biweekly basis, zeolite supplementation had no significant effect ($P > 0.05$) on pig performance (body weight, body weight gain, feed intake and feed conversion rate) within the high C.P. (crude protein) and energy group (Table 5.4 to 5.7). Within the low C.P. and energy group, the pigs fed the 4% zeolite diet (L4) had a significantly ($P < 0.05$) greater body weight than pigs on the 2% zeolite diet (L0) on week six (Table 5.4). In terms of body weight gain, feed intake and feed conversion rate, there were no significant differences amongst the different treatments (interaction between high and low protein diets supplemented with 0, 2, 4 or 6% zeolite) used throughout this experiment ($P > 0.05$).

Table 5.4 also shows that from the start of the experiment until week 6, pigs on the L4 ration consistently performed better than the pigs on the L0 and L2 ration though not statistically significant ($P > 0.05$). Significant differences ($P < 0.05$) were not seen until week 6 between the L4 and L2 rations. However, on week 6 the starter ration was substituted for a grower ration which contained less protein. This change had an effect on hog performance, and reduced the differences in body weight between pigs on the L4 and L2 rations. Differences in body weights remained and continued to increase throughout weeks 8 and 10, though not statistically significant ($P > 0.05$).

Interestingly, no significant differences ($P>0.05$) in feed intake (Table 5.6) amongst treatments (protein by zeolite interaction) was observed throughout this experiment, meaning that pigs on the L4 ration ate the same amount of feed as the pigs on the L0, L2, and L6 rations but ended up having a greater body weight at week 6 compared to pigs on the other rations. Therefore, zeolite supplementation had some beneficial effect on body weight and nutrient ingestion.

On a biweekly basis and for all pig performance factors, no significant difference was found between rations H0 and L0, although all pigs on the H0 ration performed better than those on the L0 ration. But, in the overall results, there were significant differences in feed conversion rate (Table 5.7) including that between pigs on the L0 ration, compared to those on the H0 rations.

The overall analysis of feed conversion rate (Table 5.7) did produce interesting results. It was found that pigs fed the H0, H2, and H6 diets all had a statistically better feed conversion rate ($P < 0.05$) than pigs on the L0, L2 and L6 diets, which was to be expected since they were fed a higher level of protein. However, pigs on the H0, H2 and H6 diets failed to produce significantly better ($P > 0.05$) feed conversion rates than pigs fed the L4 diet, when the L4 ration offered 8 and 10% less C.P. and energy than any of the H ration. Also, pigs fed the H4 ration had the best feed conversion rate out of all 8 rations and had a significantly better feed conversion rate ($P < 0.05$) than pigs fed L0, L2, L4 or L6 rations. These findings indicate that supplementing pig diets at the 4% zeolite inclusion level allows pigs to utilize feed more efficiently for growth. Table 5.8 shows a trend between final body weight to total feed consumption, for each treatment. Pigs receiving diets H4 and L4 had the highest final body weight to feed consumption ratio, within their respective protein groups. Furthermore, H4 had the highest ratio out of all 8 different treatments. The amount of protein and energy that was consumed by the pigs was adjusted to account for lower protein and energy diet (92% C.P. and 90% energy of the high protein and energy diet). From the analysis (Table 5.8) it was observed that hogs on the H0, H6 and L6 diets had almost identical final body weights compared to hogs fed the L4 ration, however hogs on the H0, H6 and L6 rations had to consume more crude protein and energy to achieve this body weight. This data suggests that zeolite supplemented at the 4% level helps pigs utilize nutrients more efficiently for growth.

Contradictory results have been obtained from researchers who have fed zeolite to swine. Shurson et al. (1984) found that feeding clinoptilolite at 0.5% did not significantly effect average daily gain, average daily feed intake and feed/gain ratio. However, when feeding clinoptilolite at 5% level, in a second trial, feed/gain ratio was significantly improved ($P < 0.02$) over the control diet containing no zeolite. Pond and Yen (1982) found that supplemented pig diets with % and 10% clinoptilolite at 5 and 10% had no effect on weight gain or gain/feed values obtained with animals fed a basal diet.

The findings of Shurson et al. (1984) correspond to the present findings indicating that clinoptilolite has a significant effect on pig feed conversion when fed at a level ranging between 2 and 6%. Pond and Yen (1982) found non significant improvement in feeding 5 and 10% zeolite (85% clinoptilolite) and the same amount of C.P. and energy, to hogs weighing from 15 to 45kg, and 15 to 75kg. These findings correspond to the present results obtained with the rations H4 and H6 compared to H0 indicating that, to get an advantage with feeding zeolite, the feed content has to be lowered to compensate for the great nutrient ingestion.

5.4.3 Carcass Quality

Carcass fat percentage (Table 5.9) was significantly affected by zeolite ($P < 0.01$) and sex ($P < 0.0001$) but not by room, row within rooms or protein levels ($P < 0.05$). All the interactions tested for did not show any significance ($P > 0.05$). There were no significant effects on muscle percentage ($P > 0.05$). Female pigs were found to have significantly less ($P < 0.0001$) fat % than male pigs, and as a result ended up with a significantly better ($P < 0.0001$) carcass index (Table 5.10). Pigs supplemented 0 and 2% zeolite in their diet, regardless of C.P. and energy levels, had significantly ($P < 0.05$) less fat than pigs supplemented 4 and 6% zeolite. Therefore, supplementing more than 2% zeolite can lead to fat % in carcasses ($P < 0.05$) in diets containing similar C.P. and energy levels of this experiment. This means that zeolite may have a greater impact on energy digestion, compared to protein.

Carcass index (Table 5.10) was significantly affected by zeolite ($P < 0.01$), sex ($P < 0.0001$) and room ($P < 0.05$), but not by row within rooms ($P > 0.05$) and protein ($P > 0.05$). Room 2 had a better carcass quality index than room 1, most likely due to the stress experienced by pigs in room 1 (as discussed in the pig performance section of the results and discussion). The dietary treatments (high and low C.P. and energy diets supplemented with 2, 4 or 6% zeolite) did not significantly affect the carcass index compared to the pigs fed 0% zeolite ($P > 0.05$).

Pigs fed diets supplemented with zeolite at the 2% inclusion level had the best carcass index (Table 5.10), for both low and high C.P. and energy, although not statistically different from those fed at the 0 and 4% inclusion level but statistically better than pigs fed at the 6% inclusion level ($P < 0.05$) . Beyond 2% zeolite supplementation, a trend of decreasing carcass index was observed (Table 5.10), most likely due to increased fat percentage (Table 5.9). This suggests that zeolite would have a greater effect on energy compared to protein ingestion. Therefore, zeolite supplementation requires not only the adjustment of C.P. in the diet, but also the balancing of C.P. to energy.

Other swine feeding studies reported contradictory results on carcass quality. Pearson et al. (1985) and Coffey and Pilkington (1989) found that feeding clinoptilolite to swine at the level of 4 to 8% and 0.2 to 0.6%, respectively, did not alter carcass characteristics in anyway. However, Ward et al. (1991) found that with the inclusion of sodium zeolite-A at the 0.5% level, carcass length was significantly increased ($P < 0.06$).

In this study, 2% zeolite supplementation optimized carcass index, compared to the other levels of supplementation. However, if carcass fat % is not a concern then 4% zeolite supplementation is suitable. This reinforces the fact that clinoptilolite may have a greater impact on energy digestion, compared to protein. Thus, for the effective use of 4% clinoptilolite supplementation, not only should lower C.P. and energy levels be fed but lower than standard energy to C.P. ratios should be used.

5.4.4 Heavy metal release

Samples of the liver, kidney and muscle were taken from the pigs at the Olymel slaughterhouse and analyzed for macro-nutrients and heavy metal content, to measure the effect of feed protein and zeolite level, and animal sex. From the minerals tested, (Al, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, and Zn), there was a significantly greater effect ($P < 0.05$) for Co level in the muscle tissue and for Zn level ($P < 0.05$) in the liver tissue for the pigs fed the low C.P. and energy diets than pigs fed the high C.P. and energy diet.

Significantly different heavy metal concentrations were found in pigs fed the high and low protein diet, as those the pigs on the low C.P. and energy diet consumed more feed than those on the high C.P. and energy diet, thus also consuming more zeolite.

However, zeolite supplementation even at 6% had no significant effect ($P > 0.05$) on tissue heavy metal content. Thus, zeolite was found to play any role in tissue mineral and heavy metal content, indicating an insignificant release of such elements during the digestion process.

These results agree with those found by Pond et al. (1988) who found that the addition of 2% clinoptilolite to pig diets did not significantly affect Al, Ca, Cu, Fe, Mg, Mn, Na, Zn concentrations in the liver.

5.4.5 Ameliorative effects of clinoptilolite

Pearson et al. (1985) reported that the addition of clinoptilolite to the diet of pigs did not significantly improve their growth performance and carcass quality, citing the fact that disease-control effect is a widely accepted explanation for the growth responses observed in pigs after the inclusion of antibiotics, such as zeolites. The reports of marked growth responses (34%) with inclusion of clinoptilolite in the diet of growing pigs (Cool and Willard 1982) suggest that clinical disease was being controlled by the additive and that the response in growth rate was not strictly a true growth-promoting effect.

In the majority of studies where dietary zeolites have improved pig performance, (Cool and Willard 1982), the control pigs had significantly more water in their feces ($P < 0.02$). The ameliorative effects of clinoptilolite was also reported by Vrzgula and Bartko (1984) who observed that pigs having diarrhea, after having been given a feed mixture supplemented with clinoptilolite, produced compact feces after 48 hours and the appetite of the pigs became normal, and they began to gain weight normally. In contrast, diarrheic pigs in a control group continued to scour and lose weight.

During the entire course of this feed trial, the pigs appeared to be healthy and showed no visible signs of diarrhoea or any other adverse health symptoms over other pigs receiving zeolite. This could also explain why less significant differences were observed in pig performance, as compared to other trials.

5.4.6 Tail biting

Tail biting did occur amongst 4 pigs in this feed trial in pens receiving L0, L6 and H2 diets. Fortunately, this phenomenon occurred after the data collection period (week

10). Schrøder-Petersen and Simonsen (2001) have cited factors such as gender, age and weight, rearing environment, absence of rooting materials, indoor and outdoor climate and feed type as some of the factors which trigger tail biting. Since tail biting was observed in a pen which received a 0% zeolite diet (L0), it is highly improbable that feeding zeolite contributed to tail biting, although a pig(s) from one of the adjacent pens could have been responsible for the biting.

During this experiment, indoor and outdoor climate was not a factor since both rooms in which the pigs were housed were temperature controlled. This was in the summer time and when fall comes, room temperature falls. Schrøder-Petersen and Simonsen (2001) also cite the fact that tail biting is more frequent in pigs 130 days old, which was approximately the age of the pigs when severe tail biting occurred. Pigs housed on slatted floors have been reported as having a 27% increase in incidences of tail biting as opposed to pigs housed on concrete floors (Schrøder-Petersen and Simonsen 2001). This evidence suggests that zeolite did not play a role in the promotion of tail biting, although more detailed research is required.

5.4.7 Feeder jams

Feeder jams occur when a pig(s) urinates or defecates inside the trough of the feeder, which when mixed with the feed, forms a solid lump clogging and impeding flow of fresh feed. Since fresh feed is unable to flow from the reservoir to the trough, the trough is left devoid of food until the feeder is ‘un-jammed’. In this experiment, feeder jams of significant proportion started as early as day 29 (week 4) and increased in frequency as the pigs matured and grew in size, which added variablility to the feed intake and feed conversion rate data.

Pen inspections were carried out at the end of each day, implying that less than 16h was spent before a pen would have gone without feed. The effect of such feeder jams on body weight and feed intake was not measured. However, these feeder jams may have add an impact on the variability of the data.

5.5 Conclusions

The results obtained from this feed trial indicate that zeolite supplementation, with KMI (Nevada, USA) zeolite at the 4% inclusion level (supplied by Lyrco Nutrition, Inc.; St-Valérien de Milton, PQ) showed the most potential for improving body weights and feed conversion rate of pigs. When feeding the low protein diet supplemented with 4% zeolite (L4), a statistically greater ($P < 0.05$) body weight of pigs over those supplemented with 2% zeolite (L2) in the same protein group on week 6 was observed. Pigs on the low protein and 4% zeolite feed consistently performed better than pigs on L0 and L2 rations in terms of body weight throughout the entire experiment. There were no significant differences observed in the amount of feed consumed by the pigs on the L4 ration versus any of the other rations (L0, L2, and L6) which suggests a real beneficial effect of nutrient utilization. Supplementing pig diets with 4% zeolite is also beneficial for feed conversion rate. Pigs on the H4 ration showed the best feed conversion rate while pigs fed the L4 ration did not statistically have a lower feed conversion rate than pigs fed the H0, H2 and H6 rations. These findings clearly indicate that feeding zeolite at the 4% inclusion level improves nutrient utilization of pigs for growth.

Feeding zeolite at the 4% inclusion level to pigs did not significantly ($P > 0.05$) alter carcass index from ‘zeolite-free’ pigs. The zeolite used in this experiment (KMI, Nevada, USA) also did not significantly ($P > 0.05$) contribute to heavy metal concentrations in the liver, kidney or muscle tissue.

From the feed trial carried out, it can be seen that supplementing standard pig diets with zeolite at the 4% inclusion level shows some potential for improving nutrient utilization in swine without significantly reducing carcass index and increasing heavy metal concentrations in the liver, kidney and muscle tissue, making zeolite a suitable feed additive for nutrient reduction.

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Table 5.1: Experimental feed composition

			Starter (20-50kg)		Grower (50-80kg)		Finisher (50-80kg)	
Diet	Feed Name	Zeolite Level (%)	Protein Level (%)	Energy Level (kcal/kg)	Protein Level (%)	Energy Level (kcal/kg)	Protein Level (%)	Energy Level (kcal/kg)
1	HO	0	17.2	3450	15.5	3450	14	3450
2	H2	2	17.2	3450	15.5	3450	14	3450
3	H4	4	17.2	3450	15.5	3450	14	3450
4	H6	6	17.2	3450	15.5	3450	14	3450
5	L0	0	15.5	3200	14.4	3200	13	3200
6	L2	2	15.5	3200	14.4	3200	13	3200
7	L4	4	15.5	3200	14.4	3200	13	3200
8	L6	6	15.5	3200	14.4	3200	13	3200

Note: the ration was made mainly of soybean meal and corn.

Table 5.2: Particle size analysis of feed[a]

Sieve Size (mm)	% of feed particles	Std Dev
1	45.49	1.37
0.84	5.33	1.51
0.5	13.74	4.26
0.295	8.62	2.41
0.25	1.89	0.32
0	12.03	1.30

[a] = average of 4 values

Table 5.3: Bulk compostion of zeolite (weight%)

Element	Weight (%)
Quartz (SiO_2)	Trace-1
Plagioclase ($NaAlSi_3O_8$ - $CaAl_2Si_2O_8$)	Trace-1
Calcite ($CaCO_3$)	1
Dolomite ($[CaMg]CO_3$)	Trace-1
Clinoptilolite ($KNa_2Ca_2(Si_{28}Al_7)O_{72}\cdot24H_2O$)	97-98
Opal (SiO_2 .nH_20)	0
Muscovite/Illite ($KAl_2[AlSi_3O_{10}][OH]_2$)	0

Table 5.4: Body weight analysis (kg)

	Week											
	0		2		4		6		8		10	
Effect	LS Means	SE	LS Means	SE	LS Means	SE	LS Means	SE	LS Means	SE	LS Means	SE
Pro·Zeo												
H 0	23.904^{a}	0.237	35.696^{a}	0.376	47.050^{a}	0.723	61.079^{abcde}	0.704	71.129^{a}	0.992	83.558^{a}	1.072
H 2	24.808^{a}	0.237	36.108^{a}	0.376	47.529^{a}	0.723	61.683^{ae}	0.704	72.267^{a}	1.011	84.949^{a}	1.096
H 4	24.167^{a}	0.237	35.829^{a}	0.376	48.421^{a}	0.723	61.500^{c}	0.704	72.496^{a}	0.992	84.921^{a}	1.072
H 6	23.721^{a}	0.237	35.704^{a}	0.376	48.029^{a}	0.723	60.658^{abcde}	0.704	71.154^{a}	0.992	83.741^{a}	1.072
L 0	23.804^{a}	0.237	34.704^{a}	0.376	46.158^{a}	0.723	58.683^{abcde}	0.461	68.008^{a}	0.744	80.208^{a}	1.072
L 2	23.558^{a}	0.237	34.579^{a}	0.376	45.912^{a}	0.723	58.133^{bd}	0.461	69.675^{a}	0.744	81.35^{a}	1.072
L 4	24.146^{a}	0.237	35.550^{a}	0.376	47.754^{a}	0.723	60.658^{e}	0.461	70.600^{a}	0.744	83.592^{a}	1.072
L 6	24.079^{a}	0.237	35.650^{a}	0.376	47.941^{a}	0.723	60.238^{abcde}	0.461	70.971^{a}	0.744	83.232^{a}	1.096
Room												
1	23.834	0.118	35.085^{f}	0.188	46.699^{f}	0.362	59.759^{f}	0.292	70.119^{f}	0.436	82.403^{f}	0.539
2	24.032	0.118	35.870^{g}	0.188	48.000^{g}	0.362	60.899^{g}	0.292	71.457^{g}	0.434	83.977^{g}	0.539

^{abcde} = values with different letters differ significantly from one another within Pro·Zeo interaction effect and week ($P<0.05$)

^{fg} = values with different letters differ significantly from one another within Room effect and week ($P<0.05$)

Pro·Zeo = protein by zeolite interaction

H, L = high and low protein diet, respectively

0, 2, 4, 6 = zeolite % supplementation

LS Means = least square means

SE = Standard Error

NOTE: Feed change at week 6 (starter to grower)

NOTE: Measurement taken on individual pigs

Table 5.5: Body weight gain analysis (kg)

	Week											
	2		4		6		8		10		Overall	
Effect	LS Means	SE	LS Means	SE	LS Means	SE	LS Means	SE	LS Means	SE	LS Means	SE
Pro·Zeo												
H 0	11.791^{a}	0.232	11.354^{a}	0.557	14.029^{a}	0.591	10.050^{a}	0.526	12.429^{a}	0.473	11.931^{a}	0.295
H 2	12.021^{a}	0.232	11.421^{a}	0.557	14.154^{a}	0.591	10.522^{a}	0.530	12.676^{a}	0.483	12.160^{a}	0.303
H 4	11.663^{a}	0.232	12.592^{a}	0.557	13.079^{a}	0.591	10.996^{a}	0.526	12.425^{a}	0.473	12.151^{a}	0.267
H 6	11.983^{a}	0.232	12.325^{a}	0.557	12.629^{a}	0.591	10.496^{a}	0.526	12.588^{a}	0.473	12.004^{a}	0.291
L 0	10.900^{a}	0.232	11.454^{a}	0.557	12.525^{a}	0.591	9.325^{a}	0.526	12.200^{a}	0.473	11.281^{a}	0.295
L 2	11.021^{a}	0.232	11.333^{a}	0.557	12.221^{a}	0.591	11.542^{a}	0.526	11.675^{a}	0.473	11.558^{a}	0.302
L 4	11.404^{a}	0.232	12.204^{a}	0.557	12.904^{a}	0.591	9.942^{a}	0.526	12.992^{a}	0.473	11.889^{a}	0.267
L 6	11.571^{a}	0.232	12.292^{a}	0.557	12.296^{a}	0.591	10.733^{a}	0.526	12.350^{a}	0.483	11.849^{a}	0.292
Room												
1	11.251^{b}	0.116	11.614	0.279	12.874	0.296	10.459	0.263	12.356	0.234	11.534^{b}	0.125
2	11.838^{c}	0.116	12.130	0.279	13.085	0.296	10.446	0.263	12.471	0.234	12.172^{c}	0.125

^{a} = values with different letters differ significantly from one another within Pro·Zeo interaction effect and week ($P<0.05$)

^{bc} = values with different letters differ significantly from one another within Room effect and week ($P<0.05$)

Pro·Zeo = protein by zeolite interaction

H, L = high and low protein diet, respectively

0, 2, 4, 6 = zeolite % supplementation

LS Means = least square means

SE = Standard Error

NOTE: Feed change at week 6 (starter to grower)

NOTE: Measurement taken on individual pigs

Table 5.6: Feed intake analysis (kg)

	Week											
	2		4		6		8		10		Overall	
Effect	LS Means	SE	LS Means	SE	LS Means	SE	LS Means	SE	LS Means	SE	LS Means	SE
Pro·Zeo												
H 0	21.350^{a}	0.403	26.025^{a}	0.658	31.250^{a}	0.715	30.175^{a}	0.749	35.150^{a}	0.888	28.790^{abcd}	0.433
H 2	21.800^{a}	0.403	26.675^{a}	0.658	31.150^{a}	0.715	31.350^{a}	0.749	35.175^{a}	0.888	29.230^{abcd}	0.433
H 4	21.075^{a}	0.403	27.000^{a}	0.658	30.500^{a}	0.715	30.800^{a}	0.749	35.775^{a}	0.888	29.030^{a}	0.433
H 6	21.275^{a}	0.403	26.650^{a}	0.658	29.875^{a}	0.715	30.000^{a}	0.749	36.200^{a}	0.888	28.800^{ac}	0.433
L 0	21.500^{a}	0.403	28.475^{a}	0.658	31.500^{a}	0.715	30.925^{a}	0.749	37.850^{a}	0.888	30.050^{abcd}	0.433
L 2	21.175^{a}	0.403	28.250^{a}	0.658	32.475^{a}	0.715	34.000^{a}	0.749	39.025^{a}	0.888	30.985^{abcd}	0.433
L 4	22.100^{a}	0.403	28.850^{a}	0.658	32.075^{a}	0.715	31.650^{a}	0.749	38.325^{a}	0.888	30.600^{abcd}	0.433
L 6	23.000^{a}	0.403	29.250^{a}	0.658	33.125^{a}	0.715	32.950^{a}	0.749	39.625^{a}	0.888	31.590^{b}	0.433
Room												
1	21.181^{e}	0.201	26.975^{e}	0.329	30.894^{e}	0.357	31.450	0.374	36.569	0.444	29.402^{e}	0.215
2	22.138^{f}	0.201	28.319^{f}	0.329	32.094^{f}	0.357	31.513	0.374	37.713	0.444	30.367^{f}	0.215

^{abcd} = values with different letters differ significantly from one another within Pro·Zeo interaction effect and week (P<0.05)

^{ef} = values with different letters differ significantly from one another within Room effect and week (P<0.05)

Pro·Zeo = protein by zeolite interaction

H, L = high and low protein diet, respectively

0, 2, 4, 6 = zeolite % supplementation

LS Means = Least square means

SE = Standard error

NOTE: Feed change at week 6 (starter to grower)

NOTE: Measurements taken on pens (6 pigs per pen: 3 male and 3 female)

Table 5.7: Feed conversion rate analysis

	Week											
	2		4		6		8		10		Overall	
Effect	LS Means	SE	LS Means	SE	LS Means	SE	LS Means	SE	LS Means	SE	LS Means	SE
Pro·Zeo												
H 0	1.810^{ad}	0.028	2.320^{a}	0.089	2.240^{a}	0.088	3.005^{a}	0.106	2.830^{ab}	0.091	2.441^{ac}	0.031
H 2	1.815^{ad}	0.028	2.368^{a}	0.089	2.210^{a}	0.088	3.000^{a}	0.106	2.795^{a}	0.091	2.438^{ac}	0.031
H 4	1.808^{ad}	0.028	2.140^{a}	0.089	2.332^{a}	0.088	2.805^{a}	0.106	2.888^{ab}	0.091	2.395^{a}	0.031
H 6	1.775^{a}	0.028	2.163^{a}	0.089	2.365^{a}	0.088	2.868^{a}	0.106	2.878^{ab}	0.091	2.410^{ac}	0.031
L 0	$1.975^{b(d)e}$	0.028	2.495^{a}	0.089	2.520^{a}	0.088	3.335^{a}	0.106	3.105^{ab}	0.091	2.686^{bd}	0.031
L 2	1.920^{abc}	0.028	2.508^{a}	0.089	2.685^{a}	0.088	2.983^{a}	0.106	3.360^{b}	0.091	2.691^{bd}	0.031
L 4	1.938^{bd}	0.028	2.365^{a}	0.089	2.488^{a}	0.088	3.190^{a}	0.106	2.950^{ab}	0.091	2.586^{cd}	0.031
L 6	$1.990^{(b)ce}$	0.028	2.380^{a}	0.089	2.708^{a}	0.088	3.080^{a}	0.106	3.215^{ab}	0.091	2.675^{bd}	0.031
Room												
1	1.885	0.014	2.338	0.044	2.413	0.044	3.024	0.053	2.964	0.046	2.537	0.013
2	1.873	0.014	2.346	0.044	2.474	0.044	3.043	0.053	3.041	0.046	2.543	0.013

^{abcde} = values with different letters differ significantly from one another within week ($P < 0.05$)

(d) =remove when comparing H0 and H4 with L0

(b) = include when comparing L4 and L6

Pro·Zeo = protein by zeolite interaction

H, L = high and low protein diet, respectively

0, 2, 4, 6 = zeolite % supplementation

LS Means = Least square means

SE = Standard error

NOTE: Feed change at week 6 (starter to grower)

NOTE: Measurements taken on pens (6 pigs per pen: 3 male and 3 female)

Table 5.8: Final body weight (kg) to total feed consumption (kg) ratio, crude protein ratio and energy ratio

Pro·Zeo	Total feed consumption (kg)	Final weight (kg)	Final weight to total feed ratio	C.P. ratio	Energy ratio
H0	215.8	83.6	2.42	1.02	1.05
H2	217.4	84.9	2.44	1.02	1.04
H4	218.9	84.9	2.44	1.03	1.05
H6	215.6	83.7	2.42	1.02	1.05
L0	206.9	80.2	2.21	0.99	0.99
L2	209.2	81.4	2.19	1.01	1.01
L4	214.9	83.6	2.28	1.00	1.00
L6	213.9	83.2	2.21	1.02	1.02

Pro·Zeo = Protein by Zeolite interaction

C.P. = Crude protein

Table 5.9: Analysis of the effect of sex and zeolite on carcass fat percentage carried out by Olymel Slaughter house (Princeville, PQ)

Sex	LS Means	SE	Zeo	LS Means	SE
F	16.783^{a}	0.508	0	17.355^{a}	0.750
M	21.096^{b}	0.502	2	18.059^{ad}	0.683
-	-	-	4	19.942^{bd}	0.594
-	-	-	6	20.402^{bc}	0.664

Table 5.10: Analysis of the effect of room, sex and zeolite on carcass index carried out by Olymel Slaughter house (Princeville, PQ)

Room	LS Means	SE	Sex	LS Means	SE	Zeo	LS Means	SE
1	3.344^{a}	0.156	F	2.687^{a}	0.115	0	2.930^{ab}	0.171
2	2.942^{b}	0.104	M	3.581^{b}	0.114	2	2.893^{a}	0.156
-	-	-	-	-	-	4	3.316^{ab}	0.136
-	-	-	-	-	-	6	3.343^{b}	0.152

^{ab} = values with different letters differ signficnantly from one another

LS Means = Least square means

SE = Standard error

F = Female

M = Male

0, 2, 4, 6 = zeolite % supplementation

NOTE: Smaller carcass index numbers = better carcass quality

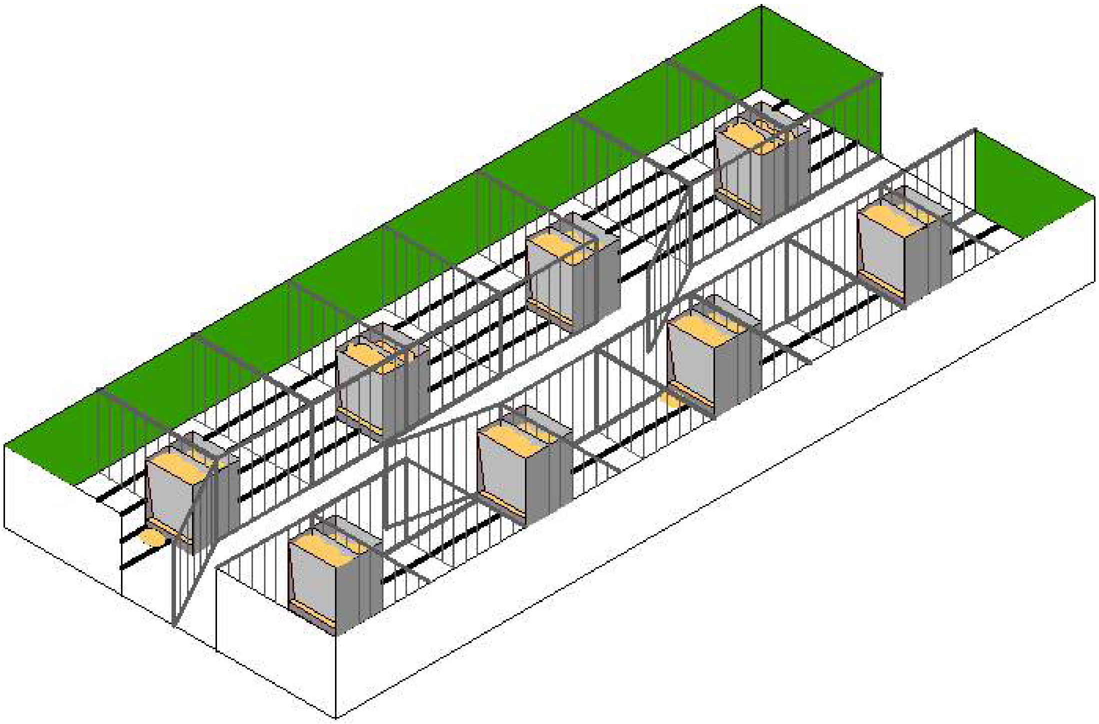

Figure 5.1: Feed room layout
NOTE: Both rooms in the Macdonald Campus Swine Unit had the exact same layout.

VI. GENERAL DISCUSSION AND CONCLUSIONS

Clinoptilolite is a species of zeolite which shows great potential as a feed additive for standard pig diets for the purpose of reducing nutrient excretion, due to their high cation exchange capacity, molecular sieving properties, and stability under high temperatures and acidity (conditions found inside the pig's stomach). Therefore zeolite could reduce nutrient overloading and some of the harmful environmental impacts associated with intensive swine operations. Zeolite's natural formation, occurrence and abundance all over the world also make its distribution feasible and economical. Thus experiments were carried out to characterize the chemical and physical properties of zeolite from different geographic sources for the purposes of nutrient reduction as a feed additive in pig diets. From these experiments an appropriate zeolite was used to supplement standard pig diets at an inclusion rate of 0, 2, 4, and 6% for a standard farrow-to-finish swine operation to test the feasibility of using zeolite as a dietary supplement and to determine optimal zeolite supplementation levels.

Chemical characterization of zeolite consisted in measuring NH_4^+ adsorption capabilities, and desorption of macro minerals on heavy metals of different types of zeolite under a neutral pH and temperature of 22^oC, as well as under a pH of 1.5 and a temperature of 39^oC, simulating conditions found inside the stomach of a pig. Due to the slightly higher clinoptilolite content, KMI zeolite was compared to Steel Head zeolite and a commercial grade zeolite of poor clinoptiolite content. KMI zeolite slightly out performed Steel Head zeolite in terms of NH_4^+ adsorption capabilities and under acidic conditions released a lower percentage of 4 out of 6 minerals (Al, Cu, Fe, and Pb) compared to the commercial grade zeolite. With the exception of Al released after 24hrs, the KMI clinoptilolite was lower than the level of heavy metals considered toxic to swine (National Academy of Science and Agriculture Canada). Even if KMI zeolite was fed to hogs at a level as high as 6%, it is expected that the amounts of heavy metals released after 24h, even for Al, would not be high enough to exceed the toxicity threshold.

The bulk shear tests carried out for the physical characterization of the zeolite indicated that neither particle size nor moisture content (between 0 and 10%) significantly affected internal angle of friction, a measure of inter particle forces. A measure of the angle of wall friction was also carried out, in order to investigate the forces between the zeolite and a piece of galvanized steel, a material commonly used in storage bins. Looking at these two results together showed that no matter how steep the hopper angle of the storage bin, funnel flow should be expected. Therefore particle size and moisture content (between 0 and 10%) had no effect on the flow properties of zeolite.

Zeolite showed favourable chemical and physical characteristics in the laboratory. However, it was important to find out how pigs being managed under standard farrow-to-finish practices would perform if fed this material. If the pigs responded poorly to zeolite (body weight, body weight gain, feed intake, feed conversion rate, and carcass quality) or showed a build up or elevated concentrations of heavy metals in their organs and tissues after slaughter, this product would not be viable as a feed additive since producers would not use this product no matter how efficient the manure nutrient removal. Therefore, a feed trial was carried out to determine how supplementing standard pig diets (high and low protein) at the zeolite inclusion level of 0, 2, 4 and 6% levels to pigs in a typical farrow-to-finish operation would impact pig performance (body weight, body weight gain, feed intake and feed conversion rate), carcass quality, and heavy metal concentrations in the liver, kidney and muscle tissue. From this feed trial, pigs given a low protein diet and zeolite supplementation of 4% performed better, in terms of body weight than other pigs within the low protein group supplemented 0, 2, or 6% zeolite.

This finding may suggest that these pigs utilized minerals within their feed more efficiently for growth. If this is the case, one would expect to find less phosphorus and definitely less nitrogen in their manure. Also, pigs on the low protein ration and 4% zeolite supplementation did not statistically consume more feed than the pigs fed the same low protein ration on the 0, 2, and 6% zeolite supplementation level, but gained as much weight. Therefore, supplementing a low protein pig diet, such as the one used in this experiment, with 4% zeolite shows potential for nutrient reduction. It was also shown that the best feed conversion rates were produced in pigs supplemented 4% zeolite in their diets. This indicates that nutrient digestion is more efficient for the purposes of weight gain when pig diets are supplemented 4% zeolite.

From the carcass index evaluation, pigs on the 2% zeolite supplementation showed the best carcass index. There was a trend of decreasing carcass index as zeolite supplementation increased beyond 2%. However, the carcass index of pigs 4% zeolite was not significantly different ($P > 0.05$) from pigs fed 2% zeolite. Carcass index of pigs fed the 2% supplementation level produced significantly better ($P < 0.05$) carcasses than pigs on 6% zeolite supplementation. This indicates that the threshold for zeolite supplementation lies between 4 and 6% before carcass index of the pigs significantly deteriorates. Samples of the liver, kidney and muscle tissues were taken from the carcases at the abattoir and analyzed for heavy metal concentrations (Al, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, and Zn). There were no significant differences in heavy metal concentrations between ($P > 0.05$) pigs fed zeolite at the 2, 4 and 6% inclusion level and pigs fed no zeolite. This feed trial has shown that zeolite can be used in the supplementation of pig diets at the 4% inclusion level giving better feed conversion rates without adversely affecting carcass quality or heavy metal concentrations in the liver, kidney and muscle tissue.

These experiments have demonstrated that zeolite is definitely a viable mineral for feed supplementation of pig diets in order to remedy the environmental impacts of swine manure, both in terms of physical and chemical properties in theory and in practice. Using this feed additive would benefit the environment as well as be advantageous for swine producers since it has shown the potential to improve pig performance through more efficient use of nutrients. In theory, this would result in lowered concentrations of nitrogen and phosphorus in the manure, alleviating the environmental impacts associated with swine operations, in particular nutrient over loading and odour.

The results obtained from these experiments have built a foundation from which further research may be carried out. In the bulk shear experiments moisture contents greater than 10% should be used to investigate its effect on angle of internal friction. Also, different silo wall materials should be used in determining angle of wall friction. During the feed trial various limitations did not allow for any nutrient concentration measurements of nitrogen and phosphorus in manure samples. Measuring these properties is crucial to research involving zeolite as a dietary supplement as a means of nutrient reduction. Quantifying ammonia gas also needs to be carried out along with a complete odour panel in order to asses the effect of zeolite on odourous compounds. Due to the strict regulations that govern feed companies the feed used in this experiment could not be pelleted. Looking at the effect of pelletization of feed with zeolite should also be carried out as well as supplement pig diets with > 250 μm particle size zeolite in the feed. For future feed trials conducted in the Macdonald Campus Swine Unit, pigs should all be housed in room 2, since other pigs move through room 1 on their way to slaughter, causing undue stress on pigs housed in room 1. A complete economic, cost to benefit analysis must also be carried out to determine if the extra money gained in the increase in carcass quality (if any) of the pigs can offset the cost of using zeolite as a feed additive in pig diets.

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