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AIR EMISSION CONTROL FROM BROILER FARMS USING A NATURAL ZEOLITE COLUMN

Submitted by

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DECLARATION OF AUTHORSHIP

I, Amanda Little declare that the work presented herein is my own, unless otherwise acknowledged. The work presented has not previously been submitted for credit at any institution.

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ABSTRACT

As the number of non-farm residents moving into rural areas increases, the number of complaints regarding the odour from broiler farms also increases. In addition to the nuisance caused by the odour, there is a growing concern that the emissions produce adverse health effects.

Although there has been sparse research into this area, one such compound which has been identified as posing serious environmental and health risks, is particularly odoriferous and is present in significant quantities at broiler farms, is ammonia.

The challenge facing this report, then, is to identify a cost-effective and viable technology to not only mitigate, but remove the ammonia content, with a view to odour reduction.
One such technology is the natural zeolite, clinoptilolite. Clinoptilolite as an abundant and relatively inexpensive recyclable natural resource which has proven effective in odour control, proves to be an attractive option.

The test performed in order to characterise the zeolite included x-ray defraction, N_2 adsorption and gravimetric ammonia adsorption. In order to determine the effectiveness of the natural zeolite column, a test using the effluent air from a broiler farm was sent through the column and the exiting air was tested by olfactometry. The results of the study indicated that the odour levels were reduced by 50% for intensity and 13% for offensiveness. Although these results are promising, it cannot conclusively be stated that reduction in ammonia caused the reduction in odour.

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1.0   INTRODUCTION

1.1   *Description of the Problem*

As the number of non-farm residents moving into rural areas increases, the number of complaints regarding the odour from broiler farms also increases. In some areas, this has resulted in increasing pressure to impose stricter controls on the extension of existing farms and the establishment of new farms and in extreme cases, law suits against the growers and the local council (Jiang, 1999). In addition to the nuisance caused by the odour, there is a growing concern that the emissions from the broiler farms produce adverse health effects. The Board of Governors of the University of North Carolina, 1998 validate this concern and state that health effects such as eye, nose and throat irritation, headaches, drowsiness, allergies, asthma and bronchitis result from exposure to odour causing substances. Consequently, reducing the impact of odours on the surrounding community is imperative.

The most cost-effective method to mitigate odour complaints resulting from broiler farms is to allow the atmosphere to dilute the odour with distance from the facility (Pacific Air and Environment, 1999). Selecting a site that provides an adequate buffer zone can achieve this. For existing facilities however, this is not an option. It is therefore necessary to turn to technology for a solution.

A technology that completely prevents or removes odour, either does not exist or is prohibitively expensive to install and/or manage (Heber, 2000). The broiler industry is a very competitive market. Growers are small profit margins and it is very difficult to pass on any environmental costs to the consumer. The challenge therefore is to develop a cost-effective technology that reduces odour levels to an appropriate level.

This report investigates the natural zeolite, clinoptilolite, and its' suitability for application as a possible air emission control technology at broiler farms.

1.2   *Objectives*

It is the aim of this thesis to:

1. characterise the natural zeolite, clinoptilolite, and establish its suitability to the application.

2. determine the performance of a natural zeolite column under site conditions.

1.3   Value of Thesis

The findings from this report are valuable for a number of reasons. These include:

1. The information regarding the equilibrium adsorption and properties of the natural zeolite, clinoptilolite, will provide practical knowledge essential for industrial application.

2. The determination of a cost-effective odour control method would influence any future town planning, cease public protest to the farms and act as a benchmark for future odour control methods.

The work performed here will be of interest to the Chicken Growers Association of Australia, Department of Primary Industries, Environmental Protection Agency and those interested in the agricultural applications of natural zeolite.

It is hoped that this report will spark further interest in the commercial application of natural zeolites

2.0   LITERATURE REVIEW

2.1   Odour

2.1.1 Source and Composition

The odour emitted from broiler farm operations is a result of animal respiration, airborne dust (derived from bedding, food and the animals themselves) and the decomposition of manure accumulated throughout the growing cycle. The latter is the most prominent source of odour on well-managed farms (Pacific Air and Environment, 1999).

There is very little information available regarding the nature and composition of the gases emitted from broiler farms. However, it is estimated that 80-200 gases are produced from the decomposition of livestock manure. Of these recognized gases, two principle classes of odorous compounds have been identified as (1) those containing sulphur, eg. Hydrogen sulphide and (2) those containing nitrogen in the amine form, eg. Ammonia (The Ohio State University, 2000).

Owing to the formative nature of the research undertaken in this area thus far, it cannot be said with any certainty which compound and/or combination of compounds are responsible for the offensive odours.   However, this report focuses primarily on the latter category of compound for the following reasons:

1. Ammonia is present in significant quantities resulting from the fact that poultry manure contains large amounts of uric acid (Harry, 1978);
2. Of the identified compounds, Ammonia is a particularly odoriferous compound; and
3. There serious environmental and health risks associated with ammonia emissions from broiler farms (Amon *et al*, 1997).

Concerns regarding the high ammonia levels in broiler sheds have sparked a number of studies aiming at quantifying ammonia levels and investigating the link between ammonia concentration and odour concentration. The results however, have not proved useful. Jiang et al, 1999, studied the spatial and temporal variations in ammonia concentration at 10 broiler sheds in New South Wales and Victoria. The ammonia levels recorded were in the range of 5-25ppm. However, Bolla, 1979 performed similar studies and reported ammonia concentrations in the range of 0-100ppm. The disparity in results highlights the variability from farm to farm.   Jiang *et* al, 1999 concluded that there is no correlation between the measured ammonia concentration and odour concentration.

2.1.2 Summary of Existing Technologies

When planning a new livestock facility or developing an existing one there are a number of factors that should be considered in order to reduce odour nuisance. These include [Board of governors Nth Carolina, Sep 1998 www.cals.ncsu.edu/waste_mgt/control.htm]:

* Appropriate site selection. This includes consideration of buffer distances; placement of buildings and manure handing with respect to neighbours; prevailing wind conditions; and air drainage.

* Suitable design of manure-handling system components.

* Operation and management practices of manure-handling and storage facilities.

However, existing facilities are not able to change their location or design and even well managed farms may suffer odour annoyances. In these situations, odour control measures must be taken. Odour control technologies fall into 3 categories [www.bae.umn.edu/extens/aeu/ae411.html, odour and odour policy criteria]:

1. Prevention of odour generation. For example, diet manipulation, litter additives, anaerobic digestion, aeration or oxidation, pH control.

2. Capture and destruction of odours before release. For example, biofilters, storage covers and organic mats.

3. Dispersion of or disguising odours. For example, masking agents, perfumes, windbreak walls, stacks.

2.1.3 Potential of Natural Zeolites in Odour Control

Natural zeolites are formed by the interaction of volcanic ash and salt deposits in alkaline lakes. As a result, zeolites are in natural abundance all over the world and can be harvested and utilised economically (http://www.cycletrol.com/cdi_zeolites.html, 2000). The wealth of resource in combination with it's inexpensiveness, proves to be an attractive option to broiler farmers, who as previously mentioned, experience low profit margins.

In addition to these benefits, the environmental impacts resulting from natural zeolites are minimal. Zeolites can easily be regenerated and studies indicate that the regeneration of natural zeolite does not reduce the adsorption properties in further trials. Furthermore, they are recyclable. Mumpton, 1978 suggests that zeolites are particularly useful as fertilisers due to their slow ammonia release properties.

Natural zeolites have also proven effective in odour control over the past three decades (Carr, 1994). Mumpton, 1978 indicates that approximately 100 tonnes of clinoptilolite is used each year in Japanese chicken houses. The zeolite is either mixed with the droppings or suspended from the ceiling in boxes packed with the zeolites. Amon *et* al, 1997 states that the clinoptilolite form of zeolite has the potential to reduce odour and ammonia emissions. In addition to their extensive agricultural usage, zeolites have, according to Carr, 1994 been particularly useful as room air cleaners and have also been used in living quarters of rest homes and similar facilities to remove urine odours.

Why are natural zeolites so applicable in these situations? A complete explanation lies within an analysis of the properties of zeolites. In short, natural zeolites particularly adsorb ammonia ions (Vaughan, 1978). As mentioned earlier, ammonia emissions present significant heath and environmental concerns. Ammonia is a particularly odoriferous compound and is thought that it is a significant contributor to odour levels. Thus, it is the ability for zeolites to capture and control ammonia emissions that makes them attractive for odour control applications.

Even though zeolites have been successful in some odour applications, it should be kept in mind, that no relationship between ammonia concentration and odour concentration has been established.

2.2   Natural Zeolites

2.2.1 Zeolite Structure

What a zeolite does, and how it does it depends on the exact shape, size and charge distribution of the lattice structure (http://sass2wlv.ac.uk:8080/zeolites/zeolite.html, 2000).

Zeolites are crystalline frameworks of oxygen, aluminium and silicon extending in a three-dimensional framework (Clifton, 1987). Figure 1 below illustrates the basic structural building blocks. Carr, 1994 states that the net charge of the structure is balanced by exchangeable cations, which are loosely held within the central cavities and surrounded by water molecules.
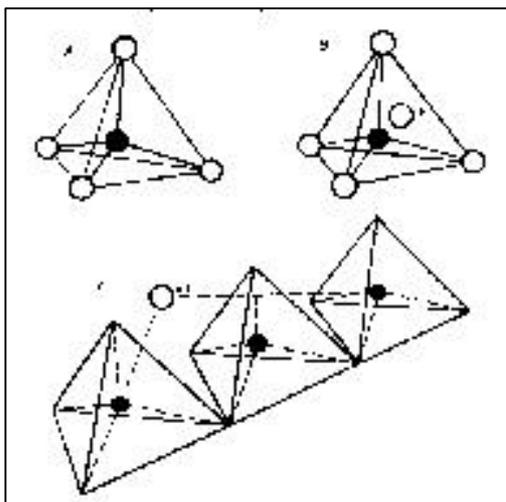
Figure 1.   Basic tetrahedron of zeolite framework.
Taken from Clifton, 1987.

The tetrahedra of the zeolites are then arranged into a crystal lattice.   Unlike other adsorbents, the resulting pores are uniform in size.   Figure 2 below suitably illustrates this.
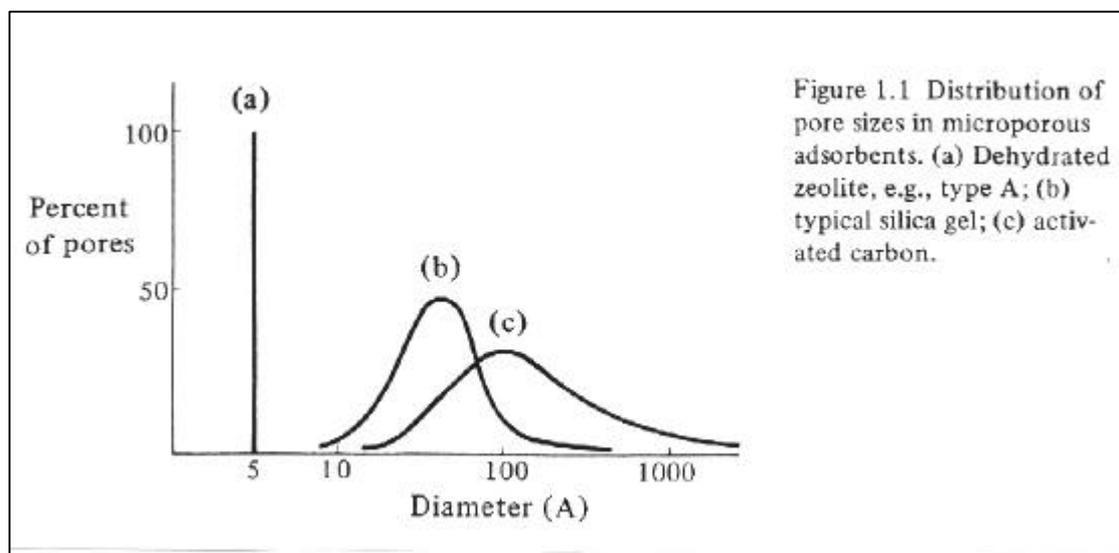
Figure 2.   Distribution of pore sizes in microporous adsorbents.
(Breck, 1974)

Breck, 1974 has summarised the structural properties clinoptilolite and the table below presents these findings.

Table 1.   Summary of clinoptilolite structural properties.
           (Breck, 1974)

Structure Group: 7

Chemical Composition
Typical Oxide Formula: $(Na_2, K_2)O \cdot Al_2O_3 \cdot 10SiO_2 \cdot 8H_2O$
Typical Unit Cell Contents: $Na_6[(AlO_2)_6(SiO_2)_{30}] \cdot 24H_2O$
Variations: Ca, K, Mg also present; Na, K>>Ca
                 Si/Al, 4.25 to 5.25

Crystallographic Data

Symmetry:	Monoclinic	Density:	2.16g/cc
Space Group:	I 2/m	Unit Cell Volume:	$2100A^3$
Unit Cell Constants:	a = 7.41 A		
	b = 17.89 A		
	c = 15.85 A		
	$\beta = 91^o29'$		

Structural Properties

Framework:	Possibly related to heulandite but not determined.		
Void Volume:	0.34 cc/cc	Framework density:	1.71 g/cc
Dehydrated -			
Effect of Dehydration:	Very stable – in air to 700^oC		
Largest Molecule Adsorbed:	O_2		
Kinetic Diameter, σ, A:	3.5		

The structure information presented by Breck, 1974 is used widely in literature and studies, such as this one, as a guide to understanding the properties of zeolites (in this case clinoptilolite). If the composition of the zeolite and hence the structure is unknown, or requires confirmation a commonly used tool is x-ray powder diffraction. A typical x-ray powder diffraction plot for clinoptilolite is shown below.
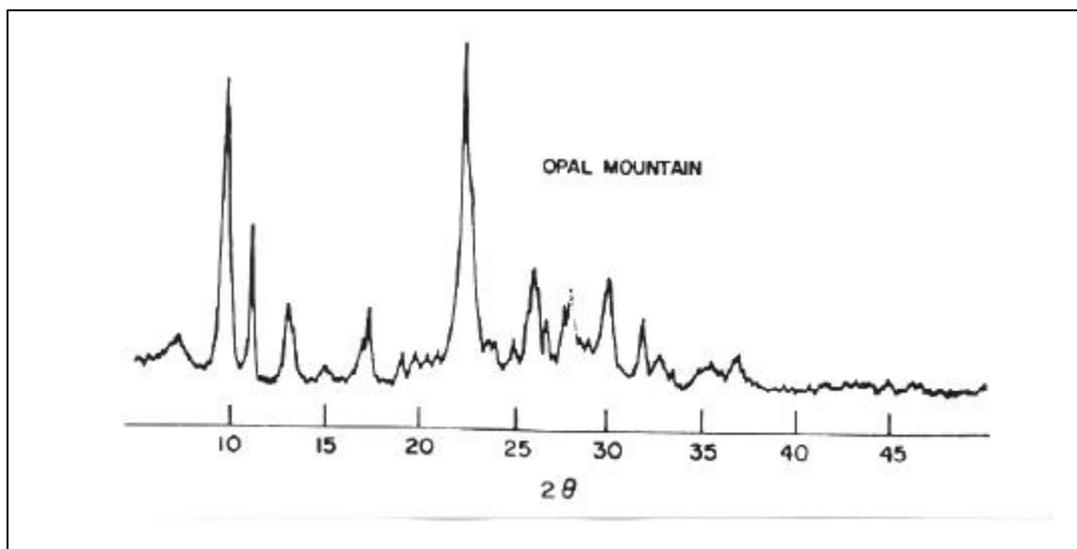
Figure 3.   X-Ray Powder Diffraction for Clinoptilolite.
(Flannigen, 1984)

The determination of pore size, shape, volume, distribution and surface area is generally through analysis of nitrogen adsorption isotherms. Studies of natural clinoptilolite in 1998 and 1999 by Hernandze-Huesca *et* al involve the used of nitrogen adsorption. The results from these studies are shown below.

Table 2.   Characterisation of Clinoptilolite.

Parameter	Hernandez-Huesca *et* al, 1998	Hernandez-Huesca *et* al 1999
Surface area (BET)	13.6 m^2/g	12 m^2/g
Total Volume	N/A	0.0660 cc/g

The shape of the particles can be determined by the shape of the isotherm and is discussed further on.

2.2.2 Properties of Zeolites

According to Breck, 1974 zeolites are characterised by the following properties:

1. High degree of hydration,
2. Low density and large void volume when dehydrated,
3. Stability of the crystal structure of many zeolites when dehydrated,
4. Cation exchange properties,
5. Uniform molecular-sized channels in the dehydrated crystals,
6. Ability to adsorb gases and vapours,
7. Catalytic properties.

Commercial applications of natural zeolites make use of one or more of several physical or chemical properties, including (1) ion exchange, (2) adsorption and related molecular sieve properties, (3) dehydration and rehydration, and (4) siliceous composition (Flanigen 1984).

2.2.2.1 Adsorption Properties

Crystalline zeolites are unique adsorbent materials (Carr, 1994). The uniform molecule-sized pores in zeolites limit adsorption on the basis of molecular size – a molecule smaller than the pore can enter the crystal structure and be adsorbed, but larger molecules are excluded from the structure and are not adsorbed (Flanigen, 1984). Thus, zeolites are considered as molecular sieves. In addition to the molecular sieving properties, adsorption favours those molecules that have relatively large energetic non-saturation (pi bonds, dipoles) (Hernandez-Huesca *et* al, 1998).

The capacity of the zeolite for adsorption is generally related to the free space or pore volume (Breck, 1974). Therefore, water must be removed from the zeolite to 'empty' the void volume before adsorption of molecules can occur. In addition, Hernandez-Huesca *et* al, 1998 suggests that the adsorption properties of zeolites tend to depend upon three things: the structure and composition of the framework, cationic form and zeolitic purity.

The majority of literature regarding clinoptilolite has been focussed on the removal of ammonia from wastewater. Quantification of gaseous ammonia adsorbed by clinoptilolite is limited. However, Amon *et* al 1997 suggest that aerial ammonia is adsorbed at a rate of between 6 and 14g/kg of zeolite.

2.2.2.2 Dehydration/Rehydration Properties

Dehydration of zeolites usually occurs at elevated temperature and under vacuum conditions. The dehydration properties of zeolites are important because they influence the adsorption characteristics of the zeolite (Clifton, 1987). Upon dehydration, the crystalline structure of some zeolites becomes distorted, affecting the volume and shape of the micropores (Carr, 1994). According to Breck, 1974 zeolites that undergo dehydration reversibly and continuously, suffer no substantial change in the topology of the framework structure.

2.3 Theoretical Background

Before the analysis of the results can proceed, it is necessary to provide the essential theoretical background.

2.3.1 Adsorption Isotherm

An equation that relates the amount of a substance attached to a surface to the equilibrium pressure, at a fixed temperature is known as an adsorption isotherm (Laidler and Meiser, 1995). In mathematical terms we may write:

$$n^a/m^s = f(p/p^o)_T \qquad \text{Eq (1)}$$

where, n^a is the gas adsorbed, m^s is the mass of the solid, p/p^o is the relative pressure and T is the temperature. There are a number of models to describe the adsorption isotherm. Of most note are the Langmuir and BET models. The explanation of such models is beyond the scope of the report. However, most adsorption texts provide such information. Reference can be made to Do, 1998.

Flanigen, 1984 continues by stating that the variation in isotherm shape reflects differences in the character of the solid surface, the size and shape of the pores, the porosity and surface area of the solid, and the energy of interaction between the adsorbed molecules at the solid surface. The majority of isotherms presented by literature can conveniently be grouped into six classes in the IUPAC classification (Rouquerol *et al*, 1999). These are illustrated in the figure below. Of these classifications, Type I and Type IV are of importance in the study of zeolites.
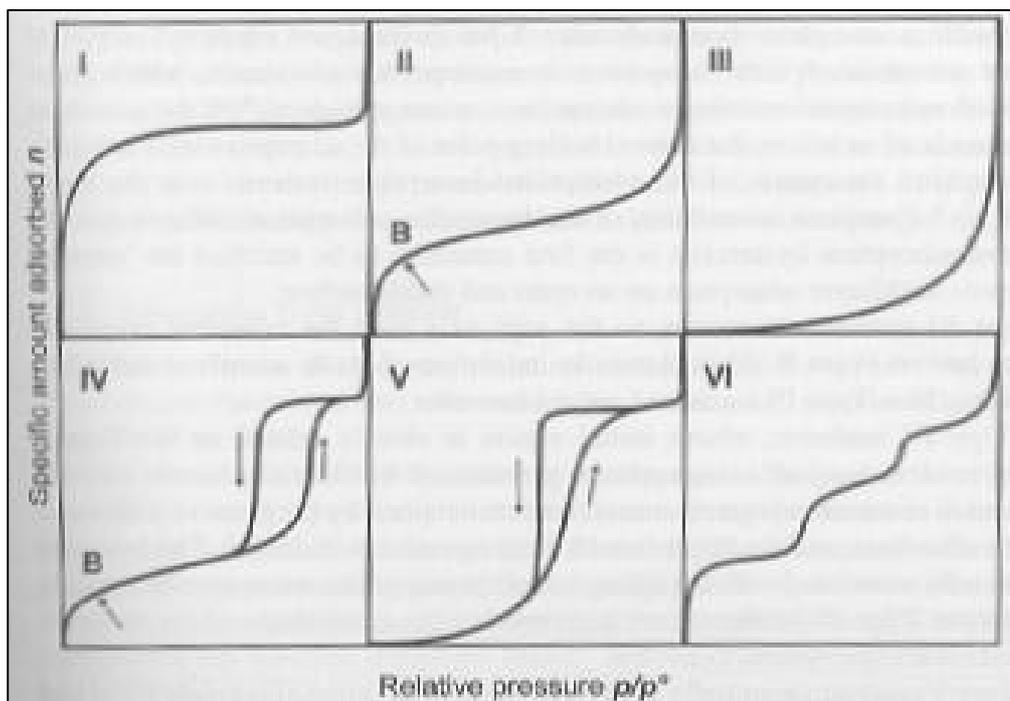
**Figure 4.   The six main types of gas physisorption isotherms, according to the
IUPAC classification.**

Sourced from Rouqerol *et* al, 1999

In its most characteristic form, the Type I isotherm is concave to the relative pressure
(p/p^o) axis. It rises sharply at low relative pressures and reaches a plateau; the amount
adsorbed the unit mass of solid, n^a/m^s, approaches a limiting value as $p/p^o \rightarrow 1$.
Adsorption is limited based on the available micropore volume (Flannigen, 1984). If the
plateau is reached at a low relative pressure, the pore size can be considered to be small.
The appearance of a nearly horizontal plateau indicates a very small external surface area
(Rouqerol *et* al, 1999)

The Type IV isotherm, The hysteresis loop shown in Type IV isotherms is usually
attributed to the filling and emptying of the mesopores by capillary condensation.
Analysis of the hysteresis loop provides information regarding pore shape.

The major forms of loop are represented in the IUPAC classification and are shown in the
figure below. A description of the meaning of each loop described below and is taken
from Rouqerol *et* al, 1999.

H1:   Produced by adsorbents having a narrow distribution of uniform pores.
H2:   In this case, the pore structure is complex and tends to be made up of
       interconnected networks of pores of different sizes and shapes.
H3:   This type of loop is usually given by the aggregates of platy particles or
       adsorbents containing slit-shaped pores.

H4:   This loop is also given by slit shaped pores, but in this case, the pore size distribution is mainly in the micropore range.
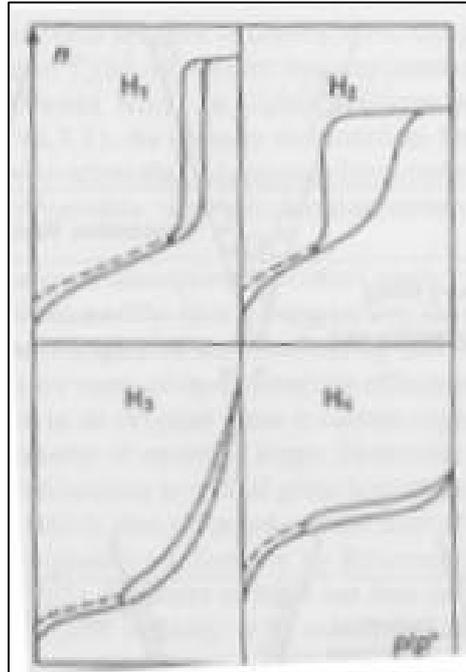
Figure 5.   The IUPAC classification of hysteresis loops.
Sourced from Rouquerol *et* al, 1999.

2.3.2 Mass Transfer Zone

When considering the suitability of the natural zeolite column to this application, it is necessary to discuss the concept of a mass transfer zone. The operation of a fixed-bed adsorber can perhaps be best understood by considering a binary fluid in which one component (C_o) is strongly adsorbed. This binary mixture is then passed through the adsorbent bed.
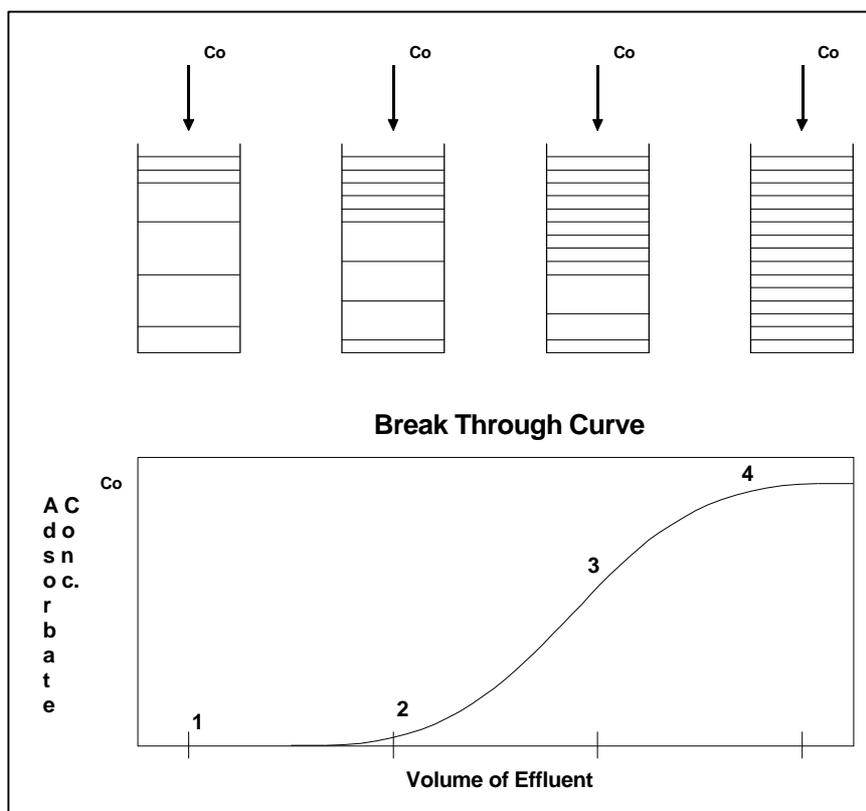
Figure 6.   Break Through Curve
(Hersh, 1961)

At point 1, the adsorbent adsorbs the solute rapidly and efficiently and the bulk of the adsorption occurs in a relatively narrow band at the uppermost layer of the bed. As the process continues, the adsorption continues further down the column as the upper most layer is filled and some of the solute entering leaves in the effluent stream. This type of volume filling is characteristic of zeolites.

The adsorption zone reaches the bottom of the column at point 3 and at this point the concentration of solute in the effluent rises rapidly. This is known as the break point. The effluent concentration reaches the influent concentration at point 4 and the bed is no longer effective.

According to Hersh, 1961 the break point generally decreases with decreased bed length, increased particle size of the adsorbent, increased rate of flow of the fluid and increased solute concentrations of the fluid feed. It is therefore important to carefully consider these parameters when designing a suitable column.

Break through can be determined theoretically as well as experimentally.

The velocity of the adsorbent or velocity of the adsorption zone can be described by the following equation.

$$u_{ad} = \frac{\dot{m}_g}{\rho_g \rho_{ad} A_{CSA}} (\alpha)^{1/\beta} \left(\frac{m_{a,o}}{V_{g,T}} \right)^{\frac{\beta-1}{\beta}}$$

Eq (2)

Then, the amount of time that will pass before break though is described by:

$$t_B = \frac{L}{u_{ad}}$$

Eq (3)

if the adsorption zone is $\ll$ the length of the bed.

Where,

U_{ad}	=	velocity of adsorbent
m_g	=	total mass feed rate of gas stream
$(m_{a,o}/V_{g,T})$	=	mass of adsorbate in incoming gas stream per unit volume of gas.
p_g	=	density of gas
p_{ad}	=	apparent density
A_{CSA}	=	cross sectional area of adsorption bed
α, β	=	empirical constants
L	=	Adsorption bed length
t_B	=	Break through time

3.0 EXPERIMENTAL PROCEDURE

The natural zeolite used for all of the tests was purchased from Neumann Group Company located at the Gold Coast. The sample was light pink in colour and measured 1-2mm in diameter. The consistency is similar to that of a common rock. Prior to testing the sample was activated by heating to 350°C for 3 hours.

3.1 Plan of Study

The experimental procedures for this study were chosen to complement the objectives of the report. In order to characterise the zeolite three tests were performed. These were x-ray diffraction, nitrogen gas adsorption and gravimetric adsorption of ammonia. The x-ray diffraction test was utilised to determine the composition of the zeolite and confirm that it was a clinoptilolite. Pore size, pore size distribution, pore volume and surface area were all determined using nitrogen gas adsorption. This information is important to predict the adsorption behaviour of the zeolite. Finally, gravimetric adsorption of an ammonia solution was used to determine how much ammonia the zeolite could adsorb.

The remaining two tests, column break through and on-site column testing were used to evaluate the performance and suitability of a natural zeolite column for odour control. The break through test was used to indicate how long the zeolites could adsorb before bed saturation. The purpose of on-site test was to give an indication of how much the odour level could be reduced if a zeolite column was used. These tests are all standard tests and an explanation beyond that given below can be found in most adsorption or experimentation texts.

Appendix A provides photographs of the zeolite sample and the apparatus used.

It should also be noted that ammonia gas is extremely hazardous. All possible care should be taken to avoid exposure by contact with skin or eyes or inhalation. Consultation of material safety data sheets is advised.

3.2 X-Ray Diffraction

The University of Queensland, Department of Mining and Metallurgy performed the X-Ray Diffraction test on the natural zeolite sample. The zeolite sample was crushed to a powder-like form before testing. As the composition of the zeolite was largely unknown, the 2θ range was chosen to be 5 to 80°. A wavelength of 1.54A (Cu), step of .04° and speed of 1° per minute was used.

3.3   N₂ Gas adsorption/desorption

Physical characterisation of zeolites was performed via nitrogen adsorption at 77K using a NOVA 1200 Quanta Chrome. From this test, the following parameters were determine:

➢ Pore size
➢ Surface area
➢ Pore volume
➢ Pore size distribution

Before testing, the sample was required to be degassed for a period of approximately 3 hours at 230°C. The resultant data was then manipulated using Novadrp software.

3.4   Gravimetric Adsorption of Ammonia

Gravimetric adsorption measurements were performed using an in-house adsorption apparatus with quartz springs, a MKS pressure transducer and a temperature-controlled oven with capability to operate up to 200°C.

A zeolite sample weighting 292.1mg was used. Prior to the experiment, the zeolite sample was degassed overnight at 200°C. The adsorbate was a 28% ammonia in water solution.   The pressure was kept constant for 20 minutes and after this time the displacement was measured. The pressure was then stepped up by 50torr and the 20 minute interval past before another measurement was taken. This was repeated until saturation was reached. The experiment was repeated for temperatures of 22°C, 50°C, 100°C and 150°C.

For each displacement measurement, 3 values were taken. If the values were not within 3μm of each other, a new set of measurements was taken. A calibration curve for the quartz spring is located in Appendix D.

3.5   Natural Zeolite Column Break Through

The activated zeolites were packed into a column. The bed height was 5cm and internal diameter of the column was also 5cm. As ammonia is being used, it was necessary to use stainless steel fittings to avoid corrosion. As mentioned, ammonia is hazardous and lack of integrity of the system may result in undesirable leaks.

A 99.9% ammonia cylinder and an air cylinder, sourced from the Department of Chemical Engineering, UQ were used. The concentration of the ammonia in air was limited by the flow meter used and, instead of being approximately 20ppm a concentration of 1.47% vol/vol ammonia in air was used. The concentration was determined using a bubble meter on each stream separately and equating the ratio.

The effluent from the column entered a container of distilled water (approximately 1L). The pH of the water was recorded at 2-minute intervals until break through occurred. Break through was considered to be a sharp increase in the pH as ammonia produces alkaline conditions when present in water.

The calibration information for the pH meter is located in Appendix F.

3.6   On-Site Testing

The same column used in the column break through tests was used on-site at a broiler farm. The bed length was 5cm for the sake of consistency. The influent air in this system however was the air emitted from one of the broiler sheds (a picture of the shed is located in Appendix A).

A plastic shroud was placed around one of the fans and the sample of undiluted air taken downstream from the fan. Appendix A provides a schematic of the operation. The effluent air was captured in a plastic bag and sent for olfactometry testing by the Department of Primary Industries (Toowoomba) to measure odour intensity and offensiveness. Appendix B provides background information about olfactometry.

Particulate and ammonia sampling was performed inside the shed by Ewan M[c]Pherson. The Department of Primary Industries sampled for ammonia at the same point for odour collection. The temperature and moisture content throughout the day was also recorded.

4.0   RESULTS AND DISCUSSION

4.1   X-Ray Diffraction

The result from the x-ray diffraction test is shown below as Figure 7.
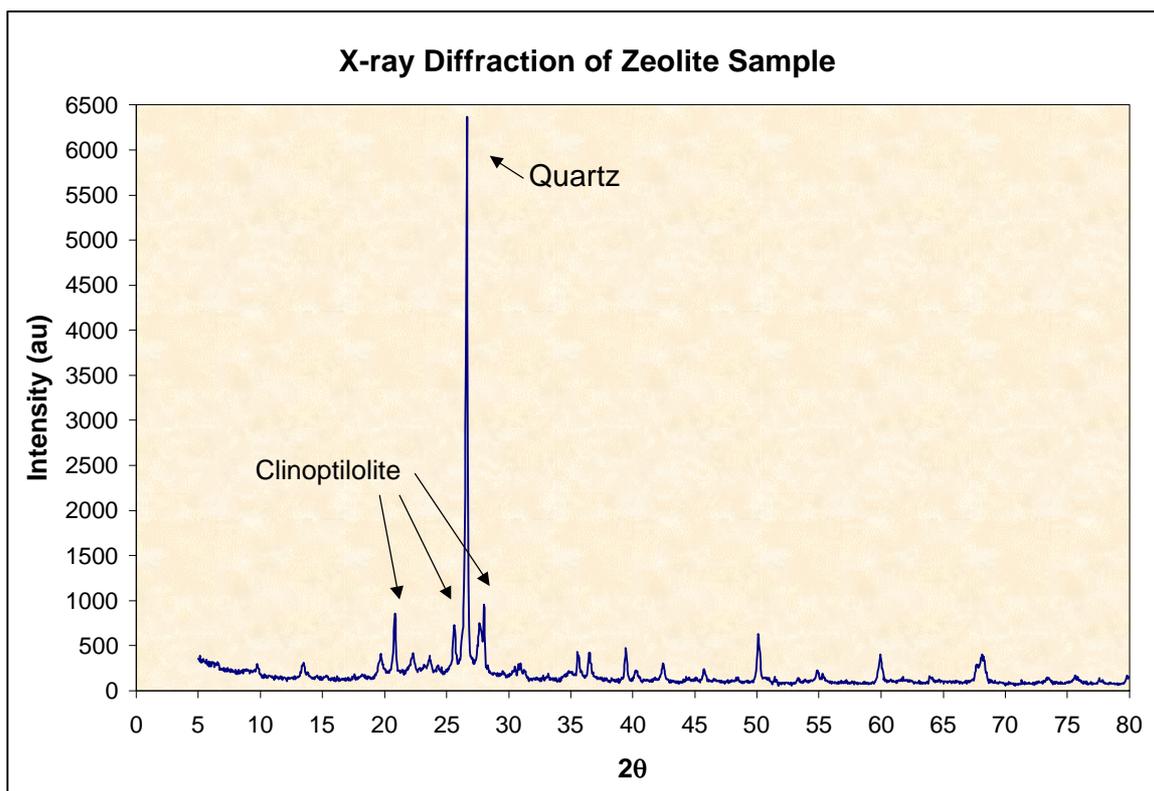
Figure 7.   X-Ray Diffraction of Natural Zeolite Sample.

The confirmation of the natural zeolite being clinoptilolite was somewhat a challenge as a result of the impurities present. Breck, 1974 encountered similar problems and states that fine-grained zeolite crystals found in sedimentary deposits are not easily identified from their optical properties. However, analysis indicated that the peaks indicated are indeed clinoptilolite. The x-ray diffraction test also indicated the presence of quartz (indicated by the large peak at 26.64°), clay impurities and possible amorphous material. The presence of such materials is not uncommon in natural zeolites (Rouquerol *et* al, 1999). However, it may impact the adsorption capacity of the zeolite.

4.2   N₂ Gas Adsorption/Desorption

4.2.1 Adsorption Isotherm

The following isotherm was produced using Novadrp software.
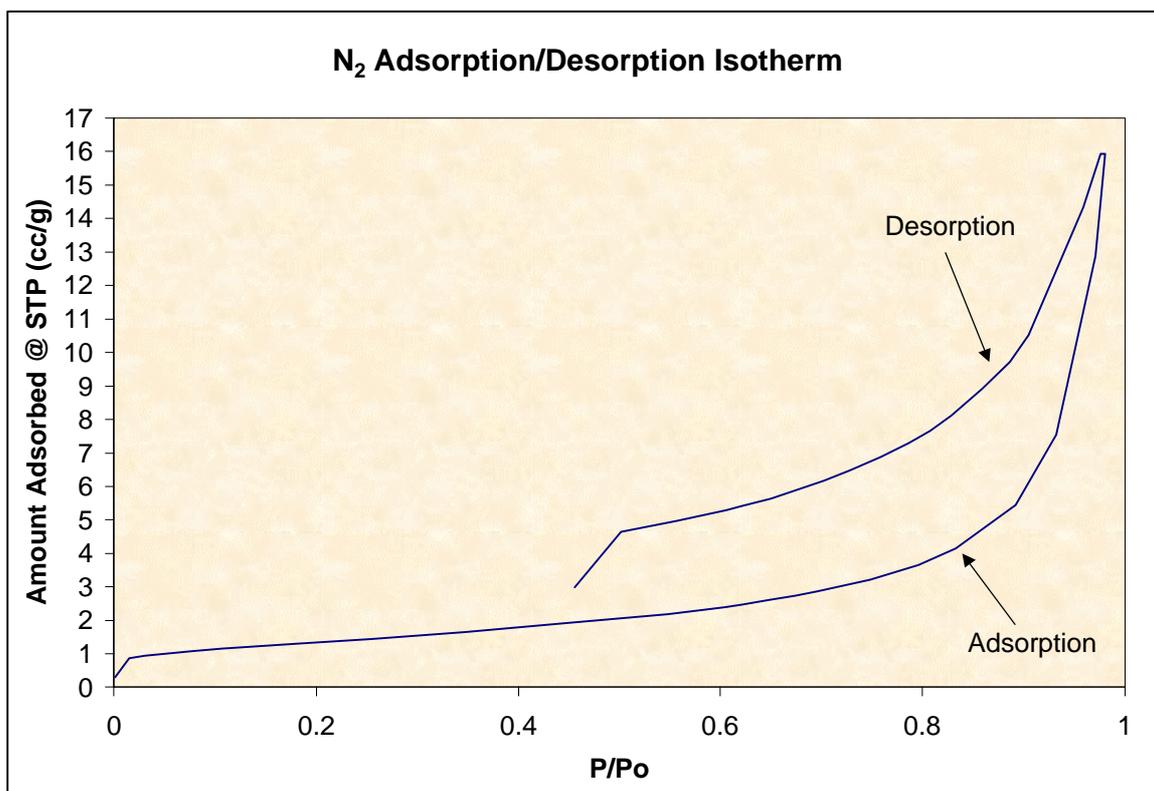
Figure 8.   N₂ Adsorption/Desorption Isotherm.

The N_2 adsorption/desorption isotherm was classified as Type IV of the IUPAC classification system. The low adsorption is a result of the N_2 molecules being unable to penetrate the zeolite channels due to the ions present.

The hysteresis shown in this plot is characteristic H3. The presence of hysteresis is usually the result of the filling and emptying of mesopores via capillary condensation. The presence of mesopores is most likely the result of the impurities present. The H3 shape of the hysteresis suggests that the particles are slit shaped and is expected due to the impurities present, especially the clay.

The very small initial adsorption indicates that the surface area of the sample is very small, and indeed it was. The surface area was calculated to be 4.8 m^2/g (BET). Hernandez-Huesca *et* al, 1998 suggest that the surface area of clinoptilolite, using the BET method, is 23m^2/g. This is almost 5 times greater than that determined in this experiment. In a later study performed by Hernandez-Huesca *et* al, 1999 surface area of natural clinoptilolite was found to be 13.6 m^2/g (BET). The difference between the results may be a result of the clinoptilolite being sourced from different deposits, and hence the levels of impurities, which influence the pore size, surface area and volume, will produce different results. In contrast, the small surface area may be the result of the N$_2$ inability to enter the passages of the zeolite.

The total pore volume in this study was calculated to be 0.026 cc/g. For the 1999 study by Hernandez-Huesca *et* al, the pore volume was calculated to be 0.0660 cc/g. The low pore volumes calculated in both cases might be a result of the N$_2$ molecules not being able to penetrate freely into the micropores of the clinoptilolite. It is for this reason, that Hernandez-Huesca *et* al, 1998 also studied water adsorption for clinoptilolite and a total pore volume of 0.1738 cc/g was then calculated from this type of adsorption, double that for the nitrogen adsorption.

4.2.2 Pore Size Distribution

A narrow pore size distribution is illustrated in Figure 9. The narrow pore size distribution is characteristic of zeolites (see Figure 2) and thus was expected. The majority of pores are found to be 3.9nm. The data presented by Breck, 1974 indicates that the pore size of clinoptilolite s 3.5nm. This is corresponds well considering the level of impurity in the zeolite. The pore size distribution ranges from 3.5nm to 65.7nm. The presence of the larger pores can be attributed to the impurities within the sample.
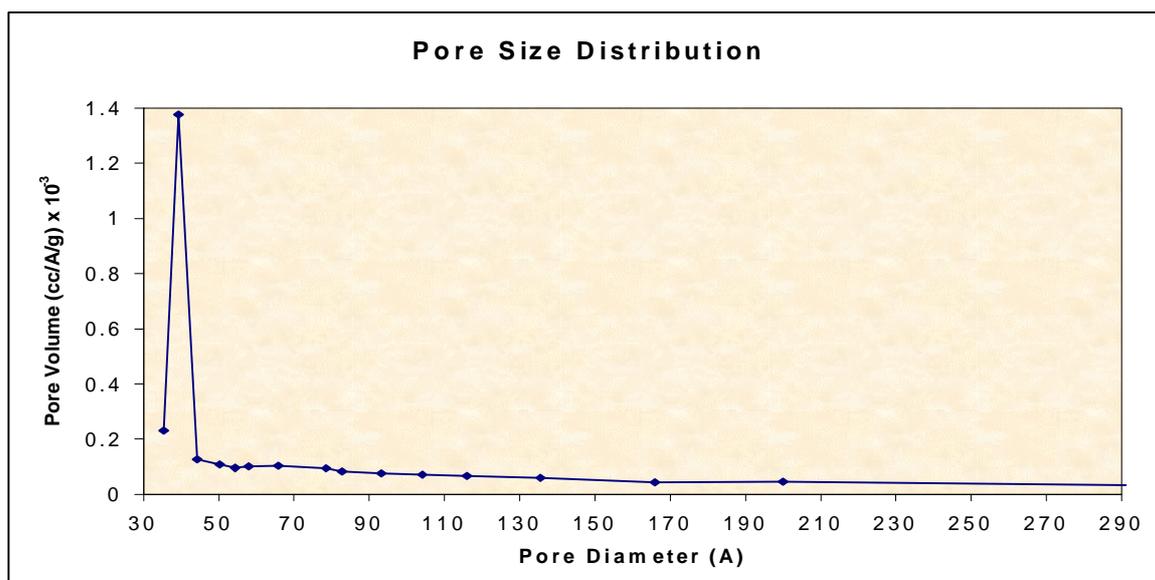
Figure 9.   Pore Size Distribution.

4.3   *Gravimetric Adsorption of Ammonia Solution*

The raw data is presented in Appendix C.

The gravimetric adsorption curve for the adsorption of ammonia solution can be described as Type I (Figure 4). This curve is as expected. Mumpton, 1978 explains that the mechanism of adsorption for zeolites is one of volume filling of the pores and where all the pores are filled at very low relative pressure. At very low pressures, the amount adsorbed increases linearly with the pressure and when pressure is sufficiently high, the amount adsorbed reaches the saturation capacity (Do, 1998). The maximum adsorption of the 28% ammonia solution was 40mg/g of clinoptilolite.

It should also be noted that an increase in temperature corresponds to a decrease in the amount adsorbed at a given pressure. This is due to the greater energy required by the adsorbed molecule to evaporate (Do, 1998).
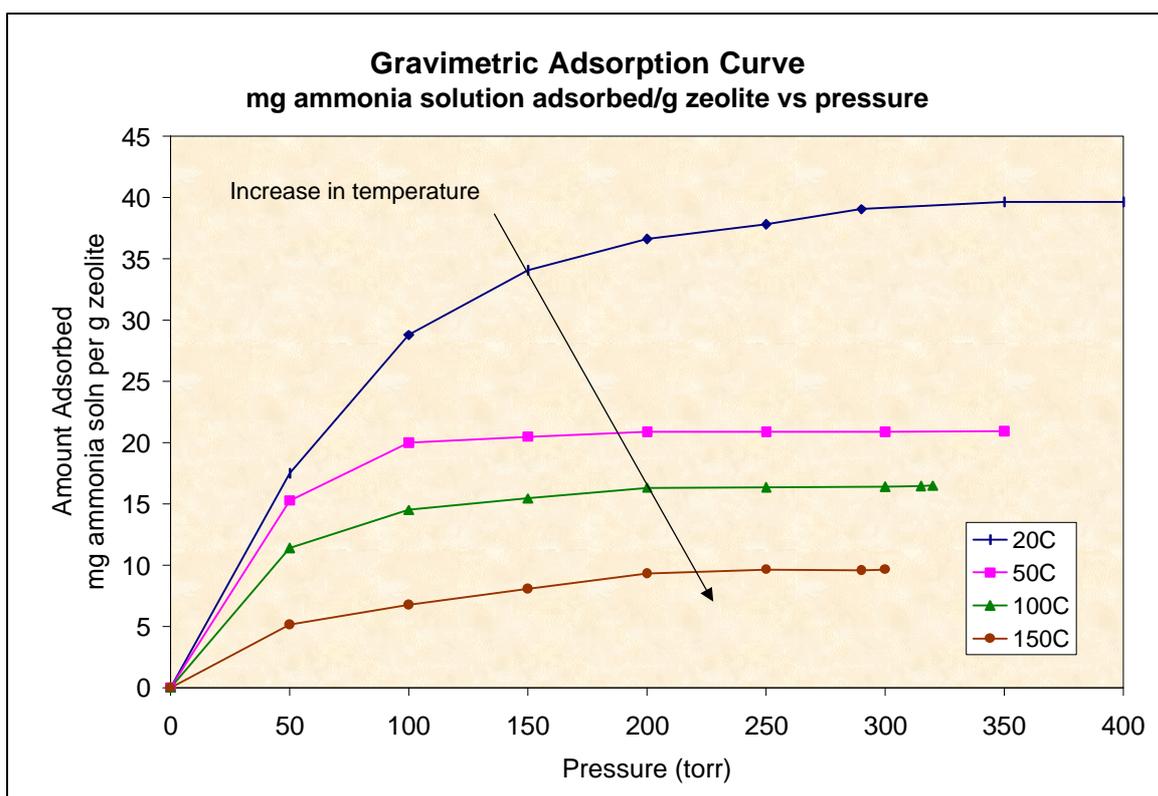
Figure 10.   Gravimetric Adsorption Curve.

4.4   Natural Zeolite Column Break Through

The following plot of pH vs time was constructed and is illustrated below.
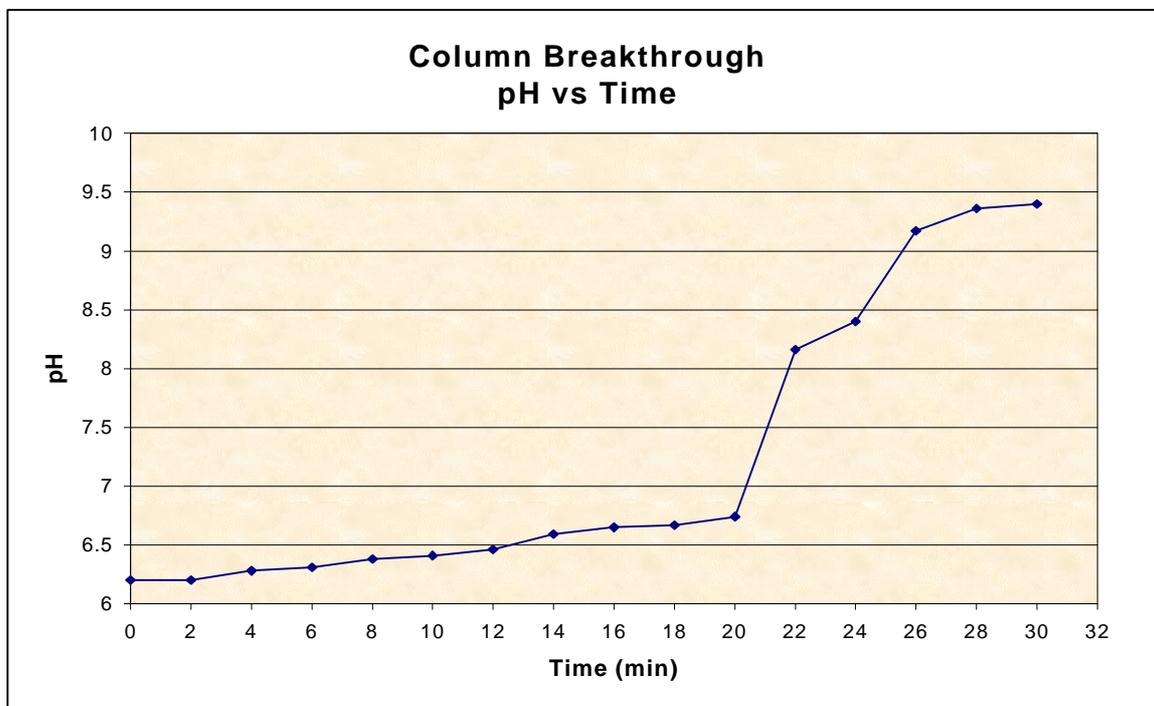
Figure 11.   Column Break Through - pH vs Time

It can be seen that this curve is similar to that in Figure 6. The curve indicates suggests that the break through occurs at approximately 30minutes. Using theoretical means to calculate break through time produces an extremely large time. The difference could be a result of the crudity of the experiment. Problems may have been the result of a small bed height. Further investigation into this type of testing will require more forethought.

The break through time is not expected to be achieved on site and hence the results of this experiment are not influential to the outcome of the report.

4.5   On-Site Testing

The results obtained by the DPI (Toowoomba) can be located in Appendix G. A summary of these results is shown below. Ammonia concentration, temperature and moisture content figures were unavailable.

Table 3.   Statistics of On-Site Testing.

Test	Av. Intensity (OU/m^3)	Std Intensity (OU/m^3)	Av. Offensiveness	Std for Offensiveness
Morning	256	72	7.0	N/A
Afternoon	223	41	7.7	N/A
Overall	239	57	7.3	N/A
Zeolite*	109	N/A	6.7	N/A

*The natural zeolite column was tested in the afternoon.

The on-site tests showed that the air emitted from the broiler sheds has a high and variable intensity. This is as expected as odour levels are highly dependent on a number of variables, which can change from day to day. As information regarding the temperature and moisture content are not provided, a relationship between these factors and the intensity cannot be determined.

The zeolite column is shown to reduce the odour intensity by > 50% (for all cases). The odour offensiveness is reduced by 13% compared with the afternoon case. The afternoon case has been used here as the zeolite sample was taken at approximately the same time. As only one test has been performed, it is uncertain why the column was so effective, or ineffective.

For instance, the reduction may indeed be due to the adsorption of ammonia and, assuming that 100% of ammonia present in the air is removed, the removal of ammonia can only bring about a reduction in intensity of approximately 50%. Literature has suggested that the removal of one component from the air stream may only serve to unmask another equally offensive and intense compound.

The assumption that 100% of ammonia is adsorbed is questionable. Firstly, any water present in the air stream will compete with ammonia for the adsorption sites and, as a result the amount of ammonia adsorbed will be hindered.

Furthermore, the presence of impurities and hence large pore sizes may enable molecules, which would normally be discarded from the bed, to be adsorbed. These molecules will therefore also compete for adsorption sites. However, the high polarity of ammonia would suggest that the potential for this scenario to occur would be low.

As reported by the Ohio State University, 1999 dust particles play a major role in the transport of odour. It is therefore possible that the reduction in odour is a result of dust particles being trapped in the bed and thus the effluent air may be perceived as less "odorous". If this is the case, the zeolite bed is an expensive and complicated type of particulate filter!

Even though it is possible to say that the zeolite column does reduce odour intensity and offensiveness, by 50 and 13% respectively, the mechanism by which this occurs is uncertain. As a result, the zeolite column may not be the best solution.

5.0 SOUCE OF ERROR

A detailed error analysis for the experimental work is not provided in this report. This is a result of the lack of information regarding the error associated with equipment and the operator. The reproducibility of results cannot be determined as only one test was performed of each type of experiment. The sections below indicate where possible propagation of error may have occurred.

5.1.1 X-Ray Diffraction

It is assumed that this test is accurate.

5.1.2 N_2 Gas Adsorption/Desorption

It is assumed that the results from this testing is accurate. However, the desorption curve does not meet back up with the adsorption curve at very low relative pressures. It is believed that the accuracy of the NOVA 1200 Quanta Chrome is questionable at very low relative pressures.

5.1.3 Gravimetric Adsorption

All possible care was taken during these experiments. However, there are a number of areas in which error may have propagated. It should firstly be noted that the integrity of the system is somewhat questionable. Due to the slight fluctuations (2 torr) in measured pressure, it is believed that there may have been a leak in the system. This will of course have an effect on the ability for the zeolite to adsorb. Some sites may have already been contaminated/filled before the testing could be performed. This limitation of the system could not be avoided however.

Furthermore, measuring the displacement was difficult. Three readings were taken for every measurement and, if the readings were not within 3 units of each other, the reading was repeated.

5.1.4 Natural Zeolite Break Through Column

The flow rate determination is questionable. A bubble meter was used to determine the flowrate of each component as the flowmeter that the gases were attached to were not easily read. There is of course error associated with reading from the burette and reaction time with the stopwatch. Once the flows were set, it is thought that there may have been some variation as there were some slight fluctuations in the pressure of the gases.

The pH meter was calibrated and appeared to be in working order. It is not thought that there were any leaks in the system as there was not notable ammonia smell.

5.1.5 On-Site Tests

It is presumed that the air was not diluted before entering the bag and that no contamination has occurred. The most obvious source of error in this test will result from the Olfactometry testing, especially for the offensiveness rating. It was assumed that the readings are consistent from one day to the next and reproducible as the same panel was used. However, there is some question regarding the validity of such an assumption especially for offensiveness testing. This doubt arises from the nature of the testing. For instance, human emotion is very difficult to predict. One of the panel may have been tired or past association with the characteristic odour may have been unpleasant. Nevertheless, this is the most appropriate way to measure the odour levels.

6.0   CONCLUSIONS

X-ray diffraction, N_2 adsorption and gravimetric ammonia adsorption were used to determine the properties of the natural zeolite. The findings from these tests are summarised below.

Table 4.   Characterisation of Clinoptilolite

Parameter	Conclusion
Composition	The zeolite was confirmed to be clinoptilolite. Quartz, clay and amorphous impurities were present in the sample.
Structure	PSD, Range 3.5nm – 67.5nm, strong peak at 3.9nm
	Total volume = 0.02 cc/g
	Specific area (BET) = 4.8 m^2/g
Ammonia adsorption	The maximum amount of 28% ammonia solution that could be adsorbed by clinoptilolite was 40mg ammonia solution/g zeolite.

The on site testing indicated that the natural zeolite column was able to reduce odour intensity by greater than 50% and offensiveness by 13%. However, the mechanism by which this happens is uncertain and further testing will be required on site.

7.0   LIMITATIONS

As a result of the limited time and funding allowed for the project, there are a number of areas in which this report could be improved. The most notable shortcoming being the uncertainty of the results. A detailed error analysis could not be performed as only one trial was performed for each type of test.   Hence, both the accuracy and the reproducibility of the results are unknown.   Moreover, the number of different experiments that could be performed was restricted.   The complete characterisation, including of the natural zeolite sample could not be determined.   Furthermore, the conclusions from the results of on-site testing are uncertain due to lack of testing.   In order to fully understand the mechanisms involved it will be necessary to create a more comprehensive testing scheme.

8.0   RECOMMENDATIONS

As mentioned earlier, this project was subject to a number of limitations. Consequently, the following is suggested to extend upon the work presented in this thesis.

1. Duplication of the experiments performed in this project to ascertain the reproducibility and accuracy of the results presented. Furthermore, it is suggested that further experiments to fully characterise the capabilities of this particular natural zeolite be explored.

2. Continued on-site monitoring in order to establish a generic description of air emitted from broiler sheds. This should include the intensity, offensiveness, composition and characteristic. From these studies it may be possible to determine the relationship between gas concentration and intensity, which has previously been uncertain.

3. Determination of the mechanism. It is still uncertain why the zeolite column reduces the odour intensity. For example, the particulate matter may be the cause of nuisance and if these particles are trapped in the bed of zeolites, the odour will be perceived to be less. Hence, the determination of the mechanism will ensure that the most appropriate technology is investigated.

4. Following from the above point, investigation in to the capabilities of combined systems may be of interest. Removal of particles via a filter, ammonia via zeolites and other organic compounds via activated carbon or other suitable adsorbent may produce an effective system.

5. Prevent the odorous compounds from entering the air. This is a far more attractive proposition than the control of such compounds once in the air stream. At present there is some work being performed on the use of zeolites in the litter to adsorb the ammonia present.

6. Upon verification of this type of technology, investigation of the most appropriate column dimensions, regeneration and reuse capabilities and required modifications to broiler sheds will be necessary.

9.0   REFERENCES

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Appendices

Appendix A

Photographs of Experimental Equipment

Figure 12. **Photograph of the NOVA 1200 Quanta Chrome used for N_2 gas adsorption/desorption testing.**

**Figure 13.   Photograph of the column used for testing on site and in the
laboratory.**
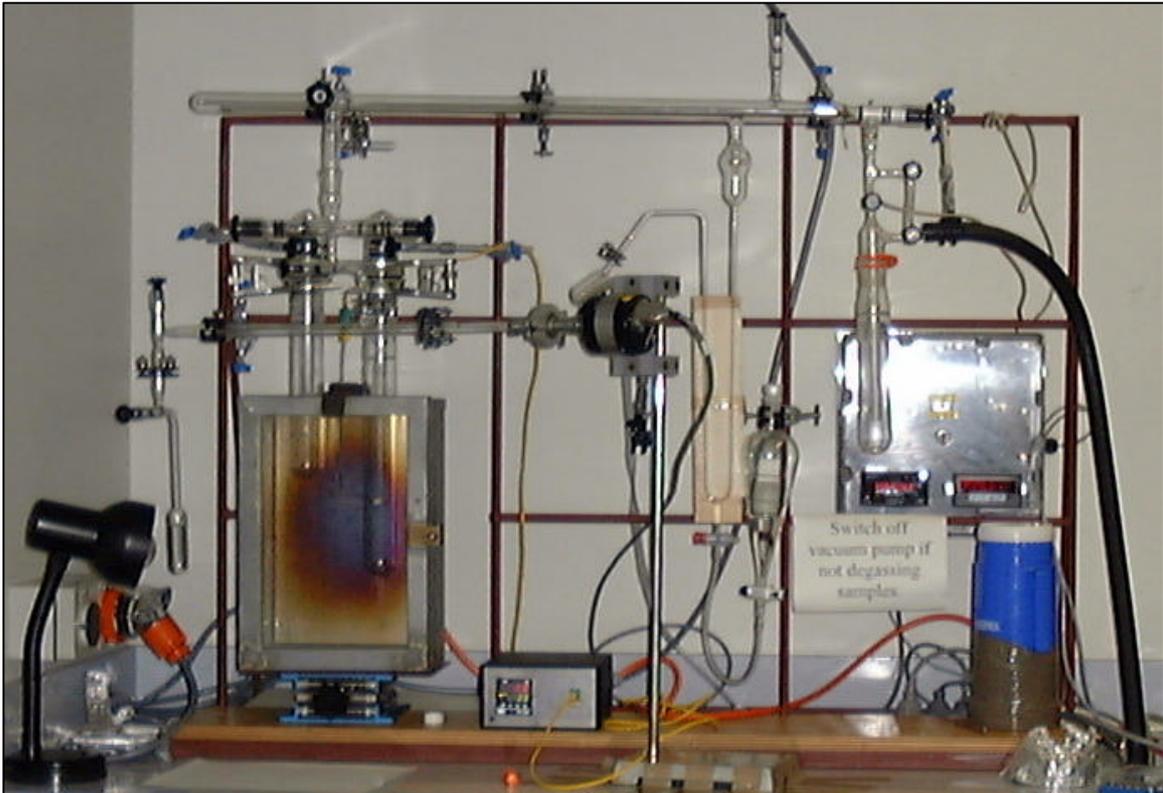
**Figure 14.   Photograph of the in house gravimetric adsorption system used for
ammonia adsorption tests.**

Appendix B

Description of Olfactometry Testing

Olfactometry

The following information regarding odour measurement via olfactometry is taken from Brockreis and Jager, 1999.

Olfactometry is the controlled presentation of odorants and the registration of the sense impression of a test panel with respect to the odorants. After taking a gas sample at the odorant source, the sample is diluted with neutral air in a defined ratio. This dilution is presented to the panel as a smell sample. Each sample is offered in several dilution steps.

The disadvantage of olfactometry is its dependence on the sense of smell of human beings. It depends on the form of the day of the test panel and for this reason is not as objective as an Electronic Nose, which is not influenced by emotions. Another problem is the selection of the test panel. In order to get an average distribution, the people in the panel should smell 'normally', not very good and not too bad. The training of the artificial neural network with the data from olfactometry is only as good as the sense of smell of the test panel during the measurements.

Appendix C

Gravimetric Adsorption Results

BACKGROUND INFORMATION

Description	
Day	Wednesday
Date	27-Sep-00
Time	12.30 pm
Temp (^{o}C)	20

Calibration	
At 0 (mm)	36.510
At 20 (mm)	36.490
Basket weight (g)	0.0765
Sample weight (g)	0.2921

RESULTS

Time	Pressure	Displacement				Mass	Note
		1	2	3	Av.		
Min	Torr	x 10^{-3} mm				mg	
0	50	108	111	107	108.7	390.601	
10	50	210	212	211	211.0	394.673	
20	50	236	238	237	237.0	395.707	
30	50	253	253	255	253.7	396.37	
40	50	271	273	271	271.7	397.087	
50	50	284	283	285	284.0	397.577	
60	50	287	289	289	288.3	397.75	
70	50	294	293	295	294.0	397.975	
80	50	295	297	295	295.7	398.041	
90	50	297	297	298	297.3	398.108	
110	100	320	321	319	320.0	399.01	
130	150	357	360	359	358.7	400.548	
150	200	379	377	377	377.7	401.304	
170	250	386	388	385	386.3	401.649	
190	290	396	396	394	395.3	402.007	
210	350	400	400	399	399.7	402.179	
230	400	400	400	399	399.7	402.179	

BACKGROUND INFORMATION

Description	
Day	Friday
Date	29-Sep-00
Time	5.00 pm
Temp (^{o}C)	50

Calibration	
At 0 (mm)	36.563
At 20 (mm)	36.543
Basket weight (g)	0.0765
Sample weight (g)	0.2921

RESULTS

Time	Pressure	Displacement				Mass	Note
		1	2	3	Av.		
Min	Torr	x 10^{-3} mm				mg	
0	50	48	47	48	47.7	386.066	
10	50	137	138	136	137.0	389.62	
20	50	159	159	161	159.7	390.522	
30	50	171	168	170	169.7	390.92	
40	50	176	175	176	175.7	391.158	
50	50	176	175	177	176.0	391.172	
60	50	176	177	176	176.3	391.185	
70	50	177	176	177	176.7	391.198	
80	50	176	177	177	176.7	391.198	
90	50	177	176	176	176.3	391.185	
110	100	194	194	195	194.3	391.901	
130	150	197	198	199	198.0	392.047	
150	200	200	201	202	201.0	392.166	
170	250	200	201	202	201.0	392.166	
190	300	201	201	201	201.0	392.166	
210	350	201	202	201	201.3	392.18	

BACKGROUND INFORMATION

Description	
Day	Tuesday
Date	19-Sep-00
Time	11.00 am
Temp (^{o}C)	100

Calibration	
At 0 (mm)	36.535
At 20 (mm)	36.515
Basket weight (g)	0.0765
Sample weight (g)	0.2921

RESULTS

Time	Pressure	Displacement				Mass	Note
		1	2	3	Av.		
Min	Torr	x 10^{-3} mm				mg	
0	50	22	25	23	23.3	382.212	
10	50	103	100	103	102.0	385.342	
20	50	108	106	107	107.0	385.541	
30	50	110	110	109	109.7	385.647	
40	50	110	112	111	111.0	385.700	
50	50	113	111	113	112.3	385.753	
60	50	113	113	114	113.3	385.792	
70	50	114	112	114	113.3	385.792	
80	50	114	114	113	113.7	385.806	
90	50	115	113	114	114.0	385.819	
110	100	129	131	129	129.7	386.442	
130	150	137	137	136	136.7	386.721	
150	200	143	144	142	143.0	386.973	
170	250	143	144	143	143.3	386.986	
190	300	143	143	145	143.7	386.999	*
210	315	145	144	143	144.0	387.013	*
230	320	144	145	144	144.3	387.026	*

*   Taking some time to reach required pressure
essentially the same pressure as taken a long time

BACKGROUND INFORMATION

Description	
Day	Wednesday
Date	20-Sep-00
Time	9.40 am
Temp (^{o}C)	150

Calibration	
At 0 (mm)	36.765
At 20 (mm)	36.745
Basket weight (g)	0.0765
Sample weight (g)	0.2921

RESULTS

Time	Pressure	Displacement				Mass	Note
		1	2	3	Av.		
Min	Torr	x 10^{-3} mm				mg	
0	50	143	144	145	144.0	381.862	
10	50	174	174	174	174.0	383.055	
20	50	181	182	182	181.7	383.36	
30	50	185	183	183	183.7	383.44	
40	50	184	183	184	183.7	383.44	
50	50	184	184	183	183.7	383.44	
60	50	184	184	184	184.0	383.453	
70	50	184	183	185	184.0	383.453	
80	50	182	185	184	183.7	383.44	
90	50	184	184	183	183.7	383.44	
110	100	194	194	193	193.7	383.838	
130	150	204	203	202	203.0	384.209	
150	200	212	213	212	212.3	384.581	
170	250	213	215	216	214.7	384.673	
190	290	215	214	214	214.3	384.66	*
210	300	215	214	215	214.7	384.673	

*   Having trouble getting to this point

Appendix D

Calibration of Quartz Spring

P=774.6 mmHg   T=20C   Right pan weight: 88.5mg

	Weight (mg)	Height (mm)	?? (cm)	
0	88.500	43.993		right equation
20	108.500	43.487		sample weight
50	138.500	42.735		(mg) y=1838.854-39.7857x
100	188.500	41.498		
145.8	234.300	40.328		Coefficients:
203.5	292.000	38.874		b[0] 1838.854 (intercept)
				b[1] -39.78569 (slope)
				r² 0.999982 (correlation coefficient)

Calibration Curve for Quartz Spring on Graimetric Rig

$y = -39.786x + 1838.9$

$R^2 = 1$

Weight (mg) vs Distance (cm)
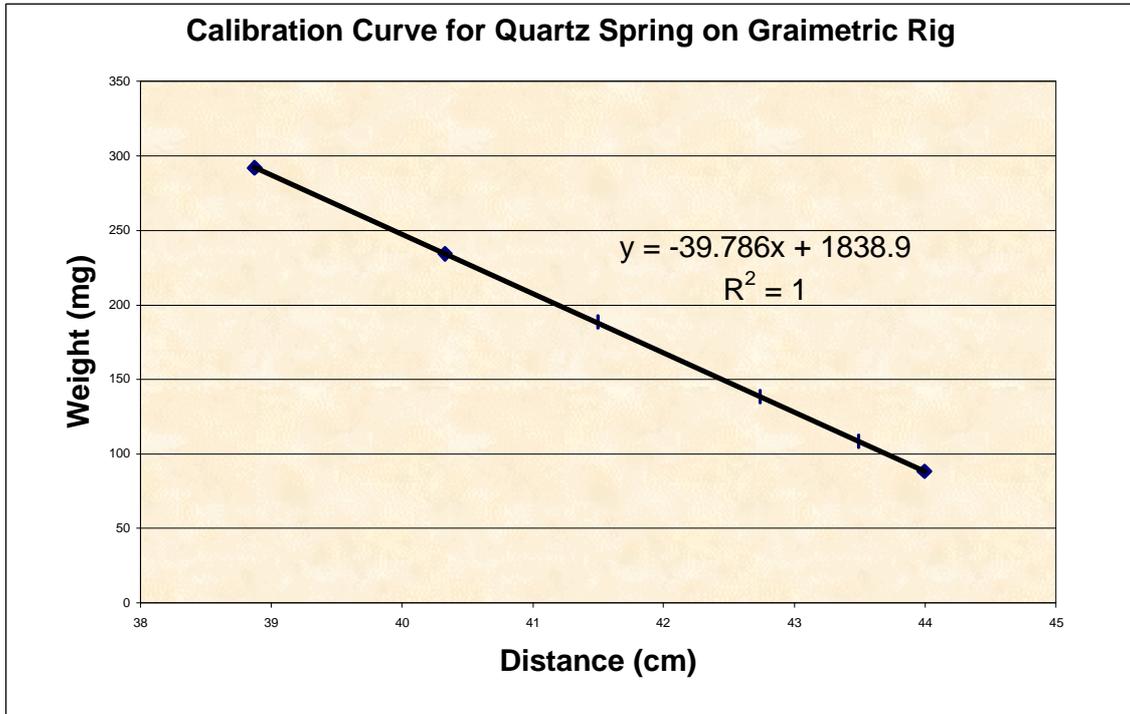
Appendix E

Break Through Column Results

Column Testing
1.47% v/v ammonia in air.

Time	pH
0	6.2
2	6.2
4	6.28
6	6.31
8	6.38
10	6.41
12	6.46
14	6.59
16	6.65
18	6.67
20	6.74
22	8.16
24	8.4
26	9.17
28	9.36
30	9.4

Column Breakthrough
pH vs Time
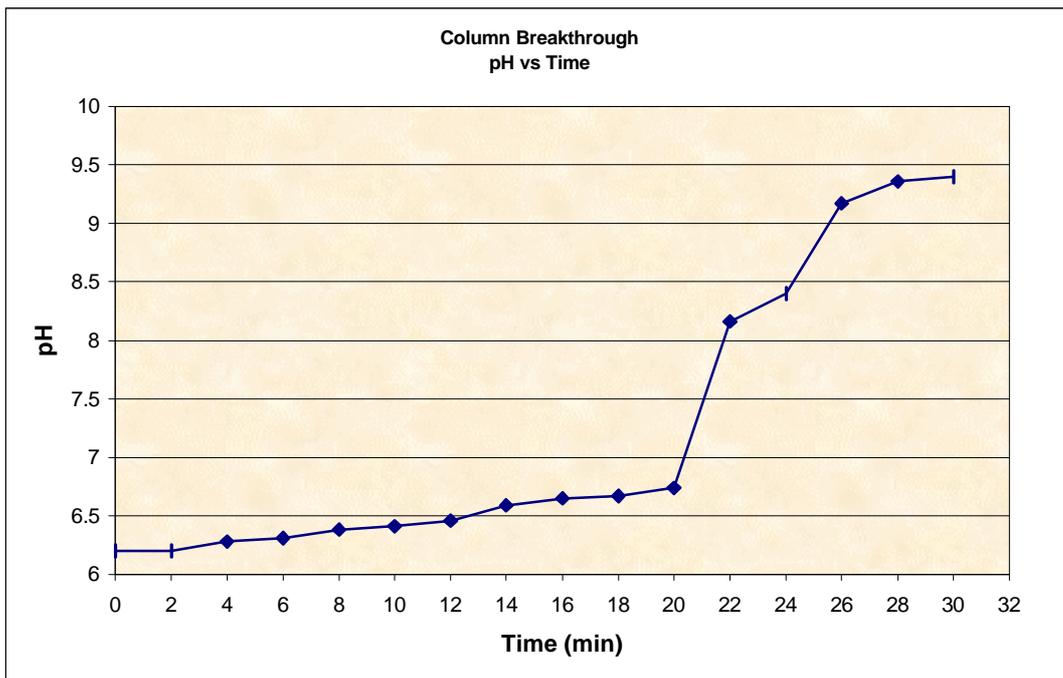
Appendix F

Calibration of pH meter

Calibration Solution pH   ⇒   7.0

Measured value of solution   ⇒   6.96   ⇒   Within tolerance.

Measured value of distilled water   ⇒   6.93   ⇒   Within tolerance.

Appendix G

On-Site Results

Summary Poultry Odour Project 2000
Day 1 - Friday 1 September

Morning	Z_ITE	Offensiveness	**Midday**	Z_ITE	Offensiveness
Control 1A	181	7.0	Control 2A	181	8.6
Control 1B	287	7.5	Control 2B	260	7.6
Mist 1A	301	6.3	Mist 2A	362	7.2
Mist 1B	304	6.3	Mist 2B	218	7.0
Control Average	234	7.3	Control Average	220	8.1
Mist Average	303	6.3	Mist Average	290	7.1

Day 2 - Monday 1

Morning	Z_ITE	Offensiveness	**Midday**	Z_ITE	Offensiveness
Control 3A	215	6.2	Control 4A	193	7.2
Control 3B	342	7.4	Control 4B	256	7.2
Mist 3A	192	7.8	Mist 4A	297	8.0
Mist 3B	342	6.0	Mist 4B	287	6.1
	Z_ITE	Offensiveness		Z_ITE	Offensiveness
Control Average	278	6.8	Control Average	224	7.2
Mist Average	267	6.9	Mist Average	292	7.1

	Z_ITE	Offensiveness
Zeolite Column Odour (ou/m3)	109	6.7

Morning	Avg	Stdev	Afternoon	Avg	Stdev
Control	256	72	Control	223	41
Mist	285	65	Mist	291	59

Overall Averages	OU/m3	Offensiveness		
Control	239	7.3	Std Dev Control	57
Mist	288	6.9	Std Dev Mist	57