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**EFFECT OF FLY ASH AND ZEOLITE AMENDMENT ON VOLATILE
AMMONIA LOSSES FROM HOG MANURE**

BY

ANDREA L. BULLINGER

**A Thesis
Submitted to the Faculty of Graduate Studies
in Partial Fulfillment of the Requirements
for the Degree of**

MASTER OF SCIENCE

**Department of Soil Science
University of Manitoba
Winnipeg, Manitoba**

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Effect of Fly Ash and Zeolite Amendment on Volatile Ammonia Losses from Hog Manure

BY

Andrea L. Bullinger

**A Thesis/Practicum submitted to the Faculty of Graduate Studies of The University
of Manitoba in partial fulfillment of the requirements of the degree
of
Master of Science**

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ABSTRACT

Bullinger, Andrea Lisa. M.Sc., The University of Manitoba, May, 2000. Fly Ash and Zeolite Effects on Volatile Ammonia Losses from Hog Manure. Major Professor; Tee Boon Goh.

Addition of waste coal fly ash to hog manure has been shown to increase ammonia (NH_3) volatilization and inhibit N mineralization. However, chemical alteration of fly ash may produce a zeolite-like mineral. Zeolites and calcium chloride (CaCl_2) have been shown to reduce NH_3 volatilization from manure. As well, chemical alteration of fly ash reduces its hazardous characteristics and improves its suitability for manure amendment and agricultural land application. The objectives of this study were (a) to chemically treat locally obtained fly ash and determine if physico-chemical changes are consistent with an increase in zeolitic character and (b) to examine the effectiveness of chemically altered and unaltered fly ash, mordenite and CaCl_2 in reducing NH_3 losses from anaerobically stored hog manure.

Fly ash was chemically altered in hot, alkaline solution for 24 hours. Physico-chemical properties of samples were determined using X-ray diffractometry (XRD), scanning-electron microscopy (SEM), heavy metal determination, cation exchange capacity (CEC), cation exchange selectivity (CES), specific surface, particle density, air dry moisture content and pH. Mean comparisons were conducted on all results. Manure properties determined included percent solids, density, total-, ammonium- (NH_4^+) and

organic-N, cation content (K^+ , Na^+ , Ca^{2+} , Mg^{2+}) and pH. Manure was amended with chemically altered and unaltered fly ash and mordenite, with and without $CaCl_2$, and stored in air-tight jars. Air removed from the jars was bubbled through acid traps. The cumulative NH_3 recovered in acid traps was determined for 86 days. Mean comparisons were conducted on cumulative NH_3 losses to days 40 and 86, NH_3 losses during individual sampling periods from days 1 to 40 and results of final destructive analyses (total-, NH_4^+ - and organic-N and pH).

XRD analysis indicated that chemical alteration of amorphous fly ash produced a crystalline aluminosilicate and SEM confirmed a change in fly ash particle shape. CEC, specific surface and air dry moisture content increased, and As and Pb levels and pH decreased after chemical alteration. All of these were consistent with an increase in the zeolitic character (due to similarities observed with mordenite) of fly ash after alteration. No changes were observed in CES or particle density after chemical alteration implying no increase in zeolitic character. In the volatilization study, unaltered fly ash (UFA), with and without $CaCl_2$, was found to increase NH_3 losses from manure (likely due to increased pH). Chemically altered fly ash (CAFA) alone was found to have no effect on volatilization but when combined with $CaCl_2$ increased total-N conserved in the manure and was as effective as mordenite. The control with $CaCl_2$ also had diminished volatile NH_3 losses which were not different than the CAFA with $CaCl_2$. However, CAFA with $CaCl_2$ had higher total-N than the control with $CaCl_2$ at the end of the study. This indicates that N was lost from the control with $CaCl_2$ samples in some form other than NH_3 . In all cases, treatments containing mordenite had the lowest volatile NH_3 losses. Even after mordenite treatments had completely dried, NH_3 losses were very low.

Calcium chloride had no apparent effect on volatilization in these treatments. In conclusion, UFA significantly increased NH_3 volatilization from anaerobically stored hog manure. Chemical alteration of fly ash increases its zeolitic character, however, benefits (in terms of reduced NH_3 losses) are not observed when amended with hog manure as compared to a control. However, CaCl_2 alone or combined with CAFA increases N conservation and is as effective as mordenite in this capacity after drying of the manure. Finally, NH_3 volatilization from mordenite was the lowest compared to all treatments. Due to health and environmental implications associated with NH_3 volatilization, mordenite is the most desirable of the hog manure amendments studied.

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FOREWARD

This thesis was prepared in the "Manuscript Style" according to the Guide to Thesis Preparation for Graduate Students in the Department of Soil Science (1996). The first manuscript (Chapter 3) will be submitted for publication in the journal *Fuel*. The second manuscript will be submitted for publication to the journal *Agricultural Wastes*.

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1. LITERATURE REVIEW

1.1 Introduction

From 1994 to 1998 hog production in Manitoba increased by approximately 9% annually (Manitoba Agriculture and Food 2000a). In 1999 Manitoba produced 4.7 million domestic hogs (Manitoba Agriculture and Food 2000b). Growing hog populations have been accompanied by a corresponding increase in hog manure production. Hog manure can be a source of air and water pollution and the unpleasant odours associated with it can diminish value of nearby properties (Ewanek 1996). Due to its high nutrient content, hog manure is slowly being reintroduced as a fertilizer in agricultural systems (Haynes 1984, McCalla 1974). However, manure handling practices can diminish the nutrient value of manure and may contribute to contamination of air and water resources. Mikkelsen (1997) and Vanderholm (1975) found that volatile ammonia (NH_3) losses from anaerobically stored hog manure can be as high as 80% and 75% respectively. Ammonia can have deleterious effects on the health of workers in livestock housing (Donham and Leininger 1984, Donham and Gustafson 1982, Donham et al. 1977) and on livestock (Drummond et al. 1980, Doig and Willoughby 1971, Strombaugh et al. 1969) and may diminish environmental quality through increased acid deposition (Verstraten et al. 1990, van Breemen et al. 1982), eutrophication (Peterjohn et al. 1996, Nohrstedt et al. 1996, Paerl 1995), terrestrial N deposition (Schlesinger 1997) and subsequent conversion and release of N_2O , a greenhouse gas and ozone depleting

substance (Duxbury 1994, Duxbury and Mosier 1993, Duxbury et al. 1993).

Amendments such as calcium chloride (CaCl_2) and zeolites have been shown to reduce NH_3 volatilization rates from manure by means of pH depression (Witter 1991, Witter and Kirchmann 1989a, Fenn et al. 1981, Fenn et al. 1980) and NH_3 or ammonium (NH_4^+) adsorption on charged mineral surfaces (Mahimairaja et al. 1994, Witter and Kirchmann 1989b, Miner 1984). Recent studies have shown that waste coal fly ash can be chemically altered, producing zeolites or zeolite-like materials (Singer and Berggaut 1995, Catalfamo et al. 1993, Mondragon et al. 1990, Hemni 1987a, Hemni 1987b, Höller and Wirsching 1985). Waste coal fly ash, produced in large quantities by thermal power stations, may contain a number of potentially hazardous materials and must be carefully managed. A rise in pH after addition of waste coal fly ash to hog manure has been shown to increase NH_3 volatilization (Vincini et al. 1994) and inhibit N mineralization (Garau et al. 1991). Treatment of fly ash may reduce its hazardous characteristics and improve its suitability for manure amendment and agricultural land application (Singer and Berggaut 1995, Catalfamo et al. 1993, Hemni 1987a, Hemni 1987b). It would therefore be useful to explore the use of altered fly ash as a manure amendment with regards to its ability to reduce NH_3 losses from hog manure. The objectives of this study were (a) to chemically alter locally obtained fly ash and determine if physico-chemical changes are consistent with an increase in zeolitic character by comparison with mordenite, a natural zeolite and (b) to examine the effectiveness of altered and unaltered fly ash, mordenite and CaCl_2 in reducing NH_3 losses from anaerobically stored hog manure.

1.2 Ammonia-N in Hog Manure

1.2.1 Manure Production

It has been estimated that in 1997, 25 million tonnes of hog manure were produced in Manitoba (Burton 2000). In the past, manure was a fundamental component of productive agroecosystems where animal husbandry and crop production went hand in hand. It was the primary source of crop nutrients in mixed farming systems. Over the last 50 years commercially produced inorganic fertilizers have replaced manure, allowing farmers to become more specialized (Eck and Stewart 1995). With an affordable source of readily available nutrients, farmers in agriculturally productive areas abandoned animal production and began to focus on crop production, whereas farmers in areas less suitable for crops have shifted to large-scale, confinement-type livestock production (Eck and Stewart 1995). Trends indicate that more livestock are being produced on less land than ever before and manure produced in these areas often exceeds the capacity of the neighbouring land for safe disposal (Manitoba Agriculture and Food 2000a, Ewanek 1988). Additionally, if the fertilizer value of manure is to be fully utilized, manure application must be timed such that it coincides with crop nutrient requirements. Accordingly, manure must be stored on site during the winter months and must be carefully managed to ensure the maintenance of its fertilizer value and protection of the neighbouring environment (Smith and Chambers, 1993).

1.2.2 Manure Composition

Taiganides and Hazen (1966) determined that livestock manure typically contains 75%, 80% and 85% respectively of the N, P, and K originally present in the feed. Baldwin (1982) recently reported a similar range for manure-N, 70-75%. However, manure composition is highly variable and may be influenced by animal physiology (e.g., size, sex, age, species, breed, and activity), nature of the feed (digestibility, protein, fibre, water intake and addition of antibiotics), environmental factors (temperature and humidity), and of course storage and handling (Smith and Chambers 1993, Burton and Beauchamp 1986, Taiganides and Hazen 1966). Hog manure is typically comprised of a large liquid fraction (urine) made up primarily of urea ($\text{CO}(\text{NH}_2)_2$) and water, and a smaller solid fraction comprised of faeces and waste feed (Klausner et al. 1994). Urea in the urine is readily hydrolyzed by urease enzymes to NH_4^+ according to the following equation where the pH ranges from 7 to 9 (Ferguson et al. 1984).



Ammonium, in turn, is readily converted to NH_3 which is prone to volatilization in the presence of hydroxide (OH^-) ions (DuPlessis and Kroontje 1964).



Analysis of a large number of manure samples by Norwest Labs, Winnipeg, has shown hog manure to contain between 69% and 71% NH_4^+ -N and between 29% and 31%

organic-N (Manitoba Agriculture and Food 2000c). Once airborne, NH_3 can pose a serious health risk to both livestock and humans and can contribute, to environmental degradation.

1.2.3 Factors Affecting NH_3 Volatilization From Hog Manure

Dewes et al. (1990) determined that total NH_3 losses from confined hog facilities ranged from 17.1 to 53.6% of total manure-N after 180 days of storage. The rate and extent of NH_3 volatilization from liquid hog manure is governed by three factors; a) the surface area of the liquid manure exposed to the air, b) the partial pressure of NH_3 in the liquid manure and c) the partial pressure of NH_3 in the overlying air. The interaction of these factors has a pronounced effect on total NH_3 losses, resulting in the variability of atmospheric NH_3 levels observed in the air of confined hog facilities (Donham et al. 1985). The model below describes NH_3 volatilization from liquid hog manure.

$$\text{NH}_3 \text{ Volatilization} = \frac{(\text{Surface Area}) * (\text{NH}_3 \text{ Partial Pressure} - \text{liquid})}{(\text{NH}_3 \text{ Partial Pressure} - \text{overlying air})} \quad [1.3]$$

Ammonia volatilization increases as the surface area of the liquid manure exposed to the air and the partial pressure of NH_3 in the manure increase. Surface area is influenced by the degree of manure agitation, whereas the partial pressure of NH_3 in the manure is influenced by pH, temperature, oxygen status and the concentration of NH_4^+ in the liquid. Conversely, NH_3 volatilization decreases as the partial pressure of NH_3 in the overlying air increases. The partial pressure of NH_3 in the overlying air is in turn influenced by the

ventilation of the stored manure. The influences mentioned above are described in greater detail below.

1.2.3.1 Manure agitation. Vlek and Stumpe (1978) demonstrated that agitating manure (i.e. by stirring before removal for land application) resulted an increase in NH_3 volatilization. When undisturbed, only the immediate surface of the manure was exposed to air and therefore available for NH_3 volatilization. However, when the manure was agitated a greater volume of the manure was exposed to air and the rate of NH_3 loss was greater. This effect was also observed by Miner and Hazen (1969), who found a considerable rise in atmospheric NH_3 levels in hog confinement facilities after manure had been stirred for removal.

1.2.3.2 Manure pH. As indicated in equation 1.2, the partial pressure of NH_3 in the liquid manure increases as solution pH increases. During the urea hydrolysis reaction (equation 1.1) H^+ ions are consumed. As a result there is a decrease in H^+ ions and a corresponding increase in pH. Thus, urea hydrolysis simultaneously increases pH as it forms NH_4^+ , increasing the potential for conversion of NH_4^+ to NH_3 and its subsequent volatilization (Fenn and Hossner 1985).

1.2.3.3 Temperature. Ammonia has a low boiling point (-33.37°C) and low heat of vaporization (5,581 cal/mole) (Jones 1973). As a result, volatilization rates increase with increasing temperature (Cotton et al. 1987). Additionally, urease activity increases linearly with increasing temperature up to 45°C , at which point enzyme functioning

begins to be impaired (Gould et al. 1973). As stated earlier, NH_3 volatilization is controlled in part by urease activity and this amplifies the effect of temperature on increased volatilization.

1.2.3.4 Oxygen status. The oxygen status of the manure is effected by temperature, ventilation and agitation of the manure. Kirchmann and Witter (1989) have shown that manure stored under aerobic conditions is more prone to NH_3 volatilization than anaerobically stored manure due to increased microbial activity. During anaerobic storage microbial activity is lower and the by-products of manure decomposition include hydrogen sulphide (H_2S), methane (CH_4), NH_4^+ and organic acids (Donham et al. 1985). The organic acids reduce manure pH and consequently NH_3 volatilization. This is illustrated in a study by Vanderholm (1975) who showed that NH_3 losses from aerobically stored manure are somewhat higher, ranging from 30% to 90%, whereas NH_3 losses from anaerobically stored manure ranged from 10% to 75%.

1.2.3.5 Ammonium concentration. As indicated in equation 1.2, the concentration of NH_4^+ in the manure will affect the partial pressure of NH_3 in the manure, influencing volatilization. Vlek and Stumpe (1978) have shown that NH_3 volatilization is higher from solutions with higher NH_4^+ ion concentrations. Thus, manure diluted by water (i.e. due to flushing of livestock houses) exhibits lower levels of NH_3 volatilization (Kroodsma et al. 1993, Veenhuizen and Qi 1992). Conversely, as manure loses moisture to evaporation, the NH_4^+ concentration becomes greater and volatilization increases until all moisture is gone. Urease activity is also controlled by the presence of moisture and ceases in the absence of water. Therefore, once the manure is completely dry, NH_3 volatilization stops.

1.2.3.6 Ventilation. Avnimelech and Laher (1977) have shown that a high partial pressure of NH_3 in the air above a solution containing aqueous NH_4^+ will hinder volatilization. In situations where NH_3 is not removed from the surface of stored manure (i.e. under poor ventilation) the partial pressure of NH_3 in the overlying air will increase until it is sufficient to stop further volatilization (i.e. when an equilibrium is established). Where ventilation is adequate, volatilized NH_3 is removed from the system and partial pressure never impedes volatilization. Several studies have illustrated this by demonstrating that an increase in NH_3 volatilization occurs with an corresponding increase in air flow rate (ventilation) (Sommer and Ersbøll 1996, Nathan and Malzer 1994, Sommer et al. 1991, Hoff et al. 1981).

1.2.4 Physiological Impacts of Increased Atmospheric NH_3

Ammonia is a ubiquitous substance and is an important component in the cycling of N between biotic and abiotic systems (Subcommittee on Ammonia 1979). However, atmospheric NH_3 elevated above ambient concentrations may have deleterious effects on the health of humans and livestock. This is problematic where animals are housed over waste pits, particularly during winter months where ventilation is reduce to limit heat losses and save energy costs (Subcommittee on Ammonia 1979, Curtis 1972). Miner and Hazen (1969) found that NH_3 levels ranged from 6 to 35 ppm in hog confinement facilities but these levels increased in winter and when manure was being stirred prior to removal. Donham et al. (1985) tested air in 23 hog confinement facilities during winter and early spring and found atmospheric NH_3 values ranged from 13 to 76 ppm with a mean of 31.4 ppm. Ammonia concentrations of 20 ppm are considered to be acceptable

but chronic exposure to higher levels have been shown to cause headaches, nausea and a reduced appetite (Subcommittee on Ammonia 1979).

1.2.4.1 Impacts on health and growth of hogs. Stombaugh et al. (1969) found that at 280 ppm, NH_3 is toxic to hogs, however, adverse effects on respiratory health and weight gain were experienced at concentrations as low as 61 ppm. Similarly, Drummond et al. (1980) found that hogs exposed to 50 ppm NH_3 for 4 weeks gained 12% less weight than a control group. Although Doig and Willoughby (1971) found no relationship between atmospheric NH_3 concentration and weight gain in hogs they did find an increase in damage to the upper respiratory tract with increasing levels of airborne NH_3 .

1.2.4.2 Human health impacts. In light of the physiological effects observed in hogs, it is not surprising that the health of workers in confinement facilities are also affected by increased levels of atmospheric NH_3 . Ammonia has a high affinity for water and therefore is preferentially absorbed by the moist tissues of the eyes, nose and upper respiratory tract causing severe irritation (Donham and Gustafson 1982, Subcommittee on Ammonia 1979, Donham et al. 1977). As well, prolonged exposure to increased levels of NH_3 has been shown to cause headaches, nausea and loss of appetite and can lead to chronic respiratory disease (Donham and Leininger 1984, Subcommittee on Ammonia 1979).

1.2.5 Environmental Impacts of Increased Atmospheric NH_3

Adverse effects from increased NH_3 emissions are not limited to within confinement facilities. An estimated 65% – 95% of the N in hog manure is lost as volatile NH_3 and later deposited on land or water (Nowlin and Boyd 1997). This deposition can have detrimental environmental effects. Ammonia emissions from livestock wastes account for approximately 43% of total global NH_3 emissions (Schlesinger and Hartley 1992). Consequently, manure management practices can have far reaching environmental impacts.

1.2.5.1 Acid deposition. In light of equation 1.2, acidification caused by deposition of atmospheric NH_3 seems counterintuitive. Indeed, acidification does not occur as a result of NH_3 dissolution into atmospheric water (ultimately falling as rain) or soil water (after dry deposition) but rather is a result of the nitrification of NH_4^+ in soil (van Breemen et al. 1982, Verstraten et al. 1990). Twice as much acidity is produced during nitrification of NH_4^+ than would be produced by simple acid dissociation of NH_4^+ to NH_3 (Paul and Clark 1996, ApSimon et al. 1987, Nihlgard 1985). As well, Schlesinger and Hartley (1992) estimate that 10% of NH_3 emissions are oxidized to nitric oxides (NO and NO_2 also called NO_x) in the atmosphere. Nitric oxides rapidly react with OH radicals, forming nitric acid (H_2NO_3) (Rodhe et al. 1981). The H_2NO_3 ultimately is deposited, contributing to soil acidification. This is of particular importance in forest soils where nitrification is performed primarily by heterotrophic microorganisms which are less acid sensitive than the autotrophic nitrifiers typically found in agricultural soils (Paul and Clark 1996). Decreased soil pH results in increased chemical weathering of soil minerals and

subsequent release of aluminium ions (Al^{3+}) into the soil solution (Schlesinger 1997). Elevated Al^{3+} in the soil solution is toxic to plants and decreases the availability of nutrients such as Ca, Mg and P for uptake by vegetation resulting in forest dieback (Likens et al. 1996, Berger and Glatzel 1994, Wright et al. 1994, Godbold et al. 1988, Shortle and Smith 1988). Additionally, atmospheric NH_3 has been shown to enhance dissolution and oxidation of acidic pollutants such as sulphur dioxide (SO_2) through acid neutralization in atmospheric water and formation of ammonium sulphate ($(\text{NH}_4)_2\text{SO}_4$) (ApSimon et al. 1987, Möller and Schieferdecker 1985, Adamowicz 1979, Scott and Hobbs 1967). This not only increases the quantity of both SO_2 and NH_3 which can be carried but also increase the distance they may be transported (ApSimon et al. 1987). Acidification of agroecosystems has not been found to be as significant as in forest ecosystems. This is likely due to the inhibition of nitrification at the relatively high pH values (6.0) encountered in agroecosystems as compared to forest ecosystems where nitrification has been found to occur at pH values as low as 3.5 (Paul and Clark 1996, Novick et al. 1984).

1.2.5.2 Terrestrial N deposition. In forest systems limited by N, NH_3 deposition may act as a fertilizer, potentially increasing productivity (Schlesinger 1997). However, as these systems become saturated with N, effects of acidification become more pronounced and dieback begins (Aber et al. 1989). Concurrently, forest systems receiving excess N from atmospheric deposition lose significant quantities of nitrate (NO_3^-) to stream waters, contributing to eutrophication (Peterjohn et al. 1996, Nohrstedt et al. 1996, Durka et al. 1994, Aber et al. 1993). Additionally, long term N deposition can cause Mg, Ca, K and P deficiencies in trees and loss of fine-root biomass in vegetation, negating the effect of

increased N availability (van Dijk et al. 1990, Schulze 1989, Mohren et al. 1986, Roelofs et al. 1985). Limited information is available regarding the effects of NH_3 deposition in agroecosystems. Langland (1992) found that atmospheric deposition of N from a livestock facility accounted for 17% of the annual N applied to neighbouring farmland. Due to the extensive use of commercially produced fertilizers, any N additions through atmospheric deposition would likely be in excess of crop requirements and would be lost either by re-volatilization, denitrification or in solution as NH_4^+ or NO_3^- exacerbating eutrophication of surrounding waterways.

1.2.5.3 Eutrophication. As stated earlier, NO_3^- additions to streams and lakes may increase from areas experiencing enhanced atmospheric deposition of NH_3 (Peterjohn et al. 1996, Nohrstedt et al. 1996, Durka et al. 1994, Aber et al. 1993). As well, inland waters receive significant contributions of NH_3 through direct atmospheric deposition (Aneja et al. 1998, Paerl 1995, Langland 1992). Combined, these N additions can lead to increased microbial activity resulting in algal blooms and depletion of dissolved oxygen causing asphyxiation of aquatic organisms (Schlesinger 1997).

1.2.5.4 Contributions to the greenhouse effect. Ammonia itself is not a greenhouse gas, however, reactions in which it participates may increase the production of other greenhouse gases (Duxbury 1994, Duxbury and Mosier 1993, Duxbury et al. 1993, Mooney et al. 1987). Schlesinger and Hartley (1992) estimate that 90% of NH_3 emissions are deposited on the earth's surface either to be re-volatilized, taken up by plants (as NH_4^+ or NO_3^-) or denitrified. The end product of denitrification is N gas (N_2) but incomplete denitrification producing N_2O or NO is not uncommon (Paul and Clark 1996). Hauck

(1984) estimated that 20-25% of applied N undergoes incomplete denitrification producing N_2O or NO. Similarly, N_2O and NO can be produced through incomplete nitrification, which occurs for up to 10% of the applied N (Paul and Clark 1996). Nitrous oxide, as a greenhouse gas, has a potential for thermal absorption approximately 300 times greater than that of CO_2 (Schlesinger 1997). However, its atmospheric concentration is much smaller and therefore contributes less to global warming (Paul and Clark 1996). This may change as N_2O emissions increase in the years to come. Current models of greenhouse gas emissions underestimate the quantity of anthropogenically produced N_2O (Eichner 1990, Duxbury et al. 1982). Robertson (1993) has suggested that the unaccounted for inputs of N_2O are most likely a product of indirect agricultural outputs such as NH_3 deposition. In addition to N_2O production, NH_3 may contribute to enhanced global warming through the production of sulphate aerosols in the atmosphere. Mitchell et al. (1995) and Kiehl and Briegleb (1993) have shown that sulphate aerosols are strong greenhouse gases and should be included in climate change models. Ammonia in the atmosphere can increase the formation of sulphate aerosols in excess of an order of magnitude (Adamowicz 1979, Scott and Hobbs 1967). Unfortunately, the impact of increased NH_3 emissions on global warming is complex and actual contributions of greenhouse gases have not been established. It is, however, clear that NH_3 does contribute to global climate change despite our inability to quantify its effect (Duxbury 1994, Duxbury and Mosier 1993, Duxbury et al. 1993).

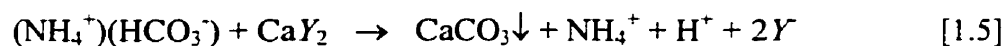
1.2.6 Reducing Volatile NH₃ Losses from Hog Manure

Concern over the environmental implications of increasing NH₃ emissions have led many researchers to explore methods by which its volatilization from manure may be reduced. Reductions have been accomplished by decreasing manure pH, by immobilization of NH₄⁺-N in microbial tissues and by adsorption of NH₃ or NH₄⁺ on to charged mineral or organic amendments.

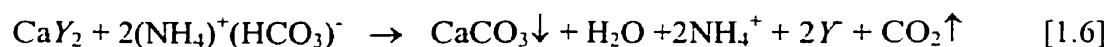
1.2.6.1 pH reduction. Several researchers have shown reduction of manure pH, by means of direct acidification, to be successful in reducing NH₃ volatilization (Bussink et al. 1994, Husted et al. 1991, Pain et al. 1990, Stevens et al. 1989). However, producers wishing to acidify manure must first address issues associated with hazardous materials handling, costs and application of acidic materials to agricultural lands. Witter and Kirchmann (1989a) have shown that the pH of stored manure is reduced when Ca-containing salts are mixed in. Carbon dioxide (CO₂) dissolved in liquid manure reacts with water producing bicarbonate (HCO₃⁻) and H⁺ ions according to the following equation (Schlesinger 1997).



Ammonium in the manure forms an unstable ion pair with the HCO₃⁻ (Jackson 1979). HCO₃⁻ can react with Ca²⁺, added in the form of a Ca-containing salt, producing calcium carbonate (CaCO₃) and a H⁺ ion according to the reaction below (Feagley and Hossner 1978).



Where Y represents a monovalent anion. Consumption of HCO_3^- in this way (equation 1.5) stimulates the reaction of CO_2 with water producing more HCO_3^- and H^+ (equation 1.4). In this way pH is reduced suppressing NH_3 volatilization. However, Fenn et al. (1981) indicate that this mechanism is effective only at pH values greater than 7.0 or where the decomposition of H_2CO_3 can act as a source of HCO_3^- . Reactions 1.4 and 1.5 were combined by Witter and Kirchmann (1989a) and are stated below,



Ammonium is included in the equation to signify that it is conserved. It is important to note that the equation is self sustaining. Production of HCO_3^- from carbonic acid produced by the dissolution of CO_2 gas results in the precipitation of CaCO_3 in the presence of a Ca-containing salt. The consequent CO_2 released is available again for dissolution.

1.2.6.2 Nitrogen immobilization. Kirchmann and Witter (1989) and Mahimairaja et al. (1994) have shown that under aerobic storage conditions, the addition of microbial substrates of high C/N ratio (e.g. straw) reduce NH_3 volatilization due to the immobilization of N in microbial tissues. Under anaerobic conditions, addition of substrates did not reduce NH_3 volatilization, likely due to diminished microbial activity (Kirchmann and Witter 1989).

1.2.6.3 Adsorption of $\text{NH}_3/\text{NH}_4^+$ on the surface of charged sorbents. Materials which have a net negative surface charge are able to retain cations and polar molecules. Cations and polar molecules held on the surface of these materials are effectively removed from the surrounding environment and do not participate in its reactions. In this way, negatively charged sorbents can adsorb NH_4^+ cations and polar NH_3 molecules in the liquid manure, thereby reducing the partial pressure of NH_3 in the manure and shifting equilibrium reactions such that NH_3 volatilization is reduced (equation 1.2). A number of adsorbents have been used in this regard with considerable success. Kemppainen (1987) and Peltola (1986) found that peat moss is highly effective at adsorbing NH_4^+ cations from manure. Peat was also found to be effective in adsorbing gaseous NH_3 and has been used as a filter, improving the quality of air vented from livestock houses (Witter and Kirchmann 1989, Scholtens et al. 1987). A number of mineral amendments have also been explored. Bentonite has been shown to reduce NH_3 volatilization from liquid cattle manure (Dewes 1987) and vermiculite has been treated with NH_4^+ and used as a slow release fertilizer (Scott et al. 1983). Both bentonite and vermiculite are clay minerals known for their cation exchange properties. However, zeolites have been found to be the most successful NH_4^+ and NH_3 adsorbents. Mahimairaja et al. (1994), Witter and Kirchmann (1989) and Ferguson and Pepper (1987) demonstrated that zeolites have a high affinity for NH_4^+ (higher than that found for peat) and are able to reduce gaseous NH_3 losses from both soil and stored manure. Miner (1983) has shown zeolites to be effective at removing gaseous NH_3 from air in livestock houses. Zeolites have also been used to reduce nitrification rates and subsequent NO_3^- leaching losses in soil by absorption of NH_4^+ (Perrin et al. 1998, Huang and Petrovic 1994, MacKown and Tucker

1985, Weber et al. 1983). Clearly, zeolites have tremendous potential for application in agricultural sciences.

1.3 Natural Zeolites

1.3.1 Formation

Hay (1966) and Sheppard and Gude (1968, 1969, 1973) have associated zeolite formation with the alteration of tuffs (consolidated volcanic ash deposits) in saline lake basins. Mineral composition of the tuffs, lake chemistry (pH and ionic strength), temperature, pressure and time were found to be dominant factors affecting the types of zeolites formed in these systems (Hay 1966). Similarly, zeolites have been found in marine sediments primarily associated with submerged tuffs from which they have formed (Hay 1978). As sediments accumulate, tuffaceous materials are buried and with time may be exposed to high temperatures and pressures. This increases the rate of zeolite diagenesis in the tuff but may also lead to the formation of more stable silicate phases (Hay 1978). Zeolites may also form from tuffs in the absence of standing water. As water percolates through the tuff it reacts with the volcanic glass, producing montmorillonite and increasing solution pH and ionic strength (Mumpton 1978). As pH and ionic strength increase, alteration of the tuff shifts to zeolite formation (Hay 1963). Zeolite formation also occurs where heated, saline water rises through amorphous tuffs, as is the case with hot springs (Honda and Muffler 1970). Salt affected soils are also sites of zeolite formation by means of the alteration of clay minerals or tuffaceous materials (Frankart and Merbillion 1970 in Ming and Mumpton 1989, Hay 1978). Exposure of

tuffaceous materials to alkaline solutions with high ionic strengths appears to be the common denominator in zeolite formation and has been manipulated for the synthetic preparation of zeolites in the laboratory.

1.3.2 Synthesis

Once established, conditions of zeolite formation were quickly reproduced by researchers in the laboratory resulting in the production of the first synthetic zeolites (Ames 1963). Zeolites were prepared by heating mixtures of silica and alumina gels and a number of strong bases (Ames 1963). Technological advancements in the field have refined these processes and led to mass production of synthetic zeolites, an industry now worth millions of dollars (Mumpton 1978). Due to its physico-chemical similarity to volcanic ashes, several researchers have explored the use of waste coal fly ash in the production of synthetic zeolites (Singer and Berkgaut 1995, Catalfamo et al. 1993, Mondragon et al. 1990, Hemni 1987a, Hemni 1987b, Höller and Wirsching 1985). This may provide an environmentally sustainable alternative to land based disposal of waste coal fly ash.

1.3.3 Physico-chemical Properties

1.3.3.1 In general. Zeolites are hydrated aluminosilicates with three-dimensional crystal structures containing channels and voids occupied by water and cations of the alkali and alkaline earth groups (Tsitsishvili et al. 1992, Ming and Mumpton 1989, Gottardi and Galli 1985). They generally follow the idealized formula (Gottardi and Galli 1985):

$$(M^+)_a(D^{2+})_d [Al_{(a+2d)}Si_{n-(a+2d)}O_{2n}] \cdot mH_2O \quad [1.7]$$

where M^+ represents monovalent cations and D^{2+} represents divalent cations. The atoms contained in the square brackets represent the permanent zeolite structure or framework, whereas atoms in the curved brackets represent extra-framework cations which are exchangeable (Ming and Mumpton 1989, Gottardi and Galli 1985). Water molecules can also be reversibly lost or gained and generally follow the rule $n \geq m$ (Gottardi and Galli 1985). As well, the ratio of Si to Al in zeolites is always greater than 1 and typically less than 6 (Tsitsishvili et al. 1992, Ming and Mumpton 1989, Gottardi and Galli 1985). The considerable substitution of Al for Si in tetrahedra produces a large net negative surface charge and consequently a high cation exchange capacity (CEC). Tetrahedra are linked to form secondary building units (SBU) which range from simple four or six membered rings to complex cubo-octahedra. SBU are arranged to form integrated crystal structures permeated by channels and voids (Ming and Mumpton 1989). The result is a very open framework (up to 50% void volume) which may explain the low densities of zeolites (2.0 - 2.3 g/cm³) relative to other tectosilicates (2.6-2.7 g/cm³) (Ming and Mumpton 1989). The open framework and interconnection of channels and voids permit the exchange of ions inside the crystal framework as well as on the external mineral surface. The capacity for internal exchange is governed by channel and void dimensions (a function of the arrangement of SBU) and the size of the exchanger. Under natural conditions, zeolites have been shown to exhibit a certain selectivity for monovalent cations such as NH_4^+ (Ames 1960, 1961). However, selectivity reversals or modifications have been observed and are known to be closely linked with structural features of the zeolite and differences

in the nature of the exchangers and the sites they occupy (Sherry 1969). Breck et al. (1956) showed that the molecular sieve properties of zeolites are dependent on the types of exchange cations held in channels and voids. In their study sorption capacities of various inorganic (including NH_3) and organic molecules on a synthetic sodium exchanged zeolite (Linde 4-A) were drastically reduced when Na^+ was replaced by larger K^+ ions on the zeolite exchange sites. The larger K^+ ions effectively blocked channel openings reducing sorption to almost zero. Similar results were observed when sorption of the same molecules dramatically increased due to the replacement of Na^+ ions by Ca^{2+} ions. The divalent Ca^{2+} replaced two Na^+ cations clearing channel entrances and permitting greater diffusion of the molecules into the zeolite lattice. Clearly, exchange reactions in zeolites are complex, being affected both by the nature of the framework and by the cations adsorbed. These reactions will certainly influence adsorption characteristics of zeolites used as amendments in manure. There will be a number of different cations in manure competing for exchange and these in turn may alter the adsorption capacity of the zeolites. Therefore, when considering zeolites as manure amendments, care should be given to select those having high NH_4^+ selectivity which is not significantly diminished in the presence of cations typically found in manure.

1.3.3.2 Mordenite. The mordenite framework is made up of six ring tetrahedral sheets positioned parallel to the *a-c* plane (see Figure 1.1) (Vaughan 1978, Meier 1978). Apices of the tetrahedra do not all point in the same direction as is the case with minerals of the mica group. Rather, tetrahedra alternate, resulting in the formation of channels running along *c* (occurs where apices point in opposite directions) and the formation of four ring

linkages between sheets (occurs where apices meet) producing a channel along b (Meier 1978, Vaughan 1978).

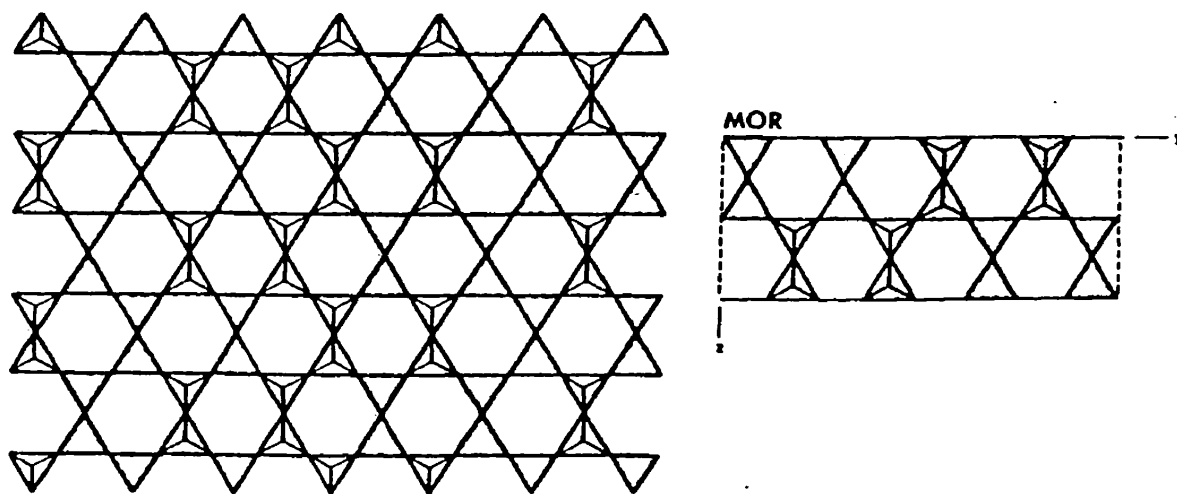


Figure 1.1 An idealized illustration of the mordenite framework depicting the six ring tetrahedral sheet in the a - c plane (from Meier 1978).

Two channels, an eight membered ring and a twelve membered ring, run parallel to c and one eight membered ring runs parallel to b (Meier 1978, Vaughan 1978). The 12 member ring is elliptical with major and minor diameters of 7.0 Å and 5.8 Å respectively, but it is only able to accommodate molecules having a maximum diameter of 4.2 Å (Tsitsishvili 1992, Nishimura and Takahashi 1970). These size limitations may be attributed to stacking faults in the framework or to the blockage of channels by quartz and iron oxides trapped in the crystals during formation (Vaughan 1978, Frilette and Rubin 1965). The smaller eight member rings (accommodate diameters of 2.4 Å) are frequently blocked by cations (Tsitsishvili 1992, Vaughan 1978). As a result, diffusion of molecules into the

mordenite framework occurs only in the largest channel (Tsitsishvili 1992, Vaughan 1978). Size limitations in mordenite can be overcome by acid treatment, which removes quartz and iron oxides from channels, or by exchange of native cations for smaller ones (Tsitsishvili 1992, Nishimura and Takahashi 1970). Nishimura and Takahashi (1970) have shown that NH_4^+ -exchanged mordenite can absorb a greater quantity of larger compounds such as benzene and n-butane than Na- or Ca-exchanged mordenite. This is a result of an increase in the effective diameter of the mordenite channels after exchange of adsorbed cations with NH_4^+ (Tsitsishvili 1992, Nishimura and Takahashi 1970). Early studies of the chemical properties of mordenite indicated that it readily adsorbs gases and small monovalent cations (Vaughan 1978). Cations most commonly associated with mordenite in nature are Na^+ (2 to 5 per unit cell), Ca^{2+} (1.6 to 2.5 per unit cell) and to a lesser extent K^+ (0.1 to 0.8 per unit cell) (Passaglia 1975). Barrer and Klinowski (1974) determined the relative cation affinity of mordenite to be $\text{Cs}^+ > \text{K}^+ > \text{NH}_4^+ > \text{Na}^+ > \text{Ba}^{2+} > \text{Li}^+$. The Si/Al ratio ranges from 4.5 to 5.5 with the majority of the isomorphous substitution occurring in the four membered rings (Tsitsishvili 1992, Meier 1978). Mordenite has a density of 2.15 g/cm^3 illustrating its large void volume relative to other tectosilicates (Tsitsishvili 1992). In nature, crystals are typically fibrous, a manifestation of the of the mordenite framework (Mumpton and Ormsby 1978).

1.3.4 Agricultural and Industrial Applications

1.3.4.1 Waste treatment. Zeolites have been successfully employed in the treatment of a wide variety of wastes. The selectivity of zeolites for NH_3 and NH_4^+ make them especially useful in the treatment of biological wastes. Zeolites have been shown to

absorb NH_4^+ cations in animal wastes, reducing NH_3 volatilization and maintaining N-fertilizer value of the manure (Mahimairaja et al. 1994, Termeer and Warman 1993, Witter and Kirchmann 1989b). Miner (1983) has shown zeolites to be successful in removing gaseous NH_3 from air in livestock housing improving air quality. Mercer et al. (1970a) and Weber et al. (1983) have demonstrated that zeolites can be used to remove NH_4^+ ions from sewage sludge and can remove hazardous metal cations in tandem. Zeolites are widely used in aquacultural systems to remove toxic NH_4^+ wastes and maintain fish health (Ciambelli et al. 1983, Colella et al. 1983, Piper and Smith 1983). Similarly, phillipsite has been used in the medical industry to clean NH_4^+ wastes from liquids in dialysis systems (Andersson et al. 1975 in Mumpton 1978). Applications of zeolites in waste treatment are not limited to NH_3 removal. Zeolites have also been used to remove radioactive Cs^{137} and Sr^{90} from the waste waters of nuclear energy production facilities (Nishita and Haug 1972, Adam et al. 1971, Mercer et al. 1970b). As well, several researchers have used mordenite and clinoptilolite to clean stack gases, due to their affinity for airborne contaminants such as SO_2 , NO_x and CO_2 (Mumpton 1978). In Japan, zeolites have been employed as adsorbents in the clean up of oil spills (Miki et al. 1974 in Mumpton 1978). Finally, zeolites are used extensively to remove heavy metal cations from hydrometallurgical waste waters (Mumpton 1978). The above examples illustrate that zeolites have considerable potential in the treatment of both biological and industrial wastes.

1.3.4.2 Energy extraction and production techniques. The potential for zeolite use in the energy extraction and production industry is dependent on the gas adsorption properties of these minerals. Zeolites have been shown to selectively absorb gases, other

than oxygen (O_2), causing a relative enrichment of O_2 in the air (Dominé and Häy 1968 in Mumpton 1978). This may find application in the mining of deep coal seams which require gasification prior to extraction. Gasification can be accomplished by pumping liquid O_2 into the seams increasing the rate of combustion. However, the cost of liquid O_2 has rendered these seams unmineable. Zeolites could be a cost effective alternative, enriching air in O_2 on site and acting as adsorbents for hazardous gases produced by the accelerated combustion (Mumpton 1978). Similarly, zeolites have been used to purify sour natural gases contaminated with CO_2 , H_2S and water (Mumpton 1978). Landfills generate a number of potentially hazardous gases including CH_4 . In 1975, the NRG Corporation in Bowie, Arizona, employed two zeolites to remove gases and moisture vented from a landfill. Methane, which is not absorbed by the zeolites, was purified by this process and sold to a local utility company (Mumpton 1978). As well, several researchers have shown zeolites to be useful in the refinement of petroleum products either as catalysts or as adsorbents of contaminant gases (Mumpton 1978). Carbon dioxide, H_2S and CH_4 , like NH_3 , are gases commonly emitted from livestock manure. Similarly, zeolites may also be used to "purify" CH_4 discharged from animal wastes for later use as an energy source (Mumpton 1978). Finally, the capacity of zeolites to absorb water has been exploited in the development of solar power cells. Heat dehydrates zeolites during the day when they are exposed to sunlight. At night water is re-adsorbed by the zeolites releasing the stored latent heat to the surrounding environment (Mumpton 1978). Several of these applications are still in developmental stages but increasing demands for environmentally sustainable energy extraction and production alternatives ensure continued exploration in this field.

1.3.4.3 Fertilizer applications. A great deal of research pertaining to application of zeolites in agricultural production systems has been completed in North America in the last 25 years. Hershey et al. (1980) demonstrated that clinoptilolite acts as a slow release source of K^+ for greenhouse plants, resulting in increased fertilizer efficiency. Similarly, NH_4^+ exchanged zeolites and zeolites combined with urea have been shown to provide crops with a more steady flux of N throughout the growing season than urea alone, resulting in increased yields and again, improved fertilizer efficiency (Lewis et al. 1983, Moore et al., Pirela et al. 1983). Lewis et al. (1983) also reported that NH_3 and nitrite (NO_2^-) toxicity effects were reduced in coarse textured soils amended with clinoptilolite and urea as opposed urea only. In order to prevent compaction, golf greens are built on sandy soil materials. When these soils are fertilized, nitrate leaching losses can be extensive (due to their inherently low cation exchange capacity) and may jeopardize groundwater quality. Several researchers have demonstrated that NO_3^- leaching losses from fertilized golf greens could be effectively reduced by incorporating coarse zeolites into sandy soils where they would improve fertilizer efficiency (Huang and Petrovic 1994, Nus and Brauen 1991, Ferguson and Pepper 1987, Ferguson et al. 1986, MacKown and Tucker 1985, Bartz and Jones 1983). This principle has been applied to sandy agricultural soils, improving crop yields and protecting groundwater resources from NO_3^- leaching (Perrin et al. 1998, Boettinger et al. 1994). Finally, zeolites have been used to facilitate the delivery of P to crops from poorly soluble fertilizers such as apatite (Allen et al. 1996, Allen et al. 1993, Barbarick et al. 1990, Chesworth et al. 1987, Lai and Eberl 1986). Dissolution of apatite releases Ca^{2+} and PO_4^{3-} ions into the soil solution. The rate of dissolution can be increased if Ca^{2+} ions are adsorbed onto zeolite mineral surfaces. If the zeolites are exchanged with NH_4^+ or K^+ prior to incorporation into the soil, adsorption

of Ca^{2+} will exchange these nutrients releasing them into the soil solution. Combined, NH_4^+ and/or K^+ exchanged zeolites and apatite are a sustained source of plant available nutrients (Allen et al. 1996, Allen et al. 1995, Allen et al. 1993, Barbarick et al. 1990, Chesworth et al. 1987, Lai and Eberl 1986).

1.3.4.4 Other agricultural applications. Zeolites have been used as livestock feed additives increasing feed efficiency and weight gain and reducing toxicity effects associated with consumption of non-protein feed sources such as urea (Roland and Dorr 1989, Nestorov 1983, Torii 1977). As well, zeolites may act as carriers for charged and polar pesticides. Yoshinaga et al. (1973 in Mumpton 1978) found clinoptilolite to be an effective carrier for benzylphosphorothioate, a fungicide used in rice production.

1.3.4.5 Industrial applications. Zeolites are used in a variety of industrial applications, however, only the two most common uses are discussed here. The ion selectivity of zeolites has been extensively exploited in the area of size and charge exclusion molecular sieving (Tsitsishvili 1992, Mumpton 1978, Breck 1974). Use of zeolite molecular sieves in chemical industries expanded rapidly with the development of synthetic homogeneous zeolites having well defined properties, resulting in an industry now worth millions of dollars annually (Mumpton 1978). Zeolites are also used widely in Japan as additives in concrete to decrease its density and increase compressive strength (Mumpton 1978).

1.4 Waste Coal Fly Ash

1.4.1 Production

Thermal power stations produce large quantities of waste ash during coal combustion. There are two types of waste coal ash. Larger, heavier ash particles collect beneath the boilers and are called bottom ash, whereas finer, lighter ash particles are carried up the stack with flue gases and are removed by dust collection systems (Bilski et al. 1995). The latter is called fly ash and is the focus of this study. In 1997, world wide production of coal ash was estimated to be approximately 650 million tonnes of which 70% (approximately 455 million tonnes) is fly ash (Slessor 2000). Annually, 35 million tonnes of fly ash (less than 8% of fly ash produced) are used as an admixture in the production of cement (Slessor 2000). The remaining fly ash is waste and is disposed of by ponding or stockpiling. As a result of growing disposal costs and environmental concerns, many recent studies have explored the use of fly ash as a soil liming agent and/or micronutrient source (Bilski et al. 1995). However, the hazardous properties of waste coal fly ash have complicated such uses.

1.4.2 Physico-chemical Properties

Fly ash particles are typically spherical with diameters ranging from 0.01 to 100 μm and average diameters of 10 μm (Bilski et al. 1995, Davison et al. 1974). Particle densities range from 2.1 to 2.7 g/cm^3 (Bern 1976 in Adriano et al. 1980, Natusch et al. 1975). Specific surface values calculated for a number of fly ashes ranged from 0.38 to

28.4 m²/g (Aitken et al. 1984, Kaakinen et al. 1975). Fly ash composition is a function of combustion conditions (rate, air:fuel ratio, etc.), chemical composition of the coal, efficiency of dust collection systems and storage/disposal methods employed (Berry and Malhotra 1986, Adriano et al. 1980). Generally, fly ash is a heterogeneous material composed of amorphous oxides of Si, Al, Fe, Ca and Mg, unburned coal and some crystalline phases such as quartz (SiO₂), mullite (3Al₂O₃ · 2SiO₂), hematite (Fe₂O₃) and magnetite (Fe₃O₄) (Bilski et al. 1995, El-Mogazi et al. 1988, Berry and Malhotra 1986, Adriano et al. 1980, Page et al. 1979). This has important consequences in terms of pH. Fly ashes containing high levels of Fe and S have pH values as low as 4.5 whereas high Ca and Mg varieties have pH values near 12.0 (Aitken et al. 1984, Hodgson et al. 1982, Adriano et al. 1980, Theis and Wirth 1977, Plank and Martens 1974). Similarly, fly ashes enriched in alkali and alkali earth metals can be highly saline with electrical conductivity (EC) values as high as 23.9 mS/cm (Aitken et al. 1984). CEC's tend to be low, ranging from 0.5 to 20 cmol⁺/kg (Hemni 1987b, Aitken et al. 1984).

Due to their volatility, trace elements such as As, B, Cd, Cu, Ga, Mo, Pb, S, Sb, Se and Zn are enriched in fly ash, making its disposal problematic (Page et al. 1979, Campbell et al. 1978, Davison et al. 1974). These metals are concentrated in the finer fly ash fraction which can be inhaled, posing a serious human health risk (Linton et al. 1976, Klein et al. 1975). As well, several researchers have shown that trace metals are enriched in thin layers on sphere surfaces and are relatively easily dissolved in water, a concern when exploring land disposal/amendment options (Menon et al. 1990, Elseewi et al. 1980a, Theis and Wirth 1977, Natusch et al. 1975). As in the case of trace metals, elements of the alkali and alkaline earth groups are enriched on the surface of fly ash

particles (Warren and Dudas 1984, Mattigod 1982, Elseewi et al. 1980a, Phung et al. 1979). Elements such as Na, K, Ca, and Mg can dissolve in water coming in contact with the fly ash, contributing to increased salinity and alkalinity (Menon et al. 1990, Aitken et al. 1984, Martens 1971). It should be noted that physico-chemico properties of fly ashes reported in the literature were highly variable. Conditions of combustion and coal composition strongly influence the properties of the ash and as a result each fly ash source should be evaluated prior to utilization or disposal.

1.4.3 Fly Ash Utilization, Benefits and Limitations

Limitations to fly ash utilization are a result of (a) element toxicity effects in aquatic and terrestrial macro- and micro-organisms resulting in reduced productivity or death (Menon et al. 1992, Wong and Wong 1986, Cherry et al. 1984, Van Hassel and Wood 1984), (b) toxic element accumulation at higher trophic levels (Carlson and Adriano 1993), (c) translocation of toxic elements by wind and water (Bilski et al. 1995), (d) dramatic alteration of soil/water pH (Cherry et al. 1984, Elseewi et al. 1980b, Cherry et al. 1979, Townsend and Gillham 1973), (e) increased salinity/electrical conductivity in soils/water resulting in chronic stress on aquatic and terrestrial organisms (Pitchel and Hayes 1990, Cherry et al. 1984, Townsend and Gillham 1973), and (f) cementation of soil resulting in reduced hydraulic conductivity, root penetration and water infiltration (Bradshaw and Chadwick 1980, Chang et al. 1977, Townsend and Hodgson 1973). The following section explores these limitations in terms of fly ash utilization.

1.4.3.1 Micronutrient sources for agricultural crops. Several studies have shown that fly ash can act as a source of B (Scanlon and Duggan 1979, Plank and Martens 1974, Martens 1971), Mo (Wong and Wong 1990, Elseewi and Page 1984, Elseewi et al. 1980b, Plank et al. 1975, Doran and Martens 1972), Mg (Wong and Wong 1990, Elseewi et al. 1980b), S (Page et al. 1979, Elseewi et al. 1978), P (Menon et al. 1990, Aitken et al. 1984, Martens 1971), Fe (Aitken et al. 1984), Cu (Aitken et al. 1984) and Se (Shane et al. 1988, Stoewsand et al. 1978) improving crop yields. However, positive effects are for the most part observed in soils deficient in these elements and only at relatively low amendment levels (Menon et al. 1992, Scanlon and Duggan 1979, Martens 1971). At high amendment levels, phytotoxicity effects become apparent (Menon et al. 1993b, Menon et al. 1992, Wong and Wong 1989, Pawar and Dubey 1988, Aitken and Bell 1985, Adriano et al. 1982, Scanlon and Duggan 1979, Elseewi et al. 1978, Mulford and Martens 1971, Martens 1971). As well, uptake of toxic elements such as Pb, Cd and Se often coincide with nutrient uptake (Wadge and Hutton 1986). Despite its toxicity, Se is an important crop nutrient, but caution must be used to prevent accumulation of toxic levels of Se in crops.

1.4.3.2 Liming agent. When used as a liming agent, fly ash may improve conditions for vegetative growth in acidic soils (Taylor and Schuman 1988, Riekerk 1983, Moliner and Street 1982, Elseewi et al. 1980a, Doran and Martens 1972). However, when incorporated into soils with neutral pH (for nutrient benefits) undesirable pH and salinity effects may occur. Several researchers have observed considerable reduction in the availability of plant nutrients such as Fe, Mn, P and Zn in soils amended with fly ash due to dramatic pH increases (Wong and Wong 1990, Adriano et al. 1982, Elseewi et al.

1980b, Schnappinger et al. 1975). As well, increases in pH and associated salinity can severely reduce microbial respiration rates and numbers subsequently decreasing plant growth (Pitchel 1990, Pitchel and Hayes 1990, Wong and Wong 1989 and 1986, Cervelli et al. 1987 and 1986, Arthur et al. 1984). Pitchel and Hayes (1990) and Arthur et al. (1984) indicated that reduction in microbial respiration may also be caused by high levels of toxic elements such as Cd. However, in several studies, leaching of fly ash was shown to reduce adverse pH and toxicity effects improving the suitability of fly ash as a soil amendment (Ghodrati et al. 1995, Wadge and Hutton 1986, Aitken and Bell 1985, Adriano et al. 1982, Phung et al. 1979).

1.4.3.3 Soil conditioner. Several benefits have been observed on the physical properties of soil with the addition of fly ash. Amendment of soil with fly ash has been shown to increase available water holding capacity (Jacobs et al. 1991, Sharma et al. 1990, Chang et al. 1989, Aitken and Bell 1985, Aitken et al. 1984, Campbell 1983). As well, appreciable decreases in bulk density and modulus of rupture and increases in aeration were measured in soils after amendment with fly ash (Salé et al. 1997, Chang et al. 1989, Campbell et al. 1983, Chang et al. 1977, Fail and Wochok 1977). Salé et al. (1997) found that decreases in bulk density and modulus of rupture were a result of the development of aggregates, likely due to increased Ca inputs. Fly ashes can react with water and CaCO_3 in the soil cementing aggregates together and potentially causing the formation of cemented layers. Cementation reduces soil hydraulic conductivity and can impede root growth and infiltration of water (Bradshaw and Chadwick 1980, Chang et al. 1977, Townsend and Hodgson 1973). Jacobs et al. (1991) found that banding fly ash in soil prevented cementation and improved conditions for plant growth.

1.4.3.4 Additives in biological waste. Combination of fly ash with animal manures may increase their fertilizer value. Vincini et al. (1994) found higher levels of plant available P in hog manure amended with fly ash. However, increased pH levels may contribute to increased NH_3 losses (Vincini et al. 1994). Amendment of sewage sludge with fly ash has been shown to increase germination, root growth and yield of crops in green house trials when used as a soil substitute (Wong and Su 1997a, Wong and Su 1997b). Some adverse effects of fly ash amendment on microbial activity in sewage sludge and in soil amended with fly ash-sewage sludge mixtures have been observed, but these were minimal and only reduced plant yield at very high amendment rates (Fang et al. 1999, Fang et al. 1998, Wong and Lai 1996). Several other studies demonstrated that adverse effects on soil microorganisms and heavy metal release rates may be reduced by combining fly ash with sewage sludge, manure or composts prior to land application (Menon et al. 1990, Sims et al. 1993, Schwab et al. 1991, Adriano et al. 1982).

1.4.3.5 Mining waste amendment. Acid mine drainage is a concern where spoils contain high levels of sulphides such as pyrite (FeS_2). Alkaline fly ashes have been used to buffer acids produced from the soil and improve the physical characteristics of the spoil such that revegetation is possible (Taylor and Schuman 1988, Fail 1987, Jastrow et al. 1981, Capp 1978, Fail and Wochok 1977).

1.4.3.6 Other industrial uses. Although fly ash can have deleterious effects on aquatic ecosystems under specific circumstances it can be successfully utilized to remove suspended solids, phosphate and lead from polluted waters (Tenney and Echelberger 1970 in Bilski et al. 1995, Yadava et al. 1989, Fine and Jensen 1981, Weeldreyer and Fine

1981). As well, approximately 8% of fly ash produced annually is used as an admixture in cement and concrete and as a soil stabilizer and structural fill in the construction of roads (Manz 1997, Murtha et al. 1983, Schivley 1979). Recycling fly ashes in this way increases the environmental sustainability of coal combustion as an energy source. Finally, Murtha et al. (1983), Gilliam et al. (1982) and Gabler and Stoll (1982) have developed cost effective acid extraction methods by which ores could be recovered from fly ash. However, wastes produced may prove more difficult to manage than the original fly ash and a full assessment of environmental effects is required before these methods are employed (Carlson and Adriano 1991).

1.4.3.7 Chemical alteration producing zeolite-like materials. Recently, fly ashes have been used as mineral starting materials in the synthesis of zeolites due to their similarity to tuffaceous materials from which many zeolites form in nature (Hemni 1987a). Alteration of fly ash is accomplished by dissolution and recrystallization of amorphous fly ash materials in heated, strongly alkaline solutions, mimicking and intensifying the conditions of formation which are known to form zeolites in nature. Höller and Wirsching (1985) investigated methods by which zeolites could be synthesized from fly ash under a wide variety of conditions. Reaction temperatures ranged from 50 - 250°C, reaction solutions contained sodium hydroxide (NaOH 0.1 - 5.0 mol/L), potassium hydroxide (KOH 0.1 - 4.0 mol/L), sodium chloride (NaCl), potassium chloride (KCl) or CaCl_2 (latter three concentrations of 0.1 and 1.0 mol/L), reaction systems were closed or open and reaction time ranged from 24 - 64 days. Under these varied conditions Höller and Wirsching (1985) were able to synthesize minerals equivalent to a number of natural

zeolites. These included analcime, chabazite, faujasite and phillipsite. As well, several known synthetic zeolites were also formed including zeolite G, zeolite F, zeolite J, zeolite M, zeolite P (several different phases) and the zeolite-like mineral hydroxy-sodalite. Zeolite formation did not occur in KCl solutions regardless of the other reaction conditions applied. Montmorillonite was the dominant mineral formed in CaCl_2 solutions with some minor zeolite phases. At high temperatures (minimum 200°C) zeolites formed in NaCl solutions. However, zeolite formation occurred much more readily in NaOH and KOH solutions even at the lowest temperatures. In most cases specific reaction conditions yielded a single type of zeolite. Finally, all of the zeolites, with the exception of zeolite J, could be formed in closed conditions. These findings indicate that a wide variety of zeolite-like minerals can be successfully synthesized from fly ash materials.

Hemni (1987b) found that exposing two fly ashes to a sodium hydroxide (NaOH) solution at $80 - 90^\circ\text{C}$ increased their CEC's by 30 and 8 times respectively. X-ray diffraction (XRD) indicated that the fly ash samples were initially amorphous oxides but were transformed to sodalite and/or hydroxy-sodalite and phillipsite and faujasite respectively after exposure to the heated alkaline solution. Sodalite and hydroxy-sodalite are feldspathoids, the latter containing water molecules in structural cavities which can be reversibly removed by heating or under reduced pressure without deformation of the crystal structure (Klein and Hurlbut 1993). This phenomenon is associated with zeolites and therefore, hydroxy-sodalite is considered to be zeolite-like (Hemni 1987b). Phillipsite and faujasite are zeolites commonly found in nature. A subsequent study by Hemni (1987a) determined that the greater the duration of exposure to the alkaline

solution the more extensive was the conversion of fly ash to sodalite and/or hydroxy-sodalite. As well, CEC increased with increasing duration of exposure to the alkaline solution. Hemni (1987a, 1987b) suggested that conversion of amorphous fly ash to crystalline zeolites would improve their suitability as soil conditioners.

Mondragon et al. (1990) chemically altered fly ash by reacting it with a range of NaOH solutions (2.0-13.0 mol/L), at a range of temperatures (90-100°C) and for different amounts of time (8-48 hours). They also investigated the effect of pre-treatment of the fly ash with acid (HCl or H₂SO₄) on the nature of alteration products. Mondragon et al. (1990) found that reaction of fly ash in hot, alkali solution resulted in the conversion of amorphous oxide constituents into hydroxy-sodalite. A greater proportion of fly ash was converted to hydroxy-sodalite as reaction temperature, NaOH molarity and duration of exposure to reaction conditions increased. Fly ash samples that were pre-treated with acid before exposure to the hot, alkaline reaction conditions also produced some hydroxy-sodalite but primary reaction products were zeolite X and zeolite P. And when sodium silicate was added to the NaOH, conversion of fly ash shifted to zeolite X production almost exclusively. Analysis of alkaline reaction products from acid pre-treated fly ash indicate that 50% to 70% of the fly ash was transformed to zeolite.

Catalfamo et al. (1993) investigated the nature of fly ash alteration products at different temperatures and combined with solutions of differing NaOH molarities over time. They found that alteration progressed more rapidly at higher temperatures and NaOH molarities. As well, XRD analysis indicated that in the first 5 hours fly ash was

converted to zeolite Linde A which, if alteration continued, was subsequently converted to zeolite P. Complete alteration of fly ash to zeolitic materials was not accomplished due to the insolubility of mullite ($3\text{Al}_2\text{O}_3 \bullet 2\text{SiO}_2$) under the above conditions.

Singer and Berggaut (1995) prepared two chemically altered fly ashes according to the method of Hemni (1987b). XRD analysis indicated that fly ash samples were primarily amorphous with some crystalline phases made up of quartz, mullite and to a lesser extent magnetite. After chemical alteration, approximately 50% of the fly ash had been transformed into zeolite P and hydroxy-sodalite. Complete conversion of the fly ash to zeolite was hindered by the presence of mullite which was unaltered by the chemical treatment. As well, chemical alteration reduced extractable levels of B, Cd, Cu, Mo, Ni and Se in the fly ash.

Although several studies have examined the nature, extent and factors influencing fly ash alteration to zeolitic species only two studies were found which explored the use of these alteration products in a commercial capacity. Singer and Berggaut (1995) used chemically altered fly ash to remove Pb and Zn from industrial waste waters. In a study by Jang et al. (1995) Ca and Na rich zeolites produced by the chemical alteration of fly ash were combined with phosphoric acid (H_3PO_4) and NH_4^+ -N fertilizers and amended to hydroponic media for the production of tomatoes. Plants receiving both fly ash zeolites and fertilizer exhibited greater fertilizer efficiency and greater biomass production than plants receiving fertilizer only. Increased productivity was also attributed to the buffering of phosphoric acid by the fly ash zeolites.

1.5 Conclusion

The studies discussed in the previous section indicated that waste coal fly ash can be chemically altered to produce zeolites or zeolite-like minerals. This is significant because zeolites are valuable commercial minerals used in a wide variety of industries. As well, Singer and Bergaut (1995) indicated that chemical alteration removed hazardous constituents from the fly ash they altered, improving its suitability for land application. Unaltered fly ash has been shown to increase NH_3 volatilization from hog manure (Vincini et al. 1994). Chemical alteration may reverse this effect, improving nutrient retention in hog manure and reducing environmental and health hazards associated with land application of unaltered fly ash and hog manure. The following study examines the potential use of fly ash in this capacity.

2. COMPARISON OF PHYSICO-CHEMICAL PROPERTIES OF CHEMICALLY ALTERED COAL FLY ASH AND MORDENITE

2.1 Abstract

Fly ash was reacted with 3.5 M NaOH at approximately 90°C for 24 hours after which it was cooled and acidified to pH 6.2. Physico-chemical properties of unaltered fly ash (UFA), chemically altered fly ash (CAFA) and mordenite were compared to determine if chemical alteration produced zeolites or zeolite-like minerals. X-ray diffractogram analysis identified that chemical treatment transformed amorphous fly ash to sodium aluminum silicate hydrate (SASH). SEM identified some change in fly ash microstructure, surface and morphology from spherical to irregular after alteration. As and Pb levels were lower in CAFA relative to UFA (for As 16 and 34 µg/g, for Pb 15 and 31 µg/g respectively). CAFA As and Pb levels were comparable with mordenite (9 and 16 µg/g respectively). CEC increased after chemical alteration of fly ash from 249 to 679 cmol⁻/kg, both higher than mordenite (112 cmol⁺/kg). Mordenite had higher K⁺/NH₄⁺ CES (3.1) than UFA or CAFA (both 2.1). Chemical alteration increased fly ash specific surface by more than an order of magnitude (from 27 to 273 m²/g) with mordenite intermediate (162 m²/g). Particle density was unaffected by chemical alteration (CAFA 2.5g/cm³, UFA 2.6g/cm³) and both UFA and CAFA were higher than mordenite (2.2 g/cm³). Air dry moisture content increased dramatically after alteration (UFA 0.01%, CAFA 10.59%) with mordenite again intermediate (4.57%). Finally, UFA had a much

higher pH (12.2) than mordenite or CAFA (6.6 and 6.7 respectively). These findings indicate that chemical alteration may reduce toxicity of fly ash and make it useful in a number of industrial and agricultural applications.

2.2 Introduction

Thermal power stations produce large quantities of waste ash during coal combustion. There are two types of waste coal ash. Larger, heavier ash particles collect beneath the boilers and are called bottom ash, whereas smaller, lighter ash particles are carried up the stack with flue gases and are removed by dust collection systems (Bilski et al. 1995). The latter is called fly ash and is the focus of this study. In 1997, world wide production of coal ash was estimated to be approximately 650 million tonnes of which 70% is fly ash (Slessor 2000). Annually, 35 million tonnes of fly ash, less than 8% of fly ash produced, are used as an admixture in the production of cement (Slessor 2000). The remaining fly ash is waste and is disposed of by ponding or stockpiling (Slessor 2000).

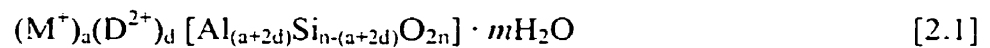
Fly ash particles are typically spherical with diameters ranging from 0.01 to 100 μm and average diameters of 10 μm (Bilski et al. 1995, Davison et al. 1974). Particle densities range from 1.99 to 2.76 g/cm^3 (Aitken et al. 1984, Natusch et al. 1975). Specific surface values calculated for a number of fly ashes ranged from 0.38 to 28.4 m^2/g (Aitken et al. 1984, Kaakinen et al. 1975). Fly ash composition is a function of combustion conditions (rate, air:fuel ratio, etc.), chemical composition of the coal, efficiency of dust collection systems and storage/disposal methods employed (Berry and Malhotra 1986, Adriano et al. 1980). Generally, fly ash is a heterogeneous material

composed of amorphous oxides of Si, Al, Fe, Ca and Mg, unburned coal and some crystalline phases such as quartz (SiO_2), mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), hematite (Fe_2O_3) and magnetite (Fe_3O_4) (Bilski et al. 1995, El-Mogazi et al. 1988, Berry and Malhotra 1986, Adriano et al. 1980, Page et al. 1979). Fly ashes containing high levels of Fe and S have pH values as low as 4.5 whereas high Ca and Mg varieties have pH values higher than 12.0 (Aitken et al. 1984, Hodgson et al. 1982, Adriano et al. 1980, Theis and Wirth 1977, Plank and Martens 1974). Similarly, fly ashes enriched in alkali and alkali earth metals can be highly saline with electrical conductivity (EC) values as high as 23.9 mS/cm (Aitken et al. 1984). CEC values tend to be low, ranging from 0.5 to 20 cmol⁺/kg (Hemni 1987b, Aitken et al. 1984).

Due to their volatility, trace elements such as As, B, Cd, Cu, Ga, Mo, Pb, S, Sb, Se and Zn are enriched in fly ash, making its disposal problematic (Page et al. 1979, Campbell et al. 1978, Davison et al. 1974). These metals are concentrated in the finer fly ash fraction which can be inhaled posing a serious human health risk (Linton et al. 1976, Klein et al. 1975). As well, several researchers have shown that trace metals are enriched in thin layers on sphere surfaces and are relatively easily dissolved in water, a concern when exploring land disposal/amendment options (Menon et al. 1990, Elseewi et al. 1980a, Theis and Wirth 1977, Natusch et al. 1975). As in the case of trace metals, elements of the alkali and alkaline earth groups are enriched on the surface of fly ash particles (Warren and Dudas 1984, Mattigod 1982, Elseewi et al. 1980a, Phung et al. 1979). Elements such as Na, K, Ca, and Mg can dissolve into water coming in contact with the fly ash contributing to salinity and increased alkalinity (Menon et al. 1990, Aitken et al. 1984, Martens 1971).

Limitations to fly ash utilization are a result of (a) toxicity effects in aquatic and terrestrial macro- and micro-organisms resulting in reduced productivity or death (Menon et al. 1992, Wong and Wong 1986, Cherry et al. 1984, Van Hassel and Wood 1984), (b) toxic element accumulation at higher trophic levels (Carlson and Adriano 1993), (c) translocation of toxic elements by wind and water (Bilski et al. 1995), (d) dramatic alteration of soil/water pH (Cherry et al. 1984, Elseewi et al. 1980b, Cherry et al. 1979, Townsend and Gillham 1973), (e) increased salinity of soils/water resulting in chronic stress on aquatic and terrestrial organisms (Pitchel and Hayes 1990, Cherry et al. 1984, Townsend and Gillham 1973), and (f) cementation of soil resulting in reduced hydraulic conductivity, root penetration and water infiltration (Bradshaw and Chadwick 1980, Chang et al. 1977, Townsend and Hodgson 1973).

In 1987, Hemni showed that fly ash could be chemically altered to produce zeolites and zeolite-like materials. Zeolites are hydrated aluminosilicates with three-dimensional crystal structures containing channels and voids occupied by water and cations of the alkali and alkaline earth groups (Tsitsishvili et al. 1992, Ming and Mumpton 1989, Gottardi and Galli 1985). They generally follow the idealized formula (Gottardi and Galli 1985):



Where M^+ represents monovalent cations and D^{2+} represents divalent cations. The atoms contained in the square brackets represent the permanent zeolite structure or framework, whereas atoms in the curved brackets represent extra-framework cations which are

exchangeable (Ming and Mumpton 1989, Gottardi and Galli 1985). Water molecules can also be reversibly lost or gained and generally follow the rule $n \geq m$ (Gottardi and Galli 1985). As well, the Si/Al ratio in zeolites is always greater than 1 and typically less than 6 (Tsitsishvili et al. 1992, Ming and Mumpton 1989, Gottardi and Galli 1985). The considerable substitution of Al for Si in tetrahedra produces a large net negative surface charge and consequently a high cation exchange capacity (CEC). Tetrahedra are linked to form secondary building units (SBU) which range from simple four or six membered rings to complex cubo-octahedra. SBU are arranged to form integrated crystal structures permeated by channels and voids (Ming and Mumpton 1989). The result is a very open framework (up to 50% void volume) which results in the low densities of zeolites (2.0 - 2.3 g/cm³) relative to other tectosilicates (2.6-2.7 g/cm³) (Ming and Mumpton 1989). The open framework and interconnection of channels and voids permit the exchange of ions inside the crystal framework as well as on the external mineral surface. Channel and void dimensions, governed by arrangement of SBU, have been shown to exhibit a certain selectivity for monovalent cations such as ammonium (NH₄⁺) (Ames 1960, 1961).

The mordenite framework is made up of six ring tetrahedral sheets positioned parallel to the *a-c* plane (Vaughan 1978, Meier 1978). Apices of the tetrahedra do not all point in the same direction as is the case with minerals of the mica group. Rather, tetrahedra alternate resulting in the formation of channels running along *c* (occurs where apices point in opposite directions) and form four ring linkages between sheets (occurs where apices meet) producing a channel along *b* (Meier 1978, Vaughan 1978). Two channels, an eight membered ring and a twelve membered ring, run parallel to *c* and one

eight membered ring runs parallel to *b* (Meier 1978, Vaughan 1978). The 12 member ring has a diameter of 6.7 Å but it is only able to accommodate molecules having a maximum diameter of 4.2 Å (Tsitsishvili 1992, Vaughan 1978). These size limits may be attributed to stacking faults in the framework or to the blockage of channels by quartz and iron oxides trapped in the crystals during formation (Vaughan 1978, Frillette and Rubin 1965). The smaller eight member rings (accommodate diameters of 2.4 Å) are frequently blocked by cations. As a result, diffusion of molecules into the mordenite framework occurs only in the largest channel. Early studies of the chemical properties of mordenite indicated that it readily adsorbs gases and small monovalent cations (Vaughan 1978). Cations most commonly associated with mordenite in nature are Na^+ (2 to 5 per unit cell), Ca^{2+} (1.6 to 2.5 per unit cell) and to a lesser extent K^+ (0.1 to 0.8 per unit cell) (Passaglia 1975). Barrer and Klinowski (1974) determined the relative cation affinity of mordenite to be $\text{Cs}^+ > \text{K}^+ > \text{NH}_4^+ > \text{Na}^+ > \text{Ba}^{2+} > \text{Li}^+$. The Si/Al ratio of mordenite ranges from 4.5 to 5.5 and its density is 2.15 g/cm³ (Tsitsishvili 1992, Meier 1978).

The unique physico-chemical properties of zeolites have made them very useful in a wide range of applications including; a) treatment of radioactive, sewage, agricultural, and aquacultural wastewater's (Mahimairaja et al. 1994, Ciambelli et al. 1983, Weber et al. 1983, Adam et al. 1971), b) cleaning of stack gas emissions and oil spills (Mumpton 1978), c) fertilizers carriers (Perrin et al. 1998, Allen et al. 1996, Allan et al. 1995, Huang and Petrovic 1994), pesticide carriers (Yoshinaga et al. 1973 in Mumpton 1978) and animal feed supplements (Roland and Dorr 1989, Nestorov 1983, Torii 1977), d) as energy conservation methods in the gasification of coal, purification of natural gas and production of petroleum (Mumpton 1978), e) in the production of solar energy and O₂

(Mumpton 1978), and, f) as solid phase media in size and charge exclusion column chromatography (Tsitsishvili et al. 1992, Mumpton 1978, Breck 1974).

This study had two objectives. The first was to chemically treat locally obtained fly ash and assess how chemical treatment has altered its physico-chemical properties. The second objective was to determine if physico-chemical changes are consistent with an increase in zeolitic character of the treated fly ash by comparison with a mined, natural zeolite, mordenite.

2.3 Materials and Methods

2.3.1 Sources and Chemical Alteration of Samples

Waste coal fly ash from the Boundary Dam Thermal Power Station, Saskatchewan, was provided by Lafarge Canada Inc. Fly ash was stored in a sealed stainless steel drum at room temperature. The fly ash chemical alteration method was modified from Hemni (1987a). Fly ash was passed through a 38- μ m mesh sieve separating the more reactive finer mineral fraction from the less reactive coarser mineral fraction. Approximately 20 g of the sieved fly ash was weighed and transferred to a 500 mL glass Erlenmeyer flask. 160 mL of 3.5 M NaOH was added to the fly ash with stirring to ensure complete mixing. The fly ash/alkali slurry was then heated on a hot plate to 90°C, with continuous stirring, for approximately 24 hours. A reflux condenser

was used to ensure fly ash/alkali slurry did not dry out during treatment. A photograph of the treatment apparatus is shown below in Figure 2.1.

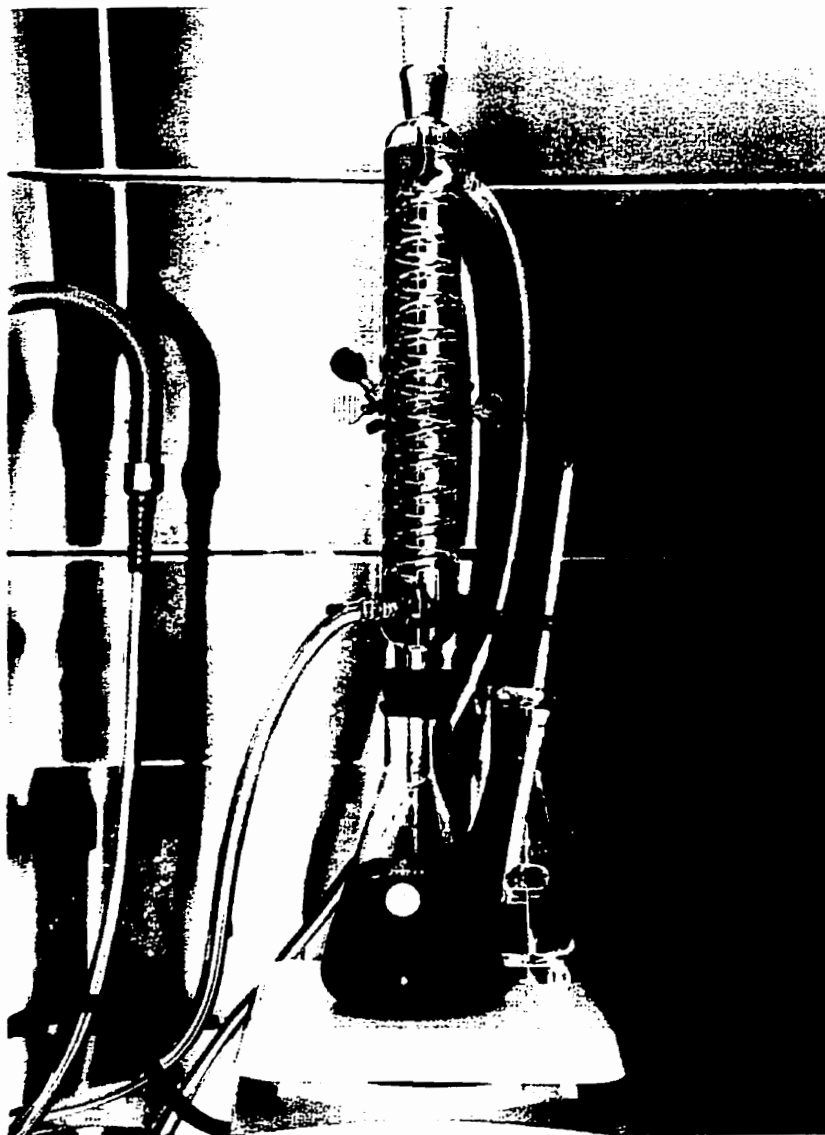


Figure 2.1 The fly ash treatment apparatus. Reaction temperature was monitored from a water bath positioned on the hot plate. Fly ash was constantly agitated with a magnetic stir bar.

Deionized-distilled water was used in all laboratory studies. After 24 hours, the fly ash/alkali slurry was removed from the hot plate and contents were immediately

transferred to a 1000 mL glass beaker, rinsing with water until a final volume of approximately 990 mL was reached. The beaker was covered with paraffin and left to stand overnight so that the treated fly ash could settle. Once settled, the supernatant liquid was decanted and fresh water was added up to the 700 mL level in the beaker. The mixture was then slowly acidified, with constant stirring, using concentrated hydrochloric acid (HCl). Acid was added in 1 to 2 mL aliquots over a four hour period until the slurry attained a pH of approximately 6.2. The beaker was then again topped up with water and left to stand overnight. Once fly ash particles had settled the supernatant was decanted and the sample was transferred to centrifuge tubes. The sample was washed (shaken, centrifuged, and decanted) five times with water. After washing the sample was filtered through Whatmann No. 4 filter papers, covered and allowed to air dry. Dry samples were scraped from filter papers and collected in an agate mortar where they were ground and mixed. Ground composite samples were then transferred to a glass jar with lid and stored at room temperature until further analysis. Mordenite $\text{Na}_3\text{K,Ca}_2(\text{Al}_8\text{Si}_{40}\text{O}_{96} \cdot 28\text{H}_2\text{O})$, a natural zeolite, was selected for comparison with the fly ash samples (Gottardi and Galli 1985). Mordenite was purchased and ground to pass through a 400 mesh sieve and stored in polyethylene bags at room temperature.

2.3.2 Physico-chemical Properties

2.3.2.1 Mineralogy. X-ray diffractometry (XRD) was conducted to identify crystalline minerals. Samples were analyzed as random powder mounts on a Phillips X-Ray Generator fully automated PW 17-10 x-ray powder system in the Department of

Geological Sciences. Initial 2θ was 4.0° for UFA and mordenite and 6.0° for CAFA. Scanning intervals increased stepwise by 0.2° every 20 seconds. Resulting x-ray diffractograms were cross-referenced with diffractograms of known inorganic substances using Fein-Marquart's micro-Powder Diffraction Search-Match (μ -PDSM) system which searches on the Powder Diffraction File published annually by the International Centre for Diffraction Data.

2.3.2.2 Scanning-electron microscopy. The microstructure, surface and morphology of UFA, CAFA and mordenite particles were observed for potential differences in form using secondary-electron (SE) micrographs. The scanning-electron microscope (SEM) employed was a Cambridge Instruments Stereoscan 120; an accelerating voltage of 20 kilovolts was used. Samples were mounted and coated with carbon prior to analysis to ensure electrical conductivity. Several SE micrographs were taken at 12,500 and 300 times magnification and dominant elements in samples were determined by means of energy-dispersive spectroscopy (EDS).

2.3.2.3 Determination of Cd, As and Pb. Heavy metal analysis for Cd, As and Pb was conducted using a Varian Liberty 2000 Inductively Coupled Plasma (ICP) Spectroscopy Unit. Samples weighing 2 to 4 grams were digested in teflon beakers with reflux at approximately 200°C . The digesting solution was made up of a 10:5:1 mixture of nitric/perchloric/hydrofluoric acids. Digested samples were diluted to 100mL and analyzed for Cd, As and Pb, the metals indicated to be most prevalent in the Boundary Dam fly ash, by Lafarge Canada Inc. (AGRA Earth and Environmental Limited 1996).

2.3.2.4 Cation exchange capacity. Cation exchange capacity (CEC) was determined according to the $\text{CaCl}_2/\text{MgCl}_2$ method of Jackson (1979). Twelve samples each of UFA, CAFA and mordenite were accurately weighed (approximately 100 mg) into pre-weighed, polyethylene centrifuge tubes. To each tube 20 mL of 0.5 mol/L CaCl_2 was added. Tubes were thoroughly agitated and allowed to stand for 30 minutes after which they were centrifuged and the supernatant liquid decanted. This was repeated 4 times to ensure complete saturation of exchange sites with Ca^{2+} . After this, 20 mL of 0.01 mol/L CaCl_2 was added to each tube followed by agitation and centrifugation. This was also repeated 4 times after which tubes were accurately weighed to determine the mass of excess CaCl_2 solution. Finally, 20 mL of 0.5 mol/L MgCl_2 were added to each tube followed by agitation, 30 minutes standing time and centrifugation. This was repeated 4 times. Decanted liquid was collected in 100 mL volumetric flasks which were topped up to 100 mL with 0.5 mol/L MgCl_2 . Replaced Ca^{2+} was determined using a Perkin Elmer 1100B Atomic Absorption Spectrophotometer (AAS) flame technique with a flow spoiler injection unit. All samples were spiked with LaCl_3 in order to minimize interference effects.

2.3.2.5 Cation exchange selectivity. The cation exchange selectivity (CES) method employed was modified from Jackson (1979). Eight samples each of UFA, CAFA and mordenite were accurately weighed (approximately 100 mg) into pre-weighed, polyethylene centrifuge tubes. To each tube 20 mL of 0.5 mol/L NaOAc of pH 7 was added. Tubes were thoroughly agitated and allowed to stand for 30 minutes after which they were centrifuged and the supernatant liquid decanted. This was repeated 4 times and once with 20 mL 0.5 mol/L NaCl to ensure complete saturation of exchange sites with

Na⁺. This was followed by 7 washings with 20 mL of a solution containing 0.025 mol/L KCl and NH₄Cl. Again, samples were agitated, allowed to stand for 30 minutes and centrifuged. After the 7th washing, the supernatant was decanted and tubes with samples were weighed to determine the mass of the excess solution. Samples were then washed 4 times with 20 mL of 0.5 mol/L MgOAc at pH 7 (agitated, let stand for 30 minutes and centrifuged). Supernatants were transferred to 100 mL volumetric flasks and topped up to 100 mL. K⁺ concentrations were determined using a Perkin Elmer 1100B Atomic Absorption Spectrophotometer (AAS) flame technique with a flow spoiler sample injection unit. All samples were spiked with LaCl₃ in order to minimize interference effects. NH₄⁺ concentrations were determined according to the colourimetric indophenol blue procedure of Maynard and Kalra (1993). Absorption of 630 nm wavelength light was measured on a Technicon AutoAnalyzer II. Relative quantities of K⁺ and NH₄⁺ displaced allowed for determination of the K⁺/NH₄⁺ selectivity coefficient (ratio of the concentrations).

2.3.2.6 Specific surface. The specific surface (SS) of samples was determined according to the ethylene glycol monoethyl ether (EGME) method described by Carter et al. (1986). Samples were dried in a vacuum desiccator with phosphorous pentoxide (P₂O₅) and then transferred to a vacuum desiccator containing a 1.5:1 EGME/CaCl₂ slurry. They were allowed to equilibrate in the vacuum chamber until a constant mass was reached. SS was calculated according to the following equation.

$$SS \text{ m}^2/\text{g} = \frac{W_a}{W_s \times 0.000286} \quad [2.2]$$

Where W_a is the mass of EGME absorbed on the sample at constant weight, W_s is the mass of the P_2O_5 -dried sample and 0.000286 is the mass of EGME needed to form a monomolecular layer on a m^2 of surface (Carter et al. 1986).

2.3.2.7 Particle density. Particle density (PD) of samples were calculated using pycnometers according to the method described by Blake and Hartge (1986).

Pycnometers were filled with water, stoppered and weighed. After which half of the water was poured out and pycnometers (with stoppers) were weighed again.

Approximately 3 g of UFA, CAFA or mordenite were added to half full pycnometers followed again by weighing. Pycnometers were then placed in a boiling water bath for 20 minutes to remove gases associated with mineral samples. After heating, pycnometers were stoppered and allowed to cool before they were filled with water and re-weighed.

PD was calculated as follows.

$$PD = \frac{\text{Oven Dry Soil (g)}}{\text{Volume Displaced Water (cm}^3\text{)}} \quad [2.3]$$

2.3.2.8 Air dry moisture content. Air dry moisture content was determined according to the method of Topp (1993). Approximately 1 g of the air dry sample was weighed to four decimal places into previously weighed drying tins with lids. Sensitivity of CAFA samples to room temperature and humidity made accurate weighing difficult. To combat this, atmospheric conditions in the weighing room were closely controlled to minimize fluctuations in mass. Weighed samples were placed in a drying oven at 105 °C for 48 hours after which samples were covered, removed and allowed to cool in a dessicator.

Once cooled to ambient temperature, samples were re-weighed and air dry moisture content calculated.

2.3.2.9 Solution pH. Mineral pH values were determined in a 3:1 mineral:water paste. Again, deionized-distilled water was used in this and all previous analyses. pH values were determined on an Acumet 950 digital pH/ion meter.

2.3.3 Statistical Analyses

Statistical analyses of all data were conducted using Systat 7.0 software. One way analysis of variance (ANOVA) was conducted on physico-chemical data and mean comparisons performed using Fisher's least significant difference (LSD) test (Systat, 1997). Samples having comparison probabilities less than 0.05 were considered to be significantly different.

2.4 Results and Discussion

2.4.1 Mineralogy

X-ray diffractograms for UFA, CAFA and mordenite are shown in Figure 2.2. UFA had only one distinctive peak. Due to its diagnostic d-spacing of 3.36, the crystalline material identified was likely quartz (SiO_2). The only other distinguishing feature of the UFA diffractogram is a hump caused by the scattered reflections from amorphous materials in the sample. Noise or interference caused by amorphous

constituents hindered the identification of any other crystalline phases and manifested itself in the low similarity index (SI) determined for quartz (48). The SI is a dimensionless number that ranks the number of matched lines in a diffractogram. With stronger/dominant mineral phases each matched line scores between 12 and 20 points, thus a SI of 48 indicates a weaker phase. The diffractogram for CAFA is very different from UFA. The amorphous hump has been replaced by several distinctive peaks (d-spacings indicated in Figure 2.2). The mineral which best matched the diffractogram pattern was sodium aluminum silicate hydrate (SASH 31-12710, $1.08\text{Na}_2\text{O}, \text{Al}_2\text{O}_3, 1.68\text{SiO}_2, 1.8\text{H}_2\text{O}$) with a SI value of 131. There were more than 60 types of 'SASH' identified within the powder diffraction file published by the International Centre for Diffraction Data, 12 of which are synthetic equivalents of natural zeolites (Ball 2000). The SASH identified in the CAFA was not a zeolite equivalent nor is it technically considered to be a mineral as it not found in nature (i.e. not formed by natural processes). It is, however, an inorganic crystalline hydrated aluminosilicate. Note that the silica peak remains in the diffractogram of the CAFA with the same relative amplitude. This may indicate that only amorphous and not crystalline materials reacted to form SASH during treatment of the fly ash. The mordenite diffractogram confirmed mordenite as the primary mineral in our sample (SI = 195) with some traces of heulandite (SI = 145). Diagnostic d-spacings for mordenite are indicated in Figure 2.2.

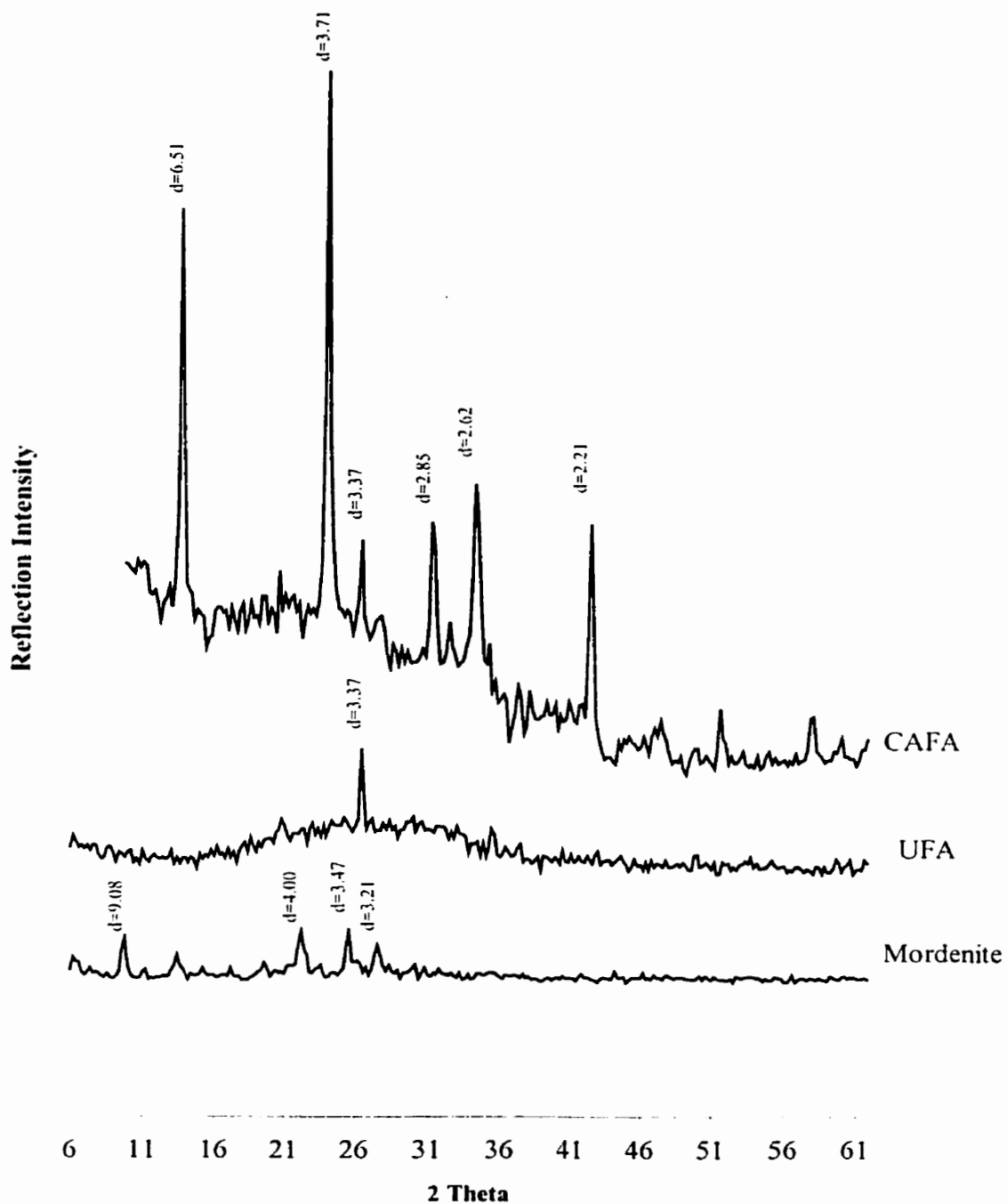


Figure 2.2 X-Ray diffractograms of unaltered fly ash (UFA), chemically altered fly ash (CAFA) and mordenite, with diagnostic d-spacings indicated

2.4.2 Scanning-electron Microscopy

SEM micrographs of UFA show spherical particles of varying sizes (Figures 2.3 and 2.4). This spherical shape is consistent for almost all UFA particles. Spheres are smooth except for the presence of white deposits on their surfaces (Figure 2.4, black arrow). Composition of the deposits could not be determined with energy-dispersive techniques, however similar studies have identified the substance to be calcium oxide (CaO) (Warren and Dudas 1984, Mattigod 1982).

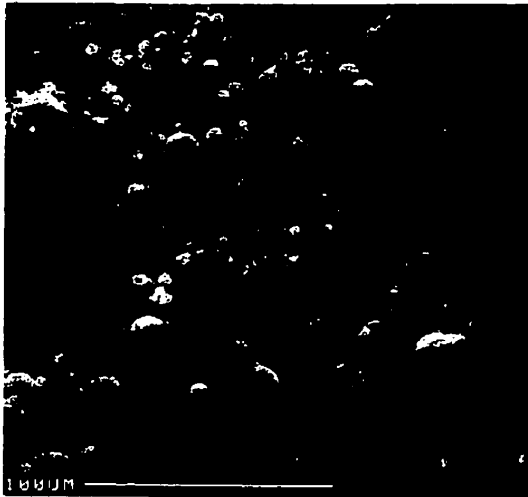


Figure 2.3 SEM micrograph of UFA spheres. Arrow indicates a shattered sphere filled with smaller spheres

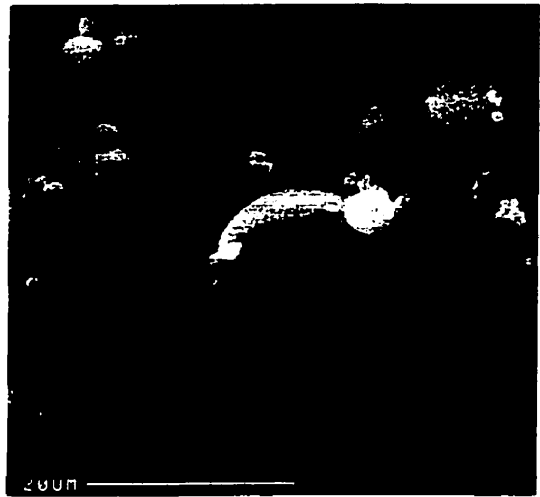


Figure 2.4 SEM micrograph of UFA spheres showing lighter surface deposits suspected to be CaO

Larger spheres were found to be hollow and were filled with smaller spheres (Figure 2.3, white arrow). According to Hulett and Weinburger (1980), sphere "shells" are primarily amorphous, but as they become smaller are filled with a web of acicular mullite crystals (Hulett and Weinberger 1980). Mullite crystals were shown to be

unaffected by chemical alteration in previous studies (Singer and Bergaut 1995, Catalfamo et al. 1993).

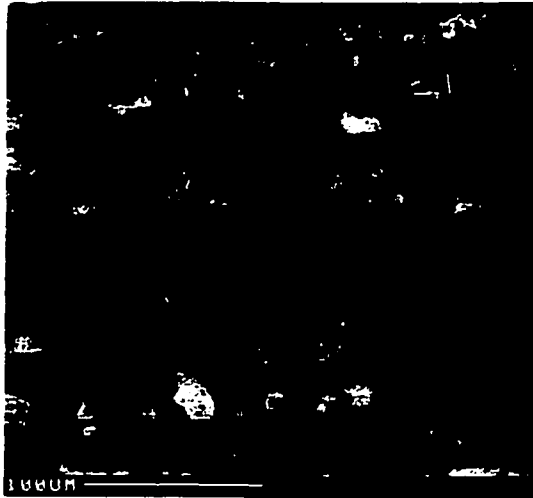


Figure 2.5 SEM micrograph of CAFA showing extensive alteration of form



Figure 2.6 SEM micrograph of CAFA particles, altered and unaltered

Figure 2.6 shows a SEM micrograph of CAFA. In the centre we see a large irregular particle (black arrow). This is not consistent with particle shapes observed for UFA and indicates some physical change as a result of alteration. Some particles in Figure 2.6 are reminiscent of their spherical parents (white arrow). This may indicate that chemical alteration of the fly ash was incomplete and a longer treatment time is required. At lower magnification it is apparent that particles are more irregular and appear to have undergone some physical alteration (Figure 2.5). SEM micrograph of mordenite (Figure 2.7) shows irregularly shaped particles as well. Mordenite crystals from sedimentary deposits (as is the case with this sample) typically form micron-sized crystals which are well to poorly developed (Mumpton and Ormsby 1978). In this case crystals were not

discernible likely do to their small size and due to the grinding of mordenite prior to analysis (Mejia pers. comm. 1997).

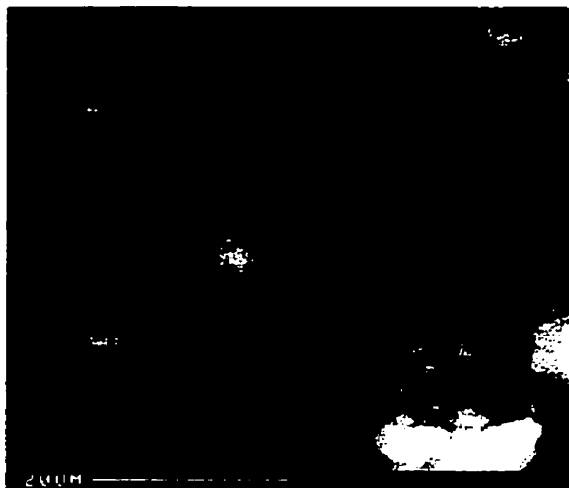


Figure 2.7 SE-micrograph of mordenite, crystals are not discernible due to their small size and grinding of the sample

Energy-dispersive spectra were determined for UFA, CAFA and mordenite. Three elements, Si, Al and Ca dominated the spectra of all samples. Outside of these, elements commonly found were (a) Fe, K and Ti in UFA, (b) Na and Fe in CAFA and (c) Na and K in mordenite.

2.4.3 Determination of Cd, As and Pb

According to information provided by Lafarge Canada, the most prevalent heavy metals found in Boundary Dam fly ash were Cd, As and Pb (AGRA Earth and Environmental Limited 1996). Heavy metal levels in UFA and CAFA may limit their suitability as soil amendments. Consequently, analyses were conducted to determine Cd,

As and Pb levels. Cadmium levels were found to be below detection limits for the ICP spectroscopy conducted, therefore only As and Pb will be discussed here.

Table 2.1 Mean comparison of As and Pb content of UFA, CAFA and mordenite.*

Sample	As ($\mu\text{g/g}$)	Standard Error	Pb ($\mu\text{g/g}$)	Standard Error
UFA	34 a	7.767	31 a	7.688
CAFA	16 b	0.854	15 b	2.398
Mordenite	9 b	0.707	16 b	2.217

*Values followed by the same letter are not significantly different ($\alpha = 0.05$)

As shown in Table 2.1, the UFA had significantly higher levels of both As and Pb as compared to CAFA or mordenite. This indicates that As and Pb in the UFA are solubilized during the treatment process and removed in the concentrated liquid waste stream. Thus treatment may improve the suitability of fly ash as a soil amendment by reducing As and Pb content to as low a concentration as in the mined, natural zeolite, mordenite.

2.4.4 Cation Exchange Capacity (CEC)

The CEC (cmol^+/kg) of UFA, CAFA and mordenite are reported in Table 2.2. CEC is an important feature in terms of suitability for manure amendment because it describes, in part, the NH_4^+ -retention capacity of the adsorbent. Based on values reported for fly ashes in the literature (maximum of $20 \text{ cmol}^+/\text{kg}$ in Hemni 1987b), the CEC determined for UFA in this study was very high. One explanation for this is that fly ash particles, made up of oxides of Si, Al and Fe, carry a charge due to the presence of

hydroxyl groups at mineral surfaces. The surface charge is strongly affected by solution pH. Generally, in acidic conditions oxide surfaces are positively charge, whereas in alkaline conditions oxide surfaces are negatively charged. The pH of the UFA was shown to be very high (12.2). As a result, oxide surfaces would carry a net negative charge and the pH-dependent CEC would be high. A second explanation is that the index cation (Ca^{2+}) used to determine CEC was inappropriate and lead to ambiguous results. In alkaline fly ashes, dominant mineral phases include oxides of the alkali and alkaline earth groups such as CaO. Several studies have found CaO to exist as deposits on sphere surfaces where it is readily solubilized (Mattigod 1982, Hulett and Weinberger 1980, Warren and Dudas 1980). Thus, Ca^{2+} in the exchange solution from the UFA may have been derived from soluble CaO on particle surfaces rather than from exchanged Ca^{2+} , despite 8 washings of the fly ash prior to exchange of Ca^{2+} by Mg^{2+} . Hemni (1987b) used Ca^{2+} as the CEC indicator ion in his study and the values he determined were comparable to others presented in the literature. This may be accounted for by the variability of fly ash composition. Not all fly ashes contain high levels of Ca^{2+} . Acidic fly ashes, which are rich in Fe and S, contain little Ca^{2+} . Therefore CEC determinations for acidic fly ashes may be unaffected by the use of Ca^{2+} as an indicator ion whereas CEC determinations for alkaline fly ashes may be overestimated when Ca^{2+} is used.

Table 2.2 Mean comparison of CEC (cmol^+/kg) values for UFA, SASH and mordenite.*

Sample	CEC (cmol^+/kg)	Standard Error
UFA	249 b	4.147
CAFA	679 a	6.006
Mordenite	112 c	1.920

*Values followed by the same letter are not significantly different ($\alpha = 0.05$)

The CEC determined for CAFA (679 cmol⁺/kg) was significantly greater than that of UFA (249 cmol⁺/kg) and both had a higher CEC than that of mordenite (112 cmol⁺/kg). This supports the finding that alteration of fly ash results in the formation of an aluminosilicate with considerable substitution of Al₃⁺ for Si₄⁺. If the particles were still oxides, one would expect the CEC of CAFA, at its lower pH, to be much less than UFA at its high pH. Difference between CAFA and mordenite may be explained in terms of Al and Fe content. The greater the isomorphous substitution of Si₄⁺ by Al₃⁺ and/or Fe₃⁺ the greater the deficit of positive charge in the mineral. Zeolites can have Si/Al ratios as high as 1/1. In the case of mordenite the Si/Al ratio is approximately 5/1 (Gottardi and Galli 1985). According to compositional data provided by Lafarge Canada, Boundary Dam waste coal fly ash contains as much as 28.2% Al₂O₃ and Fe₂O₃ combined (AGRA Earth and Environmental Limited 1996). If extensive isomorphous substitution occurred, alteration of the fly ash would result in a mineral with a large negative surface charge and hence a high CEC. This may be the case for the CAFA although further mineralogical investigations are required to confirm this hypothesis. The higher CEC of UFA relative to mordenite may be due to overestimation or to the low isomorphous substitution found in mordenite.

2.4.5 Cation Exchange Selectivity (CES)

The CES coefficient is the ratio of cmol K⁺/cmol NH₄⁺ absorbed on a Na⁺ saturated mineral surface from a dilute solution containing equal normalities of both cations. It is a unit-less measure of the affinity of a mineral for either K⁺ or NH₄⁺. If the CES coefficient is equal to 1, exchange on the mineral surface is random (neither cation is

favoured). If the coefficient is greater than one, sorption of K^+ on the surface is favoured and if the coefficient is less than 1 sorption of NH_4^+ is favoured. Table 2.3 contains K^+/NH_4^+ CES values calculated for UFA, CAFA and mordenite.

Table 2.3 Mean comparison of CES values for UFA, CAFA and mordenite.*

Sample	CES	Standard Error
UFA	2.1 a	0.166
CAFA	2.1 a	0.289
Mordenite	3.1 b	0.119

*Values followed by the same letter are not significantly different ($\alpha = 0.05$)

Cation selectivity is a function of channel sizes, configuration and occurrence and differences in selectivity can indicate differences in crystal chemistry (Tsitsishvili 1992). All samples have CES coefficients larger than 1 and therefore have a greater affinity for K^+ than for NH_4^+ . The CES coefficients for mordenite were significantly greater than those of UFA and CAFA. The mordenite cation affinity sequence is well documented, $Cs^+ > K^+ > NH_4^+ > Na^+ > Ba^{2+} > Li^+$, and its selectivity for K^+ was expected (Vaughan, 1978). CES coefficients for UFA and CAFA were not significantly different. This indicates that alteration did not affect K^+/NH_4^+ selectivity. The cause of the observed K^+ selectivity is not clear. It may be that K^+ measured in the exchange solution was derived from K_2O adsorbed onto fly ash spheres in UFA and from unreacted fly ash remaining in CAFA, however actual causes of K^+ selectivity could not be determined.

2.4.6 Specific Surface

Carter et al. (1986) defined specific surface as surface area per unit mass (m^2/g). Clay minerals, especially expanding clays like montmorillonite, have large specific surfaces (up to $810 \text{ m}^2/\text{g}$) due to internal surface available in interlayer spaces (Carter et al. 1986). Nonexpanding clays, such as kaolinite, are similar to tectosilicates in that specific surface is limited to the external surface and ranges from 10 to $70 \text{ m}^2/\text{g}$ (Carter et al. 1986). Although zeolitic materials are tectosilicates, and therefore not platy, they have a substantial internal surface in the form of channels and voids which would subsequently increase their specific surface. Specific surface values for UFA, CAFA and mordenite are listed in Table 2.4.

Table 2.4 Mean comparison of specific surface values for UFA, CAFA and mordenite.*

Sample	Specific Surface (m^2/g)	Standard Error
UFA	27 c	10.412
CAFA	273 a	37.684
Mordenite	162 b	14.026

*Values followed by the same letter are not significantly different ($\alpha = 0.05$)

All three materials have significantly different values of specific surface. UFA had the lowest specific surface at $27 \text{ m}^2/\text{g}$. Mordenite had a much higher specific surface at $162 \text{ m}^2/\text{g}$. This was expected since it is known that the mordenite crystal structure contains void and channels which increase the surface area of the mineral. In fact, it would seem logical for mordenite to have the highest specific surface due to this additional internal source. However, the CAFA had significantly greater specific surface

than even mordenite. One of two scenarios may account for this finding. First, alteration of fly ash may reduce particle sizes increasing the specific surface (this was not observed in the scanning-electron micrographs and can be discounted). The other possibility is that chemical treatment has altered fly ash morphology such that the surface available for sorption has been substantially enhanced (i.e. through development of internal voids and channels). This could be confirmed by testing the molecular sieving ability of CAFA. Ions small enough to pass into channels would have longer elution times than ions too large to enter channels provided they were of identical charge. Successive trials with ions of progressively smaller sizes would also permit determination of channel diameters (Breck 1974).

2.4.7 Particle Density

Particle density is the mass of a given unit of material divided by its volume. Zeolite mineral densities range from 1.93 g/cm³ to 2.75 g/cm³, the majority falling between 2.00 g/cm³ and 2.30 g/cm³ (Ming and Mumpton 1989). Table 2.5 reports particle density values for UFA, CAFA and mordenite.

Table 2.5 Mean comparison of particle density values for UFA, CAFA and mordenite.*

Sample	Particle Density (g/cm ³)	Standard Error
UFA	2.6 a	0.012
CAFA	2.5 a	0.033
Mordenite	2.2 b	0.006

*Values followed by the same letter are not significantly different ($\alpha = 0.05$)

The mordenite had a significantly lower particle density (2.20 g/cm^3) as compared to UFA or CAFA (2.6 and 2.5 g/cm^3 respectively). Zeolite mineral densities are generally low because of the high void volume in the minerals. The UFA and CAFA particle densities were not found to be significantly different from each other. This may indicate that they have a more dense crystal structure (less void volume) and/or that they are comprised of heavier elements (although the latter was not observed during SEM electron-backscatter).

2.4.8 Air Dry Moisture Content

Zeolites have the capacity to retain large amounts of water in channels and voids within the crystal. It is this feature which earned zeolites their name which means "boiling stone" in ancient Greek (Gottardi and Galli 1985). Zeolitic water can be removed by heating the mineral. As a result, zeolites have higher air dry moisture contents than other tectosilicates. Table 2.6 reports air dry moisture contents determined for UFA, CAFA and mordenite.

Table 2.6 Mean comparison of air dry moisture content for UFA, CAFA and mordenite.*

Sample	Air Dry Moisture Content (%)	Standard Error
Unaltered fly ash	0.01 c	0.001
SASH	10.59 a	0.124
Mordenite	4.57 b	0.206

*Values followed by the same letter are not significantly different ($\alpha = 0.05$)

The CAFA had a significantly higher air dry moisture content (10.59%) than mordenite (4.57%). The CAFA required as much as a week to dry completely and its mass fluctuated dramatically in response to minor changes in air temperature and humidity, making it difficult to obtain accurate sample weights to four decimal places. The air dry moisture content of CAFA increased 1000 times relative to UFA (0.01%) indicating an increase in zeolitic character of fly ash after chemical alteration.

2.4.9 Solution pH

It was important to include the pH of the minerals due to their potential effect on CEC. Table 2.7 contains pH values determined for UFA, CAFA and mordenite. The UFA had a significantly higher pH than CAFA or mordenite (12.2 relative to 6.7 and 6.6 respectively). The low pH of CAFA can be attributed to the acidification step in the alteration process. As stated earlier, pH is important with respect to exchange phenomenon for oxide minerals. The high pH of the UFA would produce a net negative surface charge on oxide minerals potentially resulting in the high CEC calculated.

Table 2.7 Mean comparison of pH values for UFA, CAFA and mordenite.*

Sample	pH	Standard Error
UFA	12.2 a	0.124
CAFA	6.7 b	0.206
Mordenite	6.6 b	0.001

*Values followed by the same letter are not significantly different ($\alpha = 0.05$)

2.5 Conclusions

The objective of this study was to determine if the mineralogical and physico-chemical changes following chemical alteration of waste coal fly ash were consistent with an increase in zeolitic character. Chemical alteration transforms amorphous fly ash constituents producing a hydrated crystalline aluminosilicate (SASH) with significantly higher CEC, specific surface, and air dry moisture content and lower As and Pb levels and pH. These changes are consistent with an increase in the zeolitic character of fly ash after chemical alteration. The word zeolite means "boiling stone" in ancient Greek, referring to the tendency of zeolitic minerals to froth when heated. The frothing was caused by the expulsion of water entrained in channels and voids (Gottardi and Galli 1985). However, no changes were observed in CES or particle density, in these respects suggesting no increase in zeolitic character after treatment. Clearly, we cannot at this time classify CAFA as a synthetic zeolite without conclusive crystallographic evidence, although we can refer to its physiochemical properties as having enhanced zeolitic character.

Zeolites are being increasingly recognized as useful tools in the management of agroecosystems. They have been used to increase the nutrient and water holding capacities and decrease nitrate leaching from coarse textured soils (Perrin et al. 1998, Huang and Petrovic 1994, Nus and Brauen 1991, Ferguson and Pepper 1987, Ferguson et al. 1986, MacKown and Tucker 1985, Weber et al. 1983). They have been used as animal feed supplements to improve the efficiency of nutrient uptake, reduce malodour of faeces and improve general health of livestock (Torii, 1977). As well they have been

used as slow release K^+ , NH_4^+ and phosphate (PO_4^{3-}) fertilizers (Allen et al. 1996, Barbarick et al. 1990, Lai and Eberl 1985, Lewis et al. 1983, Hershey et al. 1980,). Finally, they have been used in the management of animal wastes in both malodour control and reduction of leaching losses of N from manure after land application (Mahimairaja et al. 1994, Witter and Kirchmann 1989, Miner 1983, Torii, 1977). This could have particular significance in Manitoba where increased hog production is becoming a heated debate. If adverse effects of malodour and manure disposal can be neutralized the hog industry can be expected to grow substantially and sustainably in Manitoba in the years to come.

3. EFFECT OF CHEMICAL AND MINERAL AMENDMENT ON AMMONIA VOLATILIZATION FROM ANAEROBICALLY STORED HOG MANURE

3.1 Abstract

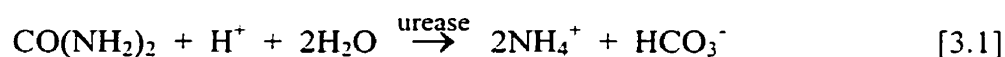
Hog manure was amended with unaltered fly ash (UFA), chemically altered fly ash (CAFA) and mordenite, with and without calcium chloride (CaCl_2). Ammonia (NH_3) volatilized from the manure, with and without added amendments, during 86 days of anaerobic storage was captured in phosphoric acid (H_3PO_4) traps. Cumulative (after 40 and 86 days) and periodic (for each sampling date) NH_3 losses determined from acid trap analysis indicate that addition of UFA to manure increased NH_3 volatilization substantially (likely due to increased pH). Addition of CAFA had no effect on NH_3 volatilization, whereas mordenite addition substantially reduced NH_3 volatilization as compared to a control. Incorporation of CaCl_2 decreased NH_3 volatilization slightly when added to manure alone or in tandem with CAFA. However, CaCl_2 had no effect on NH_3 volatilization in treatments receiving UFA or mordenite. After day 40 manure began to dry out and NH_3 volatilization increased for all treatments except those containing mordenite. Total-N losses at the end of 86 days were lowest for mordenite and CAFA with CaCl_2 containing treatments (33% and 37% respectively) whereas the control and treatments containing UFA had the highest total-N losses (64% and 68% respectively). N mass balance indicated that N losses from mordenite, and to a lesser extent from UFA

containing treatments, were greater than could be accounted for from NH_4^+ -N losses. N may have been lost from these systems in some other form (i.e. as amines).

3.2 Introduction

In 1997, 25 million tonnes of hog manure were produced in Manitoba (Burton 2000). In the past, manure was a fundamental component of productive agroecosystems where animal husbandry and crop production went hand in hand. It was the primary source of crop nutrients in these systems. Over the last 50 years, commercially produced inorganic fertilizers have replaced manure, allowing farmers to become more specialized (Eck and Stewart, 1995). With an affordable source of readily available nutrients, farmers in agriculturally productive areas abandoned animal production and began to focus on crop production, whereas farmers in areas less suitable for crops have shifted to large-scale, confinement-type livestock production (Eck and Stewart 1995). Trends indicate that more livestock are being produced on less land than ever before and manure produced in these areas often exceeds the capacity of the neighbouring land for safe disposal (Manitoba Agriculture and Food 2000a, Ewanek 1988). Additionally, if the fertilizer value of manure is to be fully utilized, manure application must be timed such that it coincides with crop nutrient requirements. Accordingly, manure must be stored on site during the winter months and must be carefully managed to ensure the maintenance of its fertilizer value and protection of the neighbouring environment (Smith and Chambers, 1993).

In order to safely and effectively store hog manure we must know its composition and reactions it may undergo during storage. Generally, livestock manure contains 75%, 80% and 85% respectively, of the N, P and K originally present in the feed (Taiganides and Hazen 1966). Consequently, manure can be an extremely valuable source of plant nutrients. More specifically, hog manure is comprised of a large liquid fraction (urine) made up primarily of urea ($\text{CO}(\text{NH}_2)_2$) and water and a smaller solid organic fraction made up primarily of faeces and undigested waste feed (Klausner et al. 1994). Urea in the urine is readily hydrolyzed by urease enzymes to ammonium (NH_4^+) according to the following equation when pH ranges from 7 to 9 (Ferguson et al. 1984).



Ammonium, in turn, is readily converted to NH_3 which is prone to volatilization in the presence of hydroxide ions (OH^-) (DuPlessis and Kroontje 1964).



Analysis of a large number of manure samples by Norvest Labs, Winnipeg, has shown hog manure to contain approximately 70% NH_4^+ -N and 30% organic-N (Manitoba Agriculture and Food 2000c).

Ammonia is a ubiquitous substance and is an important component in the cycling of N between biotic and abiotic systems (Subcommittee on Ammonia 1979). However,

atmospheric NH_3 levels in excess of ambient concentrations may have adverse effects on the functioning of natural systems and organisms. Ammonia, volatilized from hog manure stored under livestock houses (i.e. under a slatted floor), has been shown to irritate eyes, mucous membranes and respiratory tracts of workers (Donham et al. 1977, Donham and Gustafson 1982) with prolonged exposure leading to chronic lung diseases (Donham and Leininger 1984). Not surprisingly, hogs were also shown to be adversely affected by high NH_3 levels in confinement houses. Strombaugh et al. (1969) and Drummond et al. (1980) have shown that hog growth diminishes as aerial NH_3 concentrations increase. Doig and Willoughby (1971) demonstrated that damage to the upper respiratory tract increased in hogs exposed to higher levels of airborne NH_3 . Adverse effects from increased aerial NH_3 are not limited to within confinement facilities. Ammonia volatilization from stored manure and from the spreading of manure on agricultural lands has been linked with increased acid deposition (as a result of increased nitrification) (ApSimon et al. 1987, Adamowicz 1979), eutrophication (Paerl 1995, Langland 1992), increased terrestrial N deposition (Schlesinger 1977) and, as a result, an increase in the production of nitrous oxide (N_2O) a greenhouse gas and ozone depleting substance (Duxbury 1994, Duxbury and Mosier 1993, Duxbury et al. 1993).

The rate and extent of NH_3 volatilization from liquid hog manure is governed by three factors; a) the surface area of the liquid manure exposed to the air, b) the partial pressure of NH_3 in the liquid manure and c) the partial pressure of NH_3 in the overlying air. The model below describes NH_3 volatilization from liquid hog manure.

$$\text{NH}_3 \text{ Volatilization} = \frac{(\text{Surface Area}) * (\text{NH}_3 \text{ Partial Pressure} - \text{liquid})}{(\text{NH}_3 \text{ Partial Pressure} - \text{overlying air})} \quad [3.3]$$

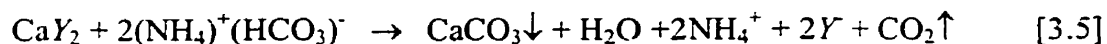
Ammonia volatilization increases as the surface area of the liquid manure exposed to the air and the partial pressure of NH_3 in the manure increase. Surface area is influenced by the degree of manure agitation (Vlek and Stumpe 1978), whereas the partial pressure of NH_3 in the manure is influenced by pH (Fenn and Hossner 1985), temperature (Cotton et al. 1987), oxygen status (Kirchmann and Witter 1989) and the concentration of NH_4^+ in the manure (Vlek and Stumpe 1978). Conversely, NH_3 volatilization decreases as the partial pressure of NH_3 in the overlying air increases. The partial pressure of NH_3 in the overlying air is in turn influenced by the ventilation of the stored manure (Sommer and Ersbøll 1996, Nathan and Malzer 1994, Sommer et al. 1991).

Due to concern over the environmental implications of increasing NH_3 emissions many researchers have begun to explore methods by which volatilization from manure may be reduced without diminishing the suitability of manure for land application. The pH of stored manure has been shown to decrease when Ca-containing salts are mixed in (Witter 1991, Witter and Kirchmann 1989a, Fenn et al. 1981, Fenn et al. 1980). Carbon dioxide (CO_2) dissolved in liquid manure reacts with water producing bicarbonate (HCO_3^-) and a hydrogen ion (H^+) (Schlesinger 1997).



As indicated in equation 3.1, NH_4^+ in the manure forms an unstable ion pair with HCO_3^- (Jackson 1979). With the addition of a Ca-containing salt, HCO_3^- can react with the Ca^{2+}

producing solid calcium carbonate (CaCO_3), water and CO_2 according to the following equation (Witter and Kirchmann, 1989a).



where Y represents the monovalent anion from the Ca-containing salt. Ammonium is included in the equation to signify that it is conserved. Consumption of HCO_3^- (equation 3.5) stimulates further reaction of CO_2 with water producing more HCO_3^- and H^+ (equation 3.4). In this way pH is reduced suppressing NH_3 volatilization. It is important to note that the equation is self sustaining. Production of HCO_3^- by dissolution of CO_2 results in the precipitation of CaCO_3 in the presence of a Ca-containing salt and subsequent release of CO_2 which is available again for dissolution.

Mahimairaja et al. (1994) and Kirchmann and Witter (1989) have shown that under aerobic storage conditions the addition of microbial substrates with high C/N ratios (e.g. straw) reduce NH_3 volatilization due to the immobilization of N in microbial tissues. Under anaerobic conditions addition of substrates did not reduce NH_3 volatilization likely due to diminished microbial activity.

The use of zeolites as $\text{NH}_3/\text{NH}_4^+$ absorbents in animal manure has only recently been explored in North America (Mumpton 1983). Zeolites are aluminosilicate minerals having three dimensional crystal structures permeated by channels and voids (Ming and Mumpton 1989, Tsitsishvili et al. 1992). They carry a net negative surface charge due to

the isomorphous substitution of Al^{3+} for Si^{4+} and therefore retain exchangeable cations on the mineral surface and within channels and voids throughout the mineral. Additionally, channel and void dimensions favour monovalent cations and therefore zeolites preferentially absorb NH_4^+ as opposed to Ca^{2+} or Mg^{2+} (Ames 1961, 1960). These characteristics have made zeolites very effective in absorbing and retaining NH_4^+ in hog manure (Mahimairaja et al. 1994, Witter and Kirchman 1989b, Miner 1983). Several recent studies have shown that waste coal fly ash, a by-product of coal combustion in thermal power stations, can be chemically altered to produce a zeolite-like material (Singer and Bergaut 1995, Catalfamo et al. 1993, Mondragon et al. 1990, Hemni 1987a, Hemni 1987b, Höller and Wirsching 1985). The objective of this study was to evaluate the effectiveness of unaltered fly ash (UFA), chemically altered fly ash (CAFA) and mordenite with and without calcium chloride (CaCl_2) in reducing NH_3 volatilization from anaerobically stored hog manure.

3.3 Materials and Methods

3.3.1 Manure Source and Collection

Hog manure was provided on the Timmerman Farm located at SE10-7-10, southwest of Treherne, Manitoba. Hogs were Yorkshire-Hampshire crosses of both genders ranging from eight weeks to six months of age. Feed consisted of a 3:16:1 ratio of wheat, barley and soy-bean meal respectively supplemented with Spectra Grower (30) Swine Premix-TYLAN as a nutritional additive. Approximately 300-325 hogs were housed in total. Manure was stored beneath the livestock housing structure in a covered, 2.5 m

deep, square, concrete pit. After three and a half months of storage manure was thoroughly stirred at the base of the pit by a mechanical arm and pumped out for land application. Due to the formation of a crust on top of the manure and the depth of the pit it can be assumed that storage conditions were primarily anaerobic. As the manure was being stirred (before pumping began) 12-12 lb. bags were filled with manure, sealed and triple bagged. Sealed bags were transferred to a large plastic bin containing ice and more ice was added to completely cover the bags. Ice was added to minimize microbial activity. Manure was transported by truck to the University of Manitoba where it was frozen. Prior to use in laboratory experiments, manure was removed from the freezer and allowed to thaw overnight in a 4°C refrigerator.

3.3.2 Manure Characterization

3.3.2.1 Percent solids and density. Thawed manure was stirred in a large plastic bin during sampling to ensure that solid matter was evenly distributed. This ensured that samples were representative of the whole. For total solids determination, manure was transferred to weighed tins with lids and then weighed again. Lids and tins with manure were placed in a drying oven at 100°C over night. Dry samples were lidded, transferred to a dessicator and allowed to cool before re-weighing. Mass of dry manure was divided by mass of wet manure and multiplied by 100 to determine the percent solids. Manure density was determined by weighing 100 mL beakers, filling them with manure and re-weighing.

3.3.2.2 Total-, NH_4^+ - and organic-N. Total-N was determined using Micro-Kjeldahl digestion followed by steam distillation as described by McGill and Figueiredo (1993). A Hengar granule, 10 mL of H_2SO_4 and 3.5 g of a K/Cu-sulphate mix were added to each of 12 - 2 mL manure samples. Samples were digested at 220°C for 1.5 hours and at 360°C for 3.5 hours. Once cool, samples were steam-distilled into 5 mL of 2% H_3BO_3 . This was then titrated with 0.05 M H_2SO_4 . Every 1 mL of 0.05 M H_2SO_4 represents 1.4 mg N in the sample. Based on this total-N was calculated as follows (McGill and Figueiredo 1993).

$$\text{Total-N}_{\text{mg/mL}} = \frac{(\text{Sample}_{\text{mL acid}} - \text{Blank}_{\text{mL acid}}) \times 1.4}{2 \text{ mL Sample}} \quad [3.6]$$

N g/mL was later converted to N g/manure g using density values (equation 3.7 below) so that they could be compared with result of the final destructive analyses.

$$\frac{[\text{Total-N (mg/mL)} \times 1 \text{ g/1000 mg}]}{\text{Manure Density g/mL}} \times 100 = \% \text{ Total-N} \quad [3.7]$$

Ammonium-N was determined by shaking 8, 2 mL samples of manure with 98 mL 2.0 M KCl for 1 hour. Samples were filtered through No. 42 Whatmann filter papers into 100mL volumetric flasks. Filtrates were immediately analyzed for NH_4^+ according to the AutoAnalyzer Indophenol Blue procedure of Maynard and Kalra (1993). Phenol reacts with NH_4^+ producing an blue colour. Automated spectrophotometric determination of NH_4^+ (based on the absorption of 630 nm wavelength light) was performed on a Technicon AutoAnalyzerII and NH_4^+ mg/mL determined according to:

$$\text{NH}_4^+ \text{ mg/mL} = \frac{\text{NH}_4^+ \mu\text{g/mL} \times 100 \text{ mL} \times 1000 \mu\text{g/mL}}{2 \text{ mL manure}} \quad [3.8]$$

Manitoba Agriculture and Food (2000c) and Schoenau (1997) have shown that inorganic N is primarily in the form of NH_4^+ in anaerobically stored hog manure. NO_3^- -N in the manure was assumed to be negligible compared to NH_4^+ -N and, as a result, organic-N was determined by subtracting the mean NH_4^+ -N content from the mean total-N content of the manure.

3.3.2.3 Aqueous K^+ , Na^+ , Ca^{2+} Mg^{2+} and H^+ . The method by which aqueous cations were determined (excluding H^+) was by extraction in water followed by filtration to remove any solids. Manure was stirred while 8, 2 mL samples were collected, to ensure representativeness of samples. Samples were transferred to 250 mL plastic containers with lids to which 1 mL of 0.015 M LaCl_3 solution and 97 mL of water were added. Containers were agitated in a side-to-side shaker for one hour to ensure complete mixing. Samples were filtered through No. 42 Whatmann filter papers into plastic vials which were afterwards sealed and refrigerated until analysis that same day. Samples were analyzed on a Perkin Elmer 1100B Atomic Absorption Spectrophotometer. Manure pH was determined directly with agitation (magnetic stirring) using an Accumet 950 pH/ion meter.

3.3.3 Physico-chemical Properties of UFA, CAFA and Mordenite

The method of fly ash chemical alteration and analytical methods used to characterize mineral amendments are discussed in detail in Chapter 2 and summarized in the following. Table 3.1 lists findings of the mineral characterization study.

Table 3.1 Selected physico-chemical properties of UFA, CAFA and mordenite.*

Sample	As μg/g	Pb μg/g	CEC cmol ⁺ /kg	CES K ⁺ /NH ₄ ⁺	SS m ² /g	PD g/m ²	ADMC %	pH
UFA	34 a	31 a	249 b	2.1 a	27 c	2.6 a	0.01 c	12.2 a
CAFA	16 b	15 b	679 a	2.1 a	273 a	2.5 a	10.59 a	6.7 b
Mordenite	9 b	16 b	112 c	3.1 b	162 b	2.2 b	4.57 b	6.6 b

*Values followed by the same letter are not significantly different ($\alpha = 0.05$)

Waste coal fly ash from the Boundary Dam Thermal Power Station, Saskatchewan, was provided by Lafarge Canada Inc. Fly ash was chemically altered according to a method modified from Hemni (1987a). Afterward, analyses were conducted on all three mineral samples including X-ray diffractometry (XRD), scanning-electron microscopy (SEM), total-As and Pb, cation exchange capacity (CEC), cation exchange selectivity (CES), specific surface (SS), particle density (PD), air dry moisture content (ADMC) and pH. XRD analysis indicated that Unaltered fly ash (UFA) consisted primarily of amorphous oxides with some crystalline material (mostly quartz). Chemically altered fly ash (CAFA) was found to be an inorganic hydrated crystalline aluminosilicate called sodium aluminum silicate hydrate. XRD confirmed the zeolite mineral to be mordenite. SEM secondary-electron micrographs indicated a change in fly ash particle shape from spherical to irregular after chemical alteration. The remaining

findings are summarized in table 3.1. For standard errors and methods please refer to Chapter 2.

3.3.4 Treatment, Composition and Calculation of Hog Manure Amendment Ratios

The volatilization study consisted of 3 replicate measurements of NH_3 volatilization from nine combinations of manure and amendments and one blank. Treatments (manure/amendment combinations) are described in the following.

- Treatment 1. Control (hog manure only)
- Treatment 2. Hog manure with UFA
- Treatment 3. Hog manure with CAFA
- Treatment 4. Hog manure with mordenite
- Treatment 5. Control with CaCl_2
- Treatment 6. Hog manure with UFA and CaCl_2
- Treatment 7. Hog manure with CAFA and CaCl_2
- Treatment 8. Hog manure with mordenite and CaCl_2
- Treatment 9. Blank

All treatments received 100 mL of hog manure which had been stirred in a plastic bin during sampling to ensure homogeneity of samples. Based on the results of the manure analysis, it was calculated that there were 0.014 mol of NH_4^+ ions in 100 mL of hog manure. Fenn and Kissel (1973) stated that addition of CaCl_2 at a ratio of 1 mol Ca^{2+} to every 2 mol NH_4^+ would be sufficient to achieve maximum reduction in NH_3

volatilization. Therefore 0.007 mol of solid, dry, reagent grade CaCl_2 (0.78 g) was mixed into manure, in treatments receiving it, prior to the addition of mineral amendments.

Quantities of minerals to be added were calculated based on their CEC and on the number of positive charges available for exchange in 100 mL of hog manure. The latter was estimated to be $2.5 \text{ cmol}^+/\text{100 mL}$ manure calculated from NH_4^+ and free cation contents (K^+ , Na^+ , Ca^{2+} and Mg^{2+}) determined in the manure analysis. Sufficient mineral was added to manure to provide CEC capable of retaining double the estimated number of positive charges present (this would compensate for an underestimation of the number of cations in solution). For example, Treatment 3 received 100 mL of hog manure and 7.4 g of CAFA. With a CEC of $0.679 \text{ cmol}^+/\text{g}$, 7.4 g of CAFA will be able to retain 5 cmol^+ - double the cmol^+ estimated to be in the manure. Positive charges coming from Ca^{2+} added in the form of CaCl_2 were incorporated into the doubled cmol^+ estimated per treatment for a total of 6.4 cmol^+ . As a result, CaCl_2 treatments received a greater quantity of mineral amendments. For example, Treatment 7 received 100 mL of hog manure, 0.78 g CaCl_2 and 9.4 g of CAFA. Mixing ratios of manure and amendments for all eight treatments and sample calculations are included in Appendix I.

3.3.5 Assembly of the Apparatus Used in the Volatilization Study

100 mL samples of hog manure were transferred to twenty-four air tight canning jars (without lids). Calcium chloride was incorporated into treatments receiving it first and samples were let stand for 15 minutes to allow for complete dissolution. Mineral amendments were added to each replicate in succession (i.e. replicate 1 first, replicate 3

last) and thoroughly stirred. Treatments were then connected to the volatilization study apparatus. Figure 3.1 is a diagrammatic representation of the apparatus.

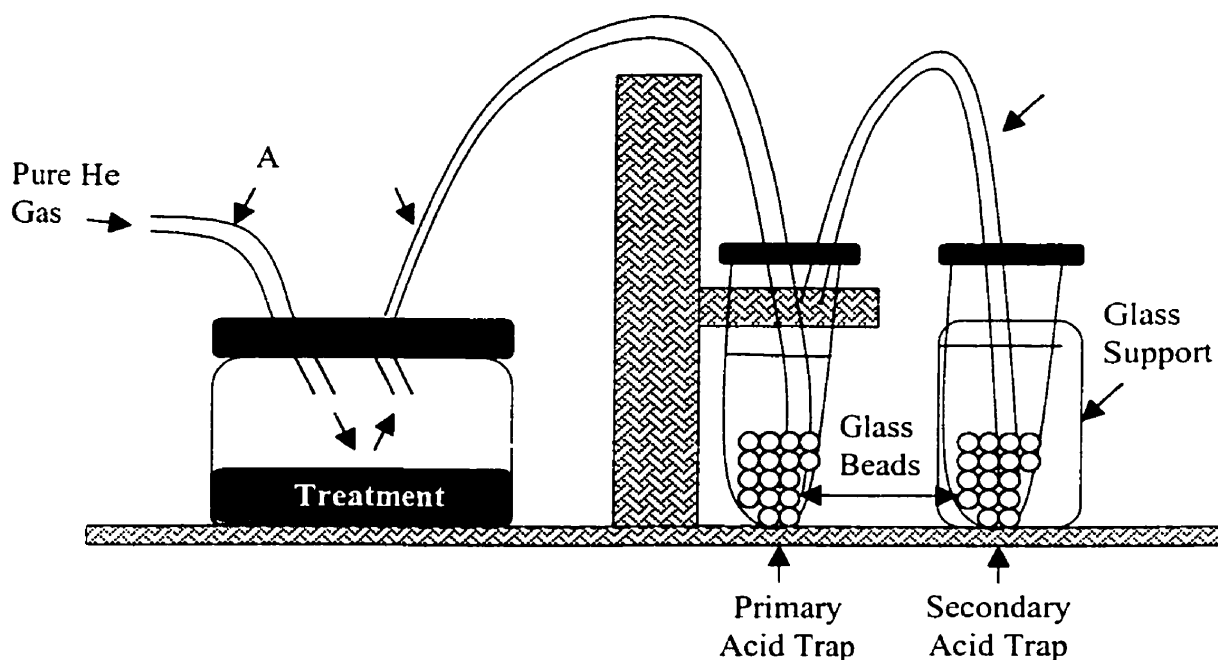


Figure 3.1 Design of the apparatus used in the volatilization study. Treatment jars and sample tubes were tightly capped and tubing inlets and outlets were sealed with silicon caulking.

The jars containing manure/amendment slurries were capped with air tight lids. Lids were fitted with one incoming tube (A) and one exit tube (B). Helium gas was passed over treatments to maintain anaerobic conditions while sweeping volatilized NH_3 away from the slurry surface. Each incoming tube was fitted with an air flow valve to allow for control of air flow rate. Valves for each replicate were stabilized on a manifold and were interconnected, receiving all their He from a single tank. Consequently, each repetition was completely isolated from the others. Helium flowing into jars from A exited through

B. The outlet of tube B was immersed in a capped centrifuge tube containing 20 mL of 1 mol/L phosphoric acid (H_3PO_4) and 20 mL of glass beads (the beads were intended to facilitate the diffusion of NH_3 into the acid by slowing down and breaking up the gas bubbles as they passed upward through the solution). This was the primary acid trap indicated in Figure 3.1. The primary acid trap was fitted with an outlet tube (C) which lead to a second centrifuge tube filled with 20 mL of 1 mol/L H_3PO_4 and 20 mL of glass beads (the secondary acid trap). The secondary acid trap trapped any remaining NH_3 that had escaped capture in the primary trap (a test of the efficiency of NH_3 removal by the primary acid trap). All inlet and outlet tubes were sealed with silicon caulking to prevent leaks excluding the secondary acid trap which was not sealed to allow the escape of gas from the apparatus.



(a)



(b)



(c)

Figure 3.2 The volatilization study apparatus showing (a) primary and secondary acid traps of all three replicates - note the helium tanks in the background each connected to one replicate, (b) side view of wooden support structure and tubing connections between treatment jars and acid traps and (c) secondary trap change on replicate 3.

Treatments were randomized within each replicate and were fitted to the apparatus in sequence, starting with replicate 1 and ending with replicate 3. Traps were changed every 24 hours after assembly (first primary traps, then secondary traps) according to this sequence up to day 34. After day 34 traps were changed every 48 hours and after day 50 traps were changed every 72 hours to compensate for anticipated reduction in NH_3 volatilization. Equal parts of the $\text{H}_3\text{PO}_4/\text{NH}_4^+$ solutions in the primary and secondary acid traps were immediately transferred to two glass scintillation vials (one duplicate) and frozen (-20°C) until analysis for NH_4^+ . These samples were removed from the freezer and allowed to thaw in a refrigerator prior to analysis. Three pictures of the volatilization study apparatus and daily trap changes are shown in Figure 3.2 (explanation on next page).

3.3.6 Analysis of Volatilized NH_3 as NH_4^+ -N Captured in Acid Traps

Phosphoric acid samples, containing NH_4^+ , were removed from the freezer (-20°C) and allowed to thaw for one to two days in a refrigerator (4°C). Ammonium content of acid traps was determined using a modified AutoAnalyzer Indophenol Blue procedure based on that of Maynard and Kalra (1993) using an absorption wavelength of 630 nm. The Brij-35 reagent (a surfactant) reacted with the acidic samples producing a white precipitate which clogged the glass tubing in the AutoAnalyzer. To counteract this Triton X-100, a surfactant used in the colourimetric determination of total-C/dissolved organic-C, was substituted for Brij-35 (Technicon Instrument Corporation 1978). Since the intensity of colour development was reduced for the acid samples the sensitivity of the

AutoAnalyzer to differences in colour was optimized. Samples of known concentration, duplicate samples and standard corrections were included in all runs to maintain quality control and quality assurance.

3.3.7 Final Destructive Analysis

The volatilization study was conducted for 86 days commencing on May 8th and ending on August 1st, 1998. After the last traps had been collected, treatments were removed from the apparatus and were analyzed for total-N, NH_4^+ -N, organic-N and pH. Drying had removed most of the liquid from treatments. Consequently, total-N and NH_4^+ -N samples were measured in grams of manure (\pm amendments) not mL as in the manure characterization study. Dry mass of combined treatment constituents were used to calculate g N (total and NH_4^+) remaining. Dry mass of treatments can be found in Appendix I. Otherwise analyses were conducted according to the methods outlined in section 3.3.2.2. Again, organic-N was determined from mean total-N and NH_4^+ -N values. Finally, pH was determined on a three decimal place Accumet 950 pH/ion meter in a 3:1 water paste. Deionized-distilled water was used for all analyses.

3.3.8 Statistical Analyses

Statistical analyses of all data were conducted using Systat 7.0 software. Means and standard errors were determined for manure characterization data. Analysis of variance (ANOVA) and Fisher's least significant difference (LSD) mean comparison tests

were conducted on cumulative NH_3 volatilized to day 40, on NH_3 volatilization during individual sampling periods from days 1 to 40, on cumulative NH_3 volatilized to day 86 and on the results of the final destructive analysis.

3.4 Results and Discussion

3.4.1 Manure Characterization

Table 3.2 contains selected physico-chemical characteristics of the manure. The low total solids (5.5%) indicated that the majority of the manure is liquid, which is not uncommon for hog manure (Manitoba Agriculture and Food 2000c). Manure density was 1.1 g/cm^3 . Manure contained 4.68 mg N/mL . This is high when compared with typical total-N values found for hog manure in Manitoba which range between 2.38 and 3.06 mg N/mL (Manitoba Agriculture and Food 2000c). Manure contained $2.51 \text{ mg NH}_4^+-\text{N/mL}$, 54% of the total-N. Organic-N was, therefore, estimated to comprise approximately 46% of the total-N (2.17 mg/mL). According to data reported by Manitoba Agriculture and Food (2000c), NH_4^+-N determined for the hog manure fell within typical ranges (1.65 - $2.19 \text{ mg NH}_4^+-\text{N/mL}$). However, due to high manure total-N, the ratio of NH_4^+-N to organic-N did not fall within normal parameters. Typically, 70% of manure total-N is in the form of NH_4^+ (Manitoba Agriculture and Food 2000c). The remainder (30%) is organic-N (Manitoba Agriculture and Food 2000c). This is important to note as the composition of N in manure will affect N losses from manure.

Table 3.2 Selected physico-chemical properties of hog manure used in the study.

	Total Solids %	Density (g/cm ³)	Nitrogen			Free Ions			pH	
			Total	NH ₄ ⁺	Organic*	K ⁺	Na ⁺	Ca ²⁺		Mg ²⁺
Mean	5.5	1.1	4.68	2.51	2.17	1.28	0.64	0.53	0.27	7.3
Stand Error	0.079	0.003	0.060	0.116	--	0.014	0.016	0.017	0.007	0.061

*Standard error was not calculated for organic-N as it was derived from mean total-N and NH₄⁺-N values.

Free cation concentrations in the hog manure were normal with K⁺ levels highest (1.28 mg/mL) followed by Na⁺ (0.64 mg/mL), Ca²⁺ (0.53 mg/mL) and Mg²⁺ (0.27 mg/mL). These values (including NH₄⁺) were used to calculate mass of mineral amendments required for each treatment. Manure pH was shown to be near neutral (7.3).

3.4.2 NH₃ Losses During the First 40 Days

The purpose of this study was to assess whether mineral and/or chemical amendments reduce NH₃ volatilization from anaerobically stored hog manure. Anaerobic storage conditions were simulated in the volatilization study apparatus and gases evolved from the manure were swept out of sealed jars by a stream of He gas into acid traps. Quantities of NH₃ trapped during individual sampling periods were summed to give cumulative NH₃ losses. Cumulative NH₃ losses from the 9 treatments were plotted against time up to day 40 and are shown in figure 3.3.

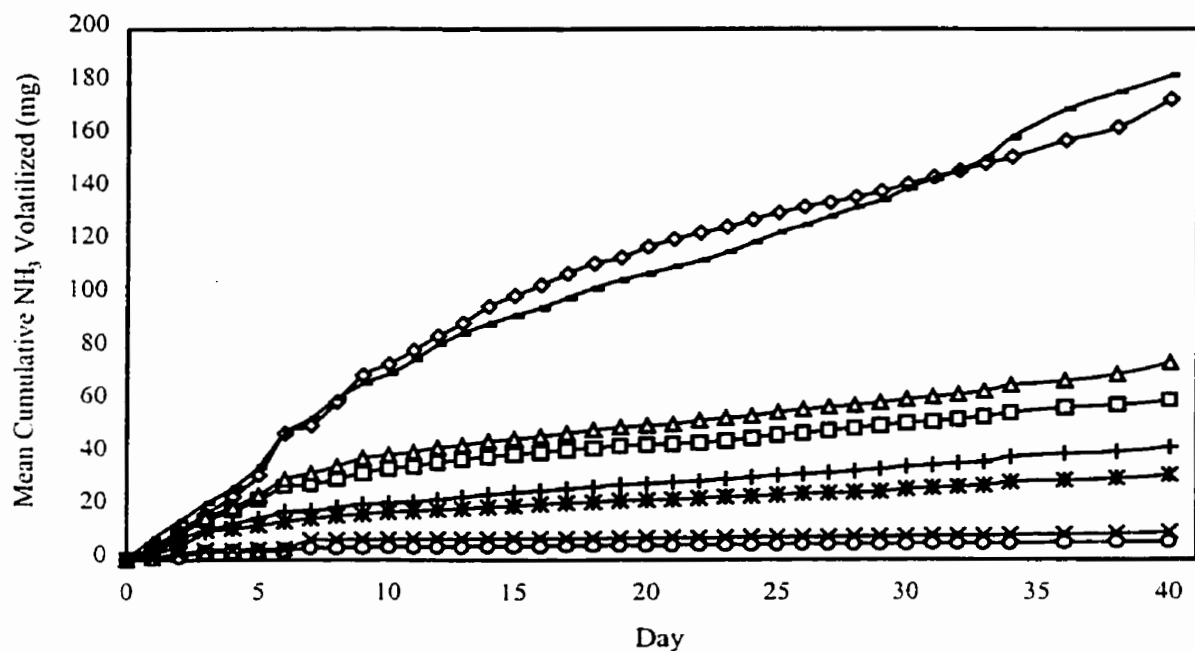


Figure 3.3 Mean cumulative NH₃ volatilized during 40 days. Where - is UFA, ◊ is UFA & CaCl₂, Δ is CAFA, □ is the Control, + is CAFA & CaCl₂, * is the Control & CaCl₂, × is mordenite & CaCl₂ and ○ is mordenite.

3.4.2.1 Cumulative NH₃ losses. Cumulative NH₃ volatilized up to day 40 was determined for each treatment. One-way ANOVA and LSD mean comparisons were conducted on results for treatments from the three replicates. It should be noted that significant differences cannot be determined for cumulative data by these means because cumulative errors are not accounted for in mean comparison tests. The data, however, help to illustrate the NH₄⁺ adsorption and retention capacities of the amendments and are included in Table 3.3.

Table 3.3 Effect of amendment on cumulative NH₃ volatilized from hog manure during 40 days of anaerobic storage.

Treatment	Cumulative Ammonia Volatilized to Day 40 (mg)	Standard Error
UFA & CaCl ₂	180 a*	29.618
UFA	170 a	26.901
CAFA	70 b	6.461
Control	60 b	4.904
CAFA & CaCl ₂	40 bc	1.755
Control & CaCl ₂	30 bc	0.654
Mordenite & CaCl ₂	10 c	1.706
Mordenite	7 c	0.719

*Mean comparison rankings. Values followed by the same letter are not significantly different ($\alpha = 0.05$)

Treatments containing UFA had significantly higher NH₃ losses as compared to all other treatments. This may be caused by an increase in the manure pH due to incorporation of UFA (pH = 12.2). Several researchers have shown that NH₃ volatilization from anaerobically stored manure increases with increasing manure pH (Termeer and Warman 1993, Dewes et al. 1990, Kirchmann and Witter 1989, Witter and Kirchman 1989). However, only the UFA treatment with CaCl₂ had a significantly higher pH at the end of the volatilization study (see Table 3.9). The treatment containing only UFA had a pH similar to that of treatments containing CAFA and the controls (with or without CaCl₂) and yet had greater NH₃ losses. This may indicate that some other factor(s) is affecting NH₃ volatilization or that NH₃ volatilization reactions have effectively reduced manure pH in the absence of CaCl₂ due to the conversion of OH⁻ ions to water (see equation 3.2). CAFA and control samples, with and without CaCl₂, did not loose significantly different amounts of NH₃ through volatilization from manure. Mordenite amendment of hog manure, on the other hand, did cause significantly lower

volatilization rates relative to CAFA and control treatments. However, when CAFA and control treatments were combined with CaCl_2 , NH_3 losses were not significantly different from either of the mordenite treatments. This implies that CAFA and control treatments coupled with CaCl_2 have lower NH_3 losses than those without although differences in volatilization were not found to be statistically significant.

3.4.2.2 Amounts of NH_3 volatilized during individual sampling periods. Although cumulative results are more informative in terms of the ability of amendments to reduce NH_3 volatilization over the long term, the cumulative error associated with these results makes their statistical significance difficult to prove. As a result, ANOVA and LSD mean comparisons were conducted on NH_3 volatilization data from individual sampling periods to day 40. These analyses provide us with an incomplete picture of amendment effects (for 24 or 48 hours only), however their statistical significance is more easily interpreted because of the much reduced error. Results of ANOVA and mean comparison tests are listed in Appendix II. A summary of these results are provided below.

In the absence of mineral amendments CaCl_2 appeared to be somewhat effective in reducing NH_3 volatilization. The control with CaCl_2 volatilized significantly less NH_3 than the control alone on 24% of the days analyzed. This may be explained in terms of the mechanism of NH_3 volatilization suppression by Ca^{2+} containing salts. According to equation 3.5, Ca^{2+} reacts with HCO_3^- in the manure forming CaCO_3 . The precipitation reaction removes HCO_3^- from the manure which stimulates the reaction of CO_2 with water producing more HCO_3^- and H^+ , the latter subsequently reducing manure pH (equation 3.4). This causes a reduction in NH_3 volatilization. Final pH values have to be

considered in order to confirm that a reduction in pH is indeed the factor causing lower NH_3 volatilization from manure amended with CaCl_2 . Destructive analysis, however, indicated that there were no pH differences between control treatments with or without CaCl_2 (Table 3.9). Therefore, some factor(s) other than pH must be affecting volatilization rates.

The addition of CaCl_2 had little effect on NH_3 volatilization in treatments containing the same mineral amendment. For example, CaCl_2 did not significantly reduce volatilization from treatments containing UFA, probably because the CaCl_2 was unable to counteract the high pH of the UFA (12.2). As can be seen in Figure 3.3, the volatilization curves for the two UFA treatments parallel each other closely. In the case of CAFA, NH_3 volatilization from the treatment containing CaCl_2 appears to be substantially lower than the treatment without (Figure 3.3). However, statistical analyses indicate that addition of CaCl_2 significantly reduces NH_3 volatilization for samples containing CAFA on only 5% of the days analyzed. The lack of statistical significance can be attributed to the variability of NH_3 volatilization observed. It should be noted that CaCl_2 was never shown to significantly increase NH_3 volatilization in treatments containing CAFA. Ammonia volatilization curves for mordenite in Figure 3.3 show that CaCl_2 did not appear to reduce NH_3 volatilization. However, some statistically significant differences were found. On 5% of the days analyzed, NH_3 volatilization was significantly higher for treatments containing CaCl_2 . Conversely, on 3% of the days analyzed, NH_3 volatilization was significantly lower for treatments containing CaCl_2 . This implies that CaCl_2 had no effect on NH_3 volatilization from treatments containing mordenite and any differences observed were as a result of variability. As indicated above, CaCl_2 appears to have no effect on

NH₃ volatilization from treatments containing the same mineral amendments. However, NH₃ volatilization from treatments containing different mineral amendments are effected by the presence of CaCl₂ as will be shown in the following section.

Ammonia volatilization from treatments containing CAFA was found to be significantly lower than from treatments containing UFA on 46% of the days analyzed, whereas treatments containing both CAFA and CaCl₂ had significantly lower amounts of NH₃ volatilization compared to UFA on 78% of the days analyzed. In other words, treatments containing CAFA and CaCl₂ had significantly lower NH₃ volatilization, as compared to UFA, more often than CAFA alone! The same trend was found for UFA with CaCl₂. Ammonia volatilization was significantly lower 49% and 84% of the time for CAFA only and CAFA and CaCl₂ treatments respectively when compared with treatments containing UFA and CaCl₂. Similar results were found for control treatments. Volatilization from the control with CaCl₂ was significantly lower than treatments containing UFA (86% of the time) more often than volatilization from the control without CaCl₂ (59% of the time). The same trend was observed for volatilization comparisons between the controls (with and without CaCl₂) and treatments containing UFA with CaCl₂ (with NH₃ volatilization from UFA and CaCl₂ greater than the control with CaCl₂ 92% of the time and greater than the control without CaCl₂ 68% of the time). Significant differences between treatments containing different mineral amendments indicate CaCl₂ reduces NH₃ volatilization somewhat. However, the mechanism by which this was achieved is not certain as pH values were not significantly different between most treatments (Table 3.6).

Generally, all other treatments displayed lower NH_3 volatilization rates than treatments containing UFA (with or without CaCl_2). Treatments amended with CAFA (with or without CaCl_2) and the control were not found to be significantly different from each other. However, the control with CaCl_2 was found to have significantly lower amounts of NH_3 volatilization than CAFA (41% of days analyzed), the control (24% of days analyzed) and CAFA with CaCl_2 (11% of all days analyzed). Treatments containing mordenite (with or without CaCl_2) were found to volatilize significantly less NH_3 relative to all other treatments on 90% or more of the days analyzed.

4.4.3 NH_3 Losses by the End of the Volatilization Study (Day 86)

Unfortunately, during the design of the volatilization study apparatus, one important factor was overlooked; that with time treatments would lose moisture to evaporation. Vlek and Stumpe (1978) have shown that NH_3 volatilization from aqueous systems increases with increasing NH_4^+ concentration. As a result, NH_3 volatilization increased dramatically as the manure dried out and became more concentrated. This was observed for all treatments except those containing mordenite (Figure 3.4).

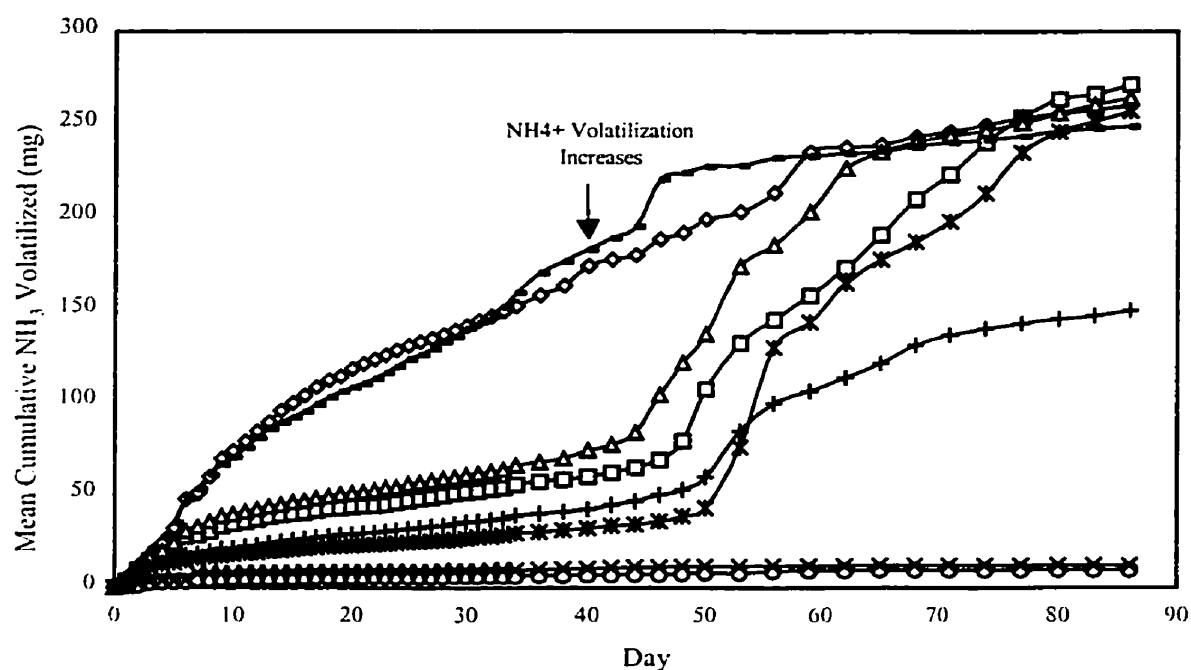


Figure 3.4 Mean cumulative NH₃ volatilized during 86 days. Where - is UFA, \diamond is UFA & CaCl₂, Δ is CAFA, \square is the Control, + is CAFA & CaCl₂, * is the Control & CaCl₂, \times is mordenite & CaCl₂ and \circ is mordenite.

Competing factors affecting NH₃ volatilization, such as drying, must be minimized so that amendment effects may be isolated. Increased rates of NH₃ volatilization occurred as early as day 42 for treatments containing UFA and as late as day 50 for the control with CaCl₂. For this reason, previous statistical analyses focused only on data up to day 40. At the end of the volatilization study (Figure 3.4) all treatments seem to have evolved similar quantities of NH₃ except for those containing mordenite (with or without CaCl₂) and CAFA with CaCl₂. For the other treatments, volatilization increases after drying and continues until approximately 250 mg of NH₃ have been lost after which volatilization abates. It is interesting to note that, based on previous calculations, 251 mg of NH₄⁺ were added to each treatment in the manure, and

that with drying all of this NH_4^+ appears to have volatilized as NH_3 . However, for the mordenite and CAFA with CaCl_2 treatments this is not the case. Mordenite treatments show no appreciable increase in volatilization even after drying even though they have significantly higher final pH values than all other treatments (7.6 and 7.5, Table 3.6). This may be a result of the high selectivity of mordenite for NH_4^+ which is only third (after Cs^+ and K^+ respectively) in the mordenite cation affinity sequence (Barrer and Kinowski, 1974). Additionally, mordenite has been shown to effectively adsorb NH_3 gas so there is even the potential for gaseous NH_3 to be held by the mineral (Vaughan, 1978). The CAFA with CaCl_2 treatment shows some increase in volatilization after day 40 but volatilization abates much sooner ($<150 \text{ mg NH}_4^+$) than for the other treatments. This indicates that CaCl_2 is in some way reducing volatilization, either by itself or in combination with CAFA. As stated earlier, CaCl_2 used by itself reduces NH_3 volatilization through a decrease in pH. However, pH results in Table 3.6 indicate that treatments containing CAFA and CaCl_2 did not have significantly different pH values (5.8) than those treatments having evolved greater quantities of NH_3 (excluding UFA which had a pH of 6.3). This may be explained if we assume the CAFA to have a zeolitic framework. Breck et al. (1956) has shown that the molecular sieve properties of zeolites are dependent on exchange cations held in channels and voids. In his study, sorption capacities of various inorganic and organic molecules on a synthetic Na-exchanged zeolite (Linde 4-A) were drastically reduced when Na^+ was replaced by larger K^+ ions on the zeolite exchange sites. The larger K^+ ions effectively blocked channel openings reducing sorption to almost zero. Similar results were observed when sorption of the same molecules drastically increased due to the replacement of Na^+ ions by Ca^{2+} ions. The divalent Ca^{2+} replaced two Na^+ cations clearing channel entrances and permitting

greater diffusion of molecules into the zeolite lattice. Ca^{2+} (from the CaCl_2) may have replaced Na^+ in channels and voids of the CAFA structure opening space for the diffusion and sorption of urea molecules, amines, NH_4^+ and NH_3 , in turn making them inaccessible for microbial breakdown or volatilization. Additionally, although the final pH values between CAFA with or without CaCl_2 were the same, the initial pH values may have been different. Perhaps the CaCl_2 containing treatment experienced a more rapid reduction in pH and had lower initial NH_3 losses until both treatments reached their final equilibrium pH. Mean comparisons of total NH_3 losses from treatments after day 86 are listed in Table 3.4.

Table 3.4 Effect of amendment on cumulative NH_3 volatilized from hog manure during 86 days of anaerobic storage.

Treatment	Cumulative Ammonia Volatilized to Day 86 (mg)	Standard Error
Control	290 a*	93.845
CAFA	260 a	39.129
UFA	260 a	4.626
Control & CaCl_2	260 a	49.480
UFA & CaCl_2	250 a	32.208
CAFA & CaCl_2	150 a	6.689
Mordenite & CaCl_2	12 b	2.223
Mordenite	10 b	0.565

*Mean comparison rankings. Values followed by the same letter are not significantly different ($\alpha = 0.05$)

The treatments containing mordenite volatilized 95% less NH_4^+ than the control (which had the highest volatile NH_3 losses) even after drying and were the only treatments found to be significantly different from the others. Interestingly, treatments containing CAFA with CaCl_2 , which had the next lowest losses of NH_3 , were not

significantly different from the other amendments (excluding mordenite). The high variability observed for total NH_3 losses between replicates (as evidenced by the large standard errors) may have hindered the identification of significant differences. At a probability of $p < 0.1$ CAFA with CaCl_2 would have been significantly different from all other treatments.

3.4.4 Destructive Analysis of Manure Slurries After 86 Days of Storage

Final destructive analyses were performed on treatments at the end of the volatilization study (after the manure had completely dried). Table 3.5 lists mean total-N, NH_4^+ -N and organic-N values.

3.4.4.1 Total-N content after 86 days of storage. In light of Figure 3.4, it is not surprising that total-N values were significantly higher for treatments containing mordenite (with or without CaCl_2) and CAFA with CaCl_2 relative to the other treatments. As well, the CAFA with CaCl_2 total-N was not significantly different from the mordenite treatments indicating that N conservation is similar although volatile NH_3 losses from CAFA with CaCl_2 were greater. This may indicate that N is being lost from mordenite amended treatments in a form other than NH_3 . The most likely alternative mode of N loss from these treatments is in the form of amines. Miner and Hazen (1969) found that gaseous N losses from hog manure stored in pits under housing structures consisted of both NH_3 and amines. Treatments containing CAFA with CaCl_2 had significantly more total-N remaining after 86 days than treatments containing CAFA alone. This indicates

Table 3.5 Total-, NH_4^+ - and organic-N remaining in treatments and their proportions relative to total-N after day 86 of the volatilization study (organic-N is the difference between total- and NH_4^+ -N and therefore has no standard error)

Treatment	Total-N (mg)	Standard Error	NH_4^+ -N (mg)	% Total-N as NH_4^+ -N	Standard Error	Organic-N (mg)	% Total-N as organic-N
Mordenite & CaCl_2	360 a*	27.171	170 abc	47	48.496	190	53
Mordenite	360 a	24.728	170 abc	47	44.187	190	53
CAFA & CaCl_2	340 a	12.566	220 a	64	14.702	120	35
Control & CaCl_2	240 b	6.861	220 ab	92	18.500	20	8
CAFA	240 b	0.422	160 abc	67	14.680	80	33
UFA & CaCl_2	240 b	23.879	90 cd	38	23.890	150	63
Control	170 c	8.882	120 bcd	71	10.404	50	29
UFA	150 c	31.377	50 d	33	21.836	100	67

*Mean comparison rankings. Values followed by the same letter are not considered to be significantly different ($\alpha = 0.05$)

that CaCl_2 was able to reduce N losses either alone or by interaction with CAFA. The control with CaCl_2 , CAFA and UFA with CaCl_2 had similar total-N content (approximately 240 mg N) and were not significantly different from each other. Similar to the case of CAFA and CaCl_2 , the control with CaCl_2 and UFA with CaCl_2 had significantly higher total-N contents after 86 days than their CaCl_2 free counterparts. This also indicates some CaCl_2 influenced reduction of N losses. Finally, the control and UFA amended manure had lowest total-N content (170 and 150 mg respectively) and were not significantly different from each other. It is interesting to note that the control and UFA amended manure had similar volatile NH_3 losses compared to treatments containing CAFA, UFA with CaCl_2 and the control with CaCl_2 despite their lower final total-N content. As in the case with the mordenite treatments, N losses from these systems may be as gaseous NH_3 and amines, resulting in their lower total-N.

Table 3.6 pH values of treatments after 86 of anaerobic storage in the volatilization study

Treatment	pH	Standard Error
Mordenite	7.6 a	0.058
Mordenite & CaCl_2	7.5 a	0.145
UFA & CaCl_2	6.3 b	0.267
CAFA	5.8 c	0.033
CAFA & CaCl_2	5.8 c	0.058
UFA	5.7 c	0.033
Control	5.6 c	0.033
Control & CaCl_2	5.6 c	0.012

*Mean comparison rankings. Values followed by the same letter are not significantly different ($\alpha = 0.05$)

3.4.4.2 NH_4^+ -N content after 86 days of storage. At the termination of the study, CAFA with CaCl_2 and the control with CaCl_2 had the highest NH_4^+ -N contents and were

found to be significantly higher than the control without CaCl_2 and UFA containing treatments. Treatments containing UFA had the lowest final NH_4^+ -N contents, significantly lower relative to treatments containing mordenite, CAFA (with or without CaCl_2) and the control with CaCl_2 . The control contained significantly lower total-N than its CaCl_2 amended counterpart despite having identical pH values (Table 3.5). However they were not found to have significantly different quantities of NH_4^+ -N. This may indicate that N was being lost from the control as NH_3 and amines. As suggested for CAFA treatments, manure containing CaCl_2 may have experienced a more rapid reduction in pH and had lower initial NH_3 -N losses.

3.4.4.3 Organic-N content after 86 days of storage. Organic-N remaining in treatments after 86 days of anaerobic storage is listed in Table 3.5. The controls, with and without CaCl_2 , have the lowest proportions of organic-N relative to other treatments (11% and 28% respectively). This may indicate that mineral amendments contribute to the conservation of N in the organic form. When molecules are adsorbed on mineral surfaces they are removed from reactions occurring in the slurry, and are therefore protected from microbial breakdown. In the absence of mineral amendments, organic-N is susceptible to microbial breakdown and a large portion of the organic-N is converted to NH_4^+ through microbial decomposition. Treatments containing CAFA, with and without CaCl_2 , had the second lowest proportions of organic-N (35 and 33% respectively) indicating that CAFA hinders the conservation of N from organic form to inorganic form somewhat (and in the case of CAFA with CaCl_2 also conserves NH_4^+ well). Treatments containing mordenite (with and without CaCl_2) conserved an even greater proportion of N in organic form (54 and 52% respectively). Based on this finding, zeolite amended manure may be a very

effective source of slow release urea-N for agricultural crops. Finally, treatments containing UFA contained the highest proportions of organic-N. This may indicate that organic-N in the manure is adsorbed on the oxide surfaces and is therefore not accessible to microorganisms. However, it is also likely that conservation of organic-N occurred initially due to the inhibition of microbial activity at high pH. UFA has a pH of 12.2 in 3:1 water paste (Table 3.1). Therefore, initial pH values in UFA containing treatments were probably high. This would have inhibited microbial and enzymatic activity reducing conversion of organic-N to NH_4^+ . As NH_3 volatilization progressed pH dropped due to the consumption of OH^- ions (equation 3.2) resulting in the lower pH values determined at that time (6.3 with CaCl_2 , 5.7 without). The extensive loss of NH_4^+ likely contributed to the high proportion of organic-N in UFA containing treatments.

3.4.5 Mass Balance of Total-N Added, Total-N Remaining and Cumulative NH_4^+ -N Lost After 86 Days

Treatments containing mordenite (with and without CaCl_2) and CAFA with CaCl_2 had the highest proportion of total-N remaining after 86 days of storage (77% and 73% respectively). The control and UFA containing treatments had the lowest total-N remaining (36% and 32% respectively). Due to the high variability observed in volatilization data N mass balance indicated an overestimation of N losses from some treatments and an underestimation of N losses from others (Table 3.7).

Table 3.7 Mass balance listing total-N added to treatments as manure, total-N remaining in treatments, total-N losses determined from this and reconciliation with cumulative NH₃ losses determined in the volatilization study.

Treatment	Total-N Added	Total-N Remaining	Total-N Lost	Cumulativ e NH ₄ ⁺ -N Lost	Difference, Total-N & NH ₄ ⁺ -N* Lost
-- mg --					
Mordenite & CaCl ₂	468	360	108	12	96
Mordenite	468	360	108	10	98
CAFA & CaCl ₂	468	340	128	150	-22
Control & CaCl ₂	468	240	228	260	-32
CAFA	468	240	228	260	-32
UFA & CaCl ₂	468	240	228	250	-22
Control	468	170	298	290	8
UFA	468	150	318	260	58

*Difference, Total-N and NH₄⁺-N refers to the difference between calculated N losses from manure characterization and destructive analyses of total-N and cumulative NH₃-N losses calculated from the volatilization study

Differences between total-N and NH₄⁺-N lost from treatments containing mordenite indicate that N losses were more extensive than was accounted for by the volatilization study. Total-N losses from mordenite containing treatments (with or without CaCl₂) were greater than NH₄⁺-N losses by 98 and 96 mg N respectively. Again this indicates that N may have been lost in some form in addition to NH₃. This may also have been the case for treatments containing UFA as the difference between total-N lost and NH₄⁺-N lost is 58. Aside from these cases, however, differences between total-N lost and NH₄⁺-N lost from treatments are not very great and considering the large variability observed in volatilization study data do not necessarily indicate discrepancies in N losses.

3.5 Conclusions

Amendment of hog manure with UFA increased NH_3 volatilization and total-N lost from the manure. UFA is not a suitable hog manure amendment. Conversely, mordenite amended hog manure lost significantly less NH_3 to volatilization than the controls. Total-N determinations after 86 days of storage indicated that treatments containing mordenite conserved the most N along with CAFA combined with CaCl_2 . CAFA amended manure volatilized comparable quantities of NH_3 as the control but total-N remaining in the CAFA amended manure after 86 days of storage was greater than in the control. This may indicate that N was lost from the control in some other form as well as in the form of NH_3 . The addition of CaCl_2 alone to hog manure had the same affect as addition of CAFA. When combined, CAFA with CaCl_2 was even more effective at conserving manure-N. Although volatile NH_3 losses after 86 days were not significantly lower then other treatments total-N conserved was equal to that of mordenite containing treatments. This indicates that mordenite containing treatments lost N in some form not measured in this study (i.e. as amines) in addition to losses as NH_3 and that N was not lost in this form from treatments containing CAFA and CaCl_2 . In conclusion mordenite and CAFA combined with CaCl_2 are the most effective hog manure amendments in terms of N conservation and further study on N release from amended manure after land application is required.

4. GENERAL SUMMARY AND CONCLUSION

The first objective of this study was to chemically alter locally obtained waste coal fly ash and determine if alteration resulted in an increase in the zeolitic character of the fly ash by comparing it with mordenite, a natural zeolite. X-ray diffractometry indicated that chemical alteration transformed amorphous unaltered fly ash (UFA) into sodium aluminum silicate hydrate, an inorganic hydrated crystalline aluminosilicate. Scanning-electron microscopy confirmed a change in particle morphology after chemical treatment, although no well developed crystals were observed. The alteration was not complete as remnants of UFA were observed. Chemical analysis demonstrated that chemically altered fly ash (CAFA) had a significantly higher cation exchange capacity (CEC), specific surface and air dry moisture content than UFA. As well, CAFA contained less As and Pb and had a lower pH than UFA. These findings are consistent with an increase in the zeolitic character of CAFA. No changes were observed in cation exchange selectivity (CES) or particle density of fly ash after chemical alteration. CAFA, UFA and mordenite all were selective for K^+ , but CAFA and UFA had significantly lower K^+ selectivity than mordenite. CAFA and UFA had similar particle densities, both significantly higher than mordenite. Therefore, some but not all of the findings in this study suggest an increase in the zeolitic character of fly ash after chemical alteration.

The second objective of this study was to examine the effectiveness of UFA, CAFA and mordenite in reducing gaseous ammonia (NH_3) volatilization from anaerobically stored hog manure. Calcium chloride (CaCl_2) had also been shown to reduce NH_3 volatilization from stored hog manure (Witter and Kirchmann 1989a). Therefore, its effect on NH_3 volatilization was also investigated alone and in combination with UFA, CAFA and mordenite. Analysis of variance (ANOVA) and Fishers Least Significant Difference mean comparison tests were conducted on cumulative NH_3 losses (to day 40 and to day 86), NH_3 losses for individual sampling days and final destructive analyses. Results from the cumulative analysis to day 40 and analysis of NH_3 volatilized during individual sampling periods indicated that the greatest volatile NH_3 losses occurred where hog manure was amended with UFA with or without CaCl_2 , indicating that UFA was ineffective. This is likely due to increased manure pH immediately after addition of UFA although final destructive analyses conducted after 3 months indicated that all treatments, excluding those containing mordenite, had pH values less than 7. Ammonia volatilization was not significantly reduced from hog manure amended with CAFA as compared to the control. However, total-N remaining in CAFA containing treatments was greater than the control at the end of the study. This may indicate that N was lost from the control in some other form in addition to NH_3 . Addition of CaCl_2 to the control and CAFA treatments reduced volatile NH_3 losses somewhat. In all cases, addition of mordenite to hog manure resulted in significantly lower volatile NH_3 losses relative to the control and all other amendments and the presence of CaCl_2 in these treatments had no further suppressive effect on NH_3 volatilization. These results suggest that despite the observed increase in zeolitic character, CAFA is still less effective than mordenite as a suppressant of NH_3 volatilization from anaerobically stored hog manure.

After day 40, treatments began to dry out and NH_3 volatilization increased except in treatments containing mordenite. Cumulative NH_3 losses to day 86 indicated that mordenite containing treatments had significantly lower NH_3 losses than the controls and other treatments. The CAFA and CaCl_2 containing treatments also exhibited lower losses than the controls and other treatments (by more than 100 mg NH_3). However, statistically significant differences were not observed.

Final destructive analyses indicated that CAFA with CaCl_2 was more effective at conserving N than could be concluded based on NH_3 volatilization study results as well as confirming the effectiveness of mordenite treatments in reducing N losses. Treatments containing mordenite and CAFA with CaCl_2 had the highest total-N remaining after 86 days of storage and were found to be significantly higher than the controls and other treatments. Differences between total-N losses and NH_3 -N losses from mordenite containing treatments indicate that N was lost from these systems in some other form in addition to NH_3 . This would explain the similar total-N values found between mordenite and CAFA with CaCl_2 containing treatments at the end of the study. The control and UFA containing treatments had significantly lower total-N remaining relative to their CaCl_2 containing counterparts after 86 days. This may indicate that N was lost from these systems in some other form not measured (i.e. as amines) in addition to NH_3 . Proportions of NH_4^+ - and organic-N determined indicate that initial high pH levels in UFA treatments may have inhibited microbial activity and increased NH_3 volatilization resulting in the high proportion of organic-N remaining in these treatments. Mordenite had NH_4^+ - and organic-N proportions similar to initial proportions indicating that N in both forms was conserved. Treatments containing CAFA had higher NH_4^+ -N proportions than existed in

the manure prior to the study, indicating that some conversion of organic-N to NH_4^+ -N occurred. Controls had the lowest proportion of organic-N after 86 days, indicating that microbial activity almost completely converted organic-N to NH_4^+ -N during storage.

In conclusion, further study on N release from amended manure after land application is required. Due to small channel sizes, $\text{NH}_4^+/\text{NH}_3$ release from mordenite may be too slow to benefit crops unless at very high amendment rates. CAFA may be able to provide a more rapid rate of $\text{NH}_4^+/\text{NH}_3$ release. Therefore the rate and duration (how rapidly and for how long can $\text{NH}_4^+/\text{NH}_3$ release from CAFA can be sustained) should be evaluated. With respect to the fly ash chemical alteration method, an alternate base should be considered (i.e. KOH) as a replacement for NaOH since sodicity problems may arise when CAFA amended manure is applied to land. As well, based on SEM micrographs and XRD data, it is the authors belief that chemical alteration was not complete and that a longer alteration time is required. With a longer alteration time and perhaps pre-treatment with acid, more complete conversion of fly ash may be achieved and products may be more zeolite-like.

5. GENERAL DISCUSSION

Mordenite and CAFA combined with CaCl_2 are the most effective hog manure amendments in terms of N conservation. However, more than just the capacity of the amendment to conserve N should be considered when selecting a hog manure amendment. One must weigh the costs with the anticipated benefits. The following details an approximate cost estimate for the amendment of a one million gallon hog manure lagoon with zeolite and with CAFA combined with CaCl_2 (hog manure composition based on typical values as reported by Norwest Labs) (Manitoba Agriculture and Foods 2000c).

Based on extensive manure analysis by Norwest Labs, hog manure typically contains 19.2 lbs of NH_3 for every 1000 gallons of manure (Manitoba Agriculture and Food 2000c). Therefore, if all the NH_3 were in the form of NH_4^+ in the liquid manure, in a one million gallon lagoon, there will be approximately 19,200 lbs of NH_4^+ (or 8,710 kg of NH_4^+). From this, there are calculated to be approximately 483,000 mols of NH_4^+ in the lagoon (48,300,000 cmol^+). Assuming a zeolite CEC of 100 cmol^+/kg , 483,000 kg of zeolite would be required to provide sufficient CEC to absorb the NH_4^+ cations in the manure. However, this number should be doubled to account for the presence of other cations (organic and inorganic) in the manure. Therefore, the total zeolite requirement would be approximately 966,000 kg or 966 tonnes. According to C₂C Mining

Corporation, Calgary, Alberta (the closest zeolite distributor), the cost of zeolite (including transportation to Manitoba) would be approximately \$215/tonne (Brandstrom pers. comm. 2001). The total cost for amendment of the lagoon would therefore be approximately \$208,000. Based on this, is there a cost benefit from using the zeolite as an amendment? To do this we must estimate the cost of the N that is lost during storage.

In the following, the author assumed that the manure in the lagoon was stored for three months and that during that time all of the $\text{NH}_4^+\text{-N}$ (19,200 lbs or 8,710 kg $\text{NH}_4^+\text{-N}$) was lost. Based on a unit cost of N of \$0.40/lb N (this is estimated from urea and anhydrous ammonia fertilizer N cost), the cost of the lost N would be \$7,680. Thus, the cost of zeolite would be greater than the cost of the N conserved and this would not be an economical option. However, the benefit associated with reducing NH_3 emissions to the atmosphere has not been considered in this estimation and is beyond the scope of this study to estimate. It should also be noted that this estimate is based on incorporation of the zeolite into the hog manure. Less zeolite may be required if it is applied only to the surface of the lagoon, creating a barrier for NH_3 volatilization (zeolite would absorb the gaseous NH_3 creating a higher partial pressure of NH_3 above the lagoon). In this last scenario it is assumed that the zeolite would float on top of the manure (not sink) and that less zeolite would be required to cover the surface of the lagoon than would be required when mixed into the manure.

A smaller volume of material will be required in the case of the CAFA with CaCl_2 due to the higher CEC of the CAFA. Assuming a CEC of $650 \text{ cmol}^+/\text{kg}$, 75,000 kg of CAFA would be required to provide sufficient CEC to absorb the NH_4^+ cations in the

manure. Again, this number should be doubled to account for the presence of other cations (organic and inorganic) in the manure. Therefore, the total CAFA requirement would be approximately 150,000 kg or 150 tonnes. Calculation of the cost of CAFA is somewhat more complex. Chemical alteration of 20 grams of fly ash would require 160 mL of 3.5 M NaOH and approximately 20 mL of concentrated HCl and would yield approximately 16 g of CAFA (80% recovery). To chemically alter a tonne of CAFA, one would require 10,000 L of 3.5 M NaOH and 1,250 L of concentrated HCl. In addition, 27 tonnes of CaCl_2 would be added to the CAFA prior to amendment. At \$650/1,000 L for 3.5 M NaOH, \$4,000/1,000 L and \$20,000/tonne CaCl_2 , the total cost for the chemical required in the treatment of one tonne fly ash would be approximately \$7,000,000 and \$1,050,000,000 for 150 tonnes (based on Fisher Scientific 2001 catalogue prices and estimated reductions due to bulk purchases). This estimate does not include the design, construction and maintenance costs of a large scale fly ash treatment facility nor does it include transportation costs associated with the delivery of the fly ash. Based on this, there is no cost benefit associated with the amendment of hog manure with CAFA and CaCl_2 assuming a total N conservation equivalent to \$7,860.

In conclusion, the cost of zeolite and CAFA with CaCl_2 used as hog manure amendments are prohibitive, and N conserved through their use would not offset the costs of the amendments. The added benefit of having reduced NH_3 losses to the atmosphere was not incorporated into estimates as it was beyond the scope of this study. If NH_3 volatilization could be accomplished with the use of a smaller quantity of zeolite (i.e. if the amendments could be spread on the surface of the manure) then the use of zeolite could become feasible. However, the cost of the CAFA with CaCl_2 amendment is prohibitive

and the use of CAFA and CaCl_2 as a hog manure amendment can only be considered if a more cost effective chemical alteration method is developed.

6. CONTRIBUTION TO KNOWLEDGE

Many studies have evaluated factors affecting the nature and extent of fly ash conversion into zeolites and zeolite-like minerals but few have explored the use of these products in a commercial capacity. More specifically, no studies were found which explore the use of chemically altered fly ash (CAFA) in the management of biological wastes. With anticipated increases in hog production, new and innovative waste management methods must be explored to ensure the environmental sustainability of Manitoba's hog industry. Amendment of hog manure with CAFA and calcium chloride (CaCl_2) can increase N conservation in manure and mitigate environmental hazards associated with its storage and potentially with land application. Additionally, this would encourage the recycling of industrial wastes and reduce the hazardous impacts associated with land filling or stockpiling of waste coal fly ash.

This paper also adds to the research available on the use of zeolites in manure management. Most studies have explored the use of zeolites as atmospheric scrubbers due to their affinity for gases such as H_2S and NH_3 (Miner 1983) or as poultry litter amendments due to high potential for NH_3 volatilization from this manure (Mahimairaja et al. 1994, Witter and Kirchmann 1989b). No studies were found looking specifically at zeolites as amendments for liquid hog manure and the results of this study indicate a great deal of potential for their use in this capacity, even after drying of the manure.

Several studies have investigated the use of waste coal fly ash as an amendment for biological wastes. However, studies conducted prior to my investigation, have focused on the addition of fly ash to sewage sludge (Fang et al. 1999, Fang et al. 1998, Wong and Su 1997a and 1997b, Wong and Lai 1996) and only one study looked at the effect of fly ash addition to hog manure (Vincini et al. 1994). The study conducted herein showed that addition of fly ash to hog manure is not useful since any micronutrient benefits which may be derived from the fly ash are offset by dramatically increased N losses.

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8. APPENDICES

Ia. Calculating positive charges in 100 mL of hog manure.

In order to calculate the cmol^+ in 100 mL of manure we need to know the mass of cations in manure. This data was collected in the manure characterization and is summarized in the Table 8.1.

Table 8.1 Aqueous cation composition of hog manure.

	Ammonium (NH_4^+)	Potassium (K^+)	Sodium (Na^+)	Calcium (Ca^{2+})	Magnesium (Mg^{2+})
Mg/mL	2.51	1.28	0.64	0.53	0.27
g/100 mL	0.251	0.128	0.064	0.053	0.027

(a) Ammonium (NH_4^+)

$$\text{mol } (\text{NH}_4^+) = \frac{0.251 \text{ g } (\text{NH}_4^+)}{18.0385} = 0.0139 \text{ mol } (\text{NH}_4^+) * 100 = \mathbf{1.4 \text{ cmol}^+}$$

(b) Potassium (K^+)

$$\text{mol } (\text{K}^+) = \frac{0.128 \text{ g } (\text{K}^+)}{39.0983} = 0.0033 \text{ mol } (\text{K}^+) * 100 = \mathbf{0.3 \text{ cmol}^+}$$


(c) Sodium (Na^+)

$$\text{mol } (\text{Na}^+) = \frac{0.064 \text{ g } (\text{Na}^+)}{22.989768} = 0.0028 \text{ mol } (\text{Na}^+) * 100 = \mathbf{0.3 \text{ cmol}^+}$$

(d) Calcium (Ca^{2+})

$$\text{mol } (\text{Ca}^{2+}) = \frac{0.053 \text{ g } (\text{Ca}^{2+})}{40.078} = 0.0013 \text{ mol } (\text{Ca}^{2+}) * 200 = \mathbf{0.3 \text{ cmol}^+}$$


Two charges
for each atom



(e) Magnesium (Mg^{2+})

$$\text{mol } (\text{Mg}^{2+}) = \frac{0.027 \text{ g } (\text{Mg}^{2+})}{24.305} = 0.0011 \text{ mol } (\text{Mg}^{2+}) * 200 = \mathbf{0.2 \text{ cmol}^+}$$

Two charges
for each atom



Estimate of cmol^+ in 100 mL of manure is based on the sum of charges contributed by each of the above cations. Therefore,

Ammonium $\text{cmol}^+/\text{100 mL}$	=	1.4
Potassium $\text{cmol}^+/\text{100 mL}$	=	0.3
Sodium $\text{cmol}^+/\text{100 mL}$	=	0.3
Calcium $\text{cmol}^+/\text{100 mL}$	=	0.3
Magnesium $\text{cmol}^+/\text{100 mL}$	=	0.2
Sum $\text{cmol}^+/\text{100 mL}$	=	2.5

Ib. Calcium chloride mixing ratios.

Witter (1991) stated that a mixing ration of 1 mol calcium to 2 mol ammonium would be sufficient to achieve maximum reduction in volatilization. From Ia we know that there are 0.014 mol ammonium in 100 mL hog manure. From this we know that 0.007 mol of calcium (and therefore 0.007 mol calcium chloride) are required.

$$\text{g CaCl}_2 = \text{mol} * \text{molecular wt.} = 0.007 * 110.984 = 0.78 \text{ g CaCl}_2$$

The calcium chloride will contribute $2 * 0.007 \text{ mol}^+ (= 1.4 \text{ cmol}^+)$ to the treatments.

Ic. Mineral amendment mixing ratios based on cation exchange capacity.

In order to compensate for the potential underestimation of positive charges in the manure, minerals amendments were added in sufficient quantities to provide twice the CEC required to exchange cations in the manure ($= 5.0 \text{ cmol}^+$ without CaCl_2 , $= 6.4 \text{ cmol}^+$ with CaCl_2). Table 8.2 contains CEC values calculated for mineral amendments.

Table 8.2 Cation exchange capacities of chemically altered and unaltered fly ash and mordenite.

	Unaltered Fly Ash	Altered Fly Ash	Mordenite
Cmol^+/kg	679	249	112
Cmol^+/g	0.679	0.249	0.112

(a) Unaltered Fly Ash

$$\text{Without CaCl}_2 \quad \frac{5.0 \text{ cmol}^+}{0.249 \text{ cmol}^+} = 20.1 \text{ g Unaltered Fly Ash}$$

$$\text{With CaCl}_2 \quad \frac{6.4 \text{ cmol}^+}{0.249 \text{ cmol}^+} = 25.7 \text{ g Unaltered Fly Ash}$$

(b) Altered Fly Ash

$$\text{Without CaCl}_2 \quad \frac{5.0 \text{ cmol}^+}{0.679 \text{ cmol}^+} = 7.4 \text{ g Altered Fly Ash}$$

$$\text{With CaCl}_2 \quad \frac{6.4 \text{ cmol}^+}{0.679 \text{ cmol}^+} = 9.4 \text{ g Altered Fly Ash}$$

(c) Mordenite

$$\text{Without CaCl}_2 \quad \frac{5.0 \text{ cmol}^+}{0.112 \text{ cmol}^+} = 44.6 \text{ g Mordenite}$$

$$\text{With CaCl}_2 \quad \frac{6.4 \text{ cmol}^+}{0.112 \text{ cmol}^+} = 57.1 \text{ g Mordenite}$$

Id. Manure and amendment mixing ratios for volatilization study treatments.

Treatment	Hog Manure (mL)	Calcium Chloride (g)	Unaltered Fly Ash (g)	Altered Fly Ash (g)	Mordenite (g)	Dry Mass (g)
1	100	--	--	--	--	6.4
2	100	--	20.1	--	--	26.5
3	100	--	--	7.4	--	13.8
4	100	--	--	--	44.6	51.0
5	100	0.76	--	--	--	7.2
6	100	0.76	25.7	--	--	32.9
7	100	0.76	--	9.4	--	16.6
8	100	0.76	--	--	57.1	64.3
9	--	--	--	--	--	--

II. ANOVA's and LSD mean comparisons of ammonia volatilized from treatments for days 1 through 40.

Log values were analyzed because of high variance in some treatments. Standard errors and mean comparisons correspond to log data. Untransformed data are included in the table for reference. Values followed by the same letter are not considered to be significantly different ($\alpha = 0.005$)

Day 1			
Treatment	Mean mg NH_4^{++}	Log Mean mg NH_4^{++}	Standard Error
Unaltered Fly Ash + CaCl_2	7.960	0.898 a	0.034
Unaltered Fly Ash	4.640	0.643 ab	0.099
Altered Fly Ash	4.227	0.614 abc	0.072
Control	3.727	0.545 bc	0.103
Control + CaCl_2	2.393	0.360 bc	0.095
Altered Fly Ash + CaCl_2	2.313	0.342 c	0.096
Mordenite + CaCl_2	0.777	0.174 d	0.162
Mordenite	0.507	0.304 d	0.064

Day 2			
Treatment	Mean mg NH_4^{++}	Log Mean mg NH_4^{++}	Standard Error
Unaltered Fly Ash + CaCl_2	9.470	2.246 a	0.069
Unaltered Fly Ash	8.945	2.190 ab	0.037
Control	5.977	1.787 ab	0.024
Control + CaCl_2	5.200	1.644 ab	0.068
Altered Fly Ash	4.913	1.570 b	0.145
Altered Fly Ash + CaCl_2	2.777	0.867 c	0.378
Mordenite + CaCl_2	1.353	0.241 d	0.241
Mordenite	0.957	0.072 d	0.164

Day 3			
Treatment	Mean mg NH_4^{++}	Log Mean mg NH_4^{++}	Standard Error
Unaltered Fly Ash + CaCl_2	10.070	2.297 a	0.161
Unaltered Fly Ash	9.500	2.248 a	0.082
Altered Fly Ash	6.637	1.884 a	0.093
Altered Fly Ash + CaCl_2	5.420	1.678 ab	0.110
Control	4.990	1.602 ab	0.075
Control + CaCl_2	3.320	1.199 b	0.034
Mordenite	1.313	0.206 c	0.265
Mordenite + CaCl_2	1.313	0.058 c	0.058

Day 4			
Treatment	Mean mg NH ⁴⁺	Log Mean mg NH ⁴⁺	Standard Error
Unaltered Fly Ash	6.610	1.848 a	0.208
Unaltered Fly Ash + CaCl ₂	5.960	1.762 a	0.151
Altered Fly Ash	3.833	1.266 ab	0.276
Control	3.700	1.287 ab	0.150
Altered Fly Ash + CaCl ₂	2.713	0.926 b	0.271
Control + CaCl ₂	0.867	0.179 c	0.190
Mordenite	0.332	1.246 d	0.392
Mordenite + CaCl ₂	0.198	1.691 d	0.278

Day 5			
Treatment	Mean mg NH ⁴⁺	Log Mean mg NH ⁴⁺	Standard Error
Unaltered Fly Ash	8.143	2.060 a	0.196
Unaltered Fly Ash + CaCl ₂	7.913	2.061 a	0.087
Altered Fly Ash	4.373	1.457 ab	0.138
Control	3.947	1.351 bc	0.152
Altered Fly Ash + CaCl ₂	2.287	0.851 c	0.110
Control + CaCl ₂	1.033	0.032 d	0.029
Mordenite	0.177	1.781 e	0.217
Mordenite + CaCl ₂	0.069	2.859 f	0.425

Day 6			
Treatment	Mean mg NH ⁴⁺	Log Mean mg NH ⁴⁺	Standard Error
Unaltered Fly Ash	14.712	2.676 a	0.113
Unaltered Fly Ash + CaCl ₂	12.512	2.510 ab	0.113
Altered Fly Ash	5.987	1.667 bc	0.376
Control	4.972	1.600 bc	0.061
Altered Fly Ash + CaCl ₂	2.358	0.789 cd	0.265
Control + CaCl ₂	1.532	0.409 d	0.128
Mordenite + CaCl ₂	0.263	1.345 d	0.977
Mordenite	0.134	1.755 d	0.568

Day 7			
Treatment	Mean mg NH ⁴⁺	Log Mean mg NH ⁴⁺	Standard Error
Unaltered Fly Ash + CaCl ₂	5.631	1.540 a	0.419
Mordenite + CaCl ₂	3.288	0.383 a	1.761
Unaltered Fly Ash	3.198	0.340 a	1.054
Altered Fly Ash	2.396	0.509 a	1.751
Control + CaCl ₂	1.188	0.621 a	0.582
Mordenite	0.930	0.886 a	1.167
Control	0.780	0.948 a	0.582
Altered Fly Ash + CaCl ₂	0.519	1.272 a	0.425

Day 8			
Treatment	Mean mg NH ⁴⁺	Log Mean mg NH ⁴⁺	Standard Error
Unaltered Fly Ash	8.759	2.120 a	0.228
Unaltered Fly Ash + CaCl ₂	7.492	0.007 a	0.082
Altered Fly Ash	2.519	0.827 b	0.313
Control	1.879	0.458 bc	0.402
Altered Fly Ash + CaCl ₂	1.165	0.138 bc	0.122
Control + CaCl ₂	0.792	0.235 c	0.041
Mordenite + CaCl ₂	0.081	2.553 d	0.204
Mordenite	0.072	2.789 d	0.407

Day 9			
Treatment	Mean mg NH ⁴⁺	Log Mean mg NH ⁴⁺	Standard Error
Unaltered Fly Ash	9.356	2.192 a	0.205
Unaltered Fly Ash + CaCl ₂	5.663	1.384 ab	0.663
Altered Fly Ash	3.103	0.905 bc	0.477
Control	2.630	0.869 bcd	0.325
Altered Fly Ash + CaCl ₂	1.056	0.001 cd	0.242
Control + CaCl ₂	0.743	0.363 d	1.261
Mordenite	0.148	2.280 e	0.656
Mordenite + CaCl ₂	0.088	2.467 e	0.185

Day 10			
Treatment	Mean mg NH^{4+}	Log Mean mg NH^{4+}	Standard Error
Unaltered Fly Ash	4.013	1.087 a	0.664
Unaltered Fly Ash + CaCl_2	3.613	1.065 a	0.482
Control	1.520	0.146 a	0.598
Altered Fly Ash	1.170	0.017 a	0.446
Control + CaCl_2	0.563	0.644 a	0.280
Altered Fly Ash + CaCl_2	0.387	0.998 ab	0.220
Mordenite	0.228	3.235 b	1.666
Mordenite + CaCl_2	0.056	3.205 b	0.660

Day 11			
Treatment	Mean mg NH^{4+}	Log Mean mg NH^{4+}	Standard Error
Unaltered Fly Ash	5.222	1.650 a	0.097
Unaltered Fly Ash + CaCl_2	5.222	1.644 a	0.053
Altered Fly Ash	1.102	0.053 b	0.220
Control	1.082	0.073 b	0.075
Altered Fly Ash + CaCl_2	0.692	0.515 b	0.225
Control + CaCl_2	0.572	0.559 b	0.030
Mordenite + CaCl_2	0.058	3.220 c	0.617
Mordenite	0.024	3.811 c	0.279

Day 12			
Treatment	Mean mg NH^{4+}	Log Mean mg NH^{4+}	Standard Error
Unaltered Fly Ash + CaCl_2	5.624	1.713 a	0.116
Unaltered Fly Ash	5.457	1.640 a	0.240
Altered Fly Ash	1.511	0.377 b	0.195
Control	1.351	0.295 b	0.075
Altered Fly Ash + CaCl_2	0.911	0.124 bc	0.170
Control + CaCl_2	0.541	0.652 c	0.199
Mordenite + CaCl_2	0.052	3.013 d	0.218
Mordenite	0.015	4.017 d	0.693

Day 13			
Treatment	Mean mg NH ⁴⁺	Log Mean mg NH ⁴⁺	Standard Error
Unaltered Fly Ash	4.740	1.479 a	0.279
Unaltered Fly Ash + CaCl ₂	4.464	1.496 a	0.008
Control	1.198	0.171 b	0.098
Altered Fly Ash	1.151	0.077 b	0.245
Altered Fly Ash + CaCl ₂	0.878	0.189 bc	0.236
Control + CaCl ₂	0.501	0.713 c	0.153
Mordenite + CaCl ₂	0.060	2.899 d	0.322
Mordenite	0.016	3.400 d	0.463

Day 14			
Treatment	Mean mg NH ⁴⁺	Log Mean mg NH ⁴⁺	Standard Error
Unaltered Fly Ash	6.253	1.820 a	0.116
Unaltered Fly Ash + CaCl ₂	3.520	1.258 ab	0.022
Altered Fly Ash	1.260	0.203 bc	0.165
Control	0.906	0.103 c	0.066
Altered Fly Ash + CaCl ₂	0.866	0.240 c	0.303
Control + CaCl ₂	0.403	0.950 c	0.203
Mordenite	0.054	3.594 d	0.982
Mordenite + CaCl ₂	0.022	4.078 d	0.496

Day 15			
Treatment	Mean mg NH ⁴⁺	Log Mean mg NH ⁴⁺	Standard Error
Unaltered Fly Ash	4.128	1.381 a	0.197
Unaltered Fly Ash + CaCl ₂	2.895	1.046 a	0.133
Altered Fly Ash	1.121	0.064 b	0.236
Control	0.868	0.192 bc	0.221
Altered Fly Ash + CaCl ₂	0.805	0.226 bc	0.092
Control + CaCl ₂	0.505	0.725 c	0.200
Mordenite	0.072	2.632 d	0.024
Mordenite + CaCl ₂	0.048	3.140 d	0.317

Day 16			
Treatment	Mean mg NH ⁴⁺	Log Mean mg NH ⁴⁺	Standard Error
Unaltered Fly Ash	3.962	1.363 a	0.118
Unaltered Fly Ash + CaCl ₂	2.962	0.991 a	0.329
Altered Fly Ash	0.902	0.104 b	0.030
Control	0.749	0.319 b	0.171
Altered Fly Ash + CaCl ₂	0.692	0.373 b	0.074
Control + CaCl ₂	0.535	0.752 b	0.380
Mordenite	0.076	2.690 c	0.339
Mordenite + CaCl ₂	0.068	2.868 c	0.457

Day 17			
Treatment	Mean mg NH ⁴⁺	Log Mean mg NH ⁴⁺	Standard Error
Unaltered Fly Ash	4.395	1.428 a	0.239
Unaltered Fly Ash + CaCl ₂	3.861	1.348 a	0.053
Altered Fly Ash	1.241	0.162 b	0.226
Control	0.955	0.075 bc	0.166
Altered Fly Ash + CaCl ₂	0.758	0.277 bc	0.016
Control + CaCl ₂	0.451	0.824 c	0.169
Mordenite	0.067	2.917 d	0.485
Mordenite + CaCl ₂	0.056	3.176 d	0.624

Day 18			
Treatment	Mean mg NH ⁴⁺	Log Mean mg NH ⁴⁺	Standard Error
Unaltered Fly Ash	3.619	1.283 a	0.197
Unaltered Fly Ash + CaCl ₂	3.619	1.249 a	0.060
Altered Fly Ash	0.983	0.089 b	0.267
Control	0.779	0.290 b	0.197
Altered Fly Ash + CaCl ₂	0.649	0.448 b	0.124
Control + CaCl ₂	0.327	1.240 c	0.376
Mordenite + CaCl ₂	0.021	3.983 d	0.353
Mordenite	0.013	3.986 d	0.214

Day 19			
Treatment	Mean mg NH ⁴⁺	Log Mean mg NH ⁴⁺	Standard Error
Unaltered Fly Ash + CaCl ₂	3.095	1.125 a	0.066
Unaltered Fly Ash	2.335	0.844 a	0.060
Altered Fly Ash	1.042	0.092 b	0.395
Altered Fly Ash + CaCl ₂	0.652	0.445 bc	0.130
Control	0.585	0.610 bc	0.124
Control + CaCl ₂	0.382	0.971 c	0.091
Mordenite + CaCl ₂	0.023	3.780 d	0.089
Mordenite	0.018	4.236 d	0.482

Day 20			
Treatment	Mean mg NH ⁴⁺	Log Mean mg NH ⁴⁺	Standard Error
Unaltered Fly Ash	4.047	1.213 a	0.415
Unaltered Fly Ash + CaCl ₂	2.327	0.803 ab	0.803
Altered Fly Ash	0.700	0.480 bc	0.350
Control	0.487	0.740 c	0.140
Altered Fly Ash + CaCl ₂	0.450	0.906 c	0.345
Control + CaCl ₂	0.324	1.134 c	0.081
Mordenite + CaCl ₂	0.056	3.375 d	0.822
Mordenite	0.023	4.280 d	0.701

Day 21			
Treatment	Mean mg NH ⁴⁺	Log Mean mg NH ⁴⁺	Standard Error
Unaltered Fly Ash	2.728	0.938 a	0.249
Unaltered Fly Ash + CaCl ₂	2.254	0.794 a	0.141
Altered Fly Ash	0.554	0.779 b	0.420
Altered Fly Ash + CaCl ₂	0.481	0.849 b	0.363
Control + CaCl ₂	0.308	1.221 b	0.205
Control	0.318	1.257 b	0.362
Mordenite + CaCl ₂	0.069	2.906 c	0.537
Mordenite	0.063	3.532 c	1.142

Day 22			
Treatment	Mean mg NH ⁴⁺	Log Mean mg NH ⁴⁺	Standard Error
Unaltered Fly Ash + CaCl ₂	2.428	0.876 a	0.107
Unaltered Fly Ash	2.435	0.803 a	0.290
Altered Fly Ash	1.282	0.244 ab	0.066
Altered Fly Ash + CaCl ₂	0.468	0.785 bc	0.168
Control	0.438	0.866 bc	0.207
Control + CaCl ₂	0.324	1.232 bc	0.333
Mordenite	0.052	3.164 d	0.453
Mordenite + CaCl ₂	0.045	3.879 d	1.168

Day 23			
Treatment	Mean mg NH ⁴⁺	Log Mean mg NH ⁴⁺	Standard Error
Unaltered Fly Ash + CaCl ₂	3.251	1.149 a	0.168
Unaltered Fly Ash	2.211	0.753 ab	0.202
Altered Fly Ash	1.077	0.036 bc	0.199
Control	0.677	0.392 c	0.054
Altered Fly Ash + CaCl ₂	0.677	0.437 c	0.212
Control + CaCl ₂	0.431	0.854 c	0.107
Mordenite	0.063	3.089 d	0.641
Mordenite + CaCl ₂	0.048	3.206 d	0.428

Day 24			
Treatment	Mean mg NH ⁴⁺	Log Mean mg NH ⁴⁺	Standard Error
Unaltered Fly Ash + CaCl ₂	3.485	1.182 a	0.251
Unaltered Fly Ash	2.631	0.950 ab	0.136
Control	0.991	0.133 abc	0.345
Altered Fly Ash + CaCl ₂	0.718	0.586 bc	0.505
Control + CaCl ₂	0.365	1.078 c	0.256
Altered Fly Ash	0.645	1.352 c	1.307
Mordenite + CaCl ₂	0.048	3.256 d	0.512
Mordenite	0.038	3.301 d	0.200

Day 25			
Treatment	Mean mg NH ⁴⁺	Log Mean mg NH ⁴⁺	Standard Error
Unaltered Fly Ash + CaCl ₂	3.877	1.261 a	0.299
Unaltered Fly Ash	2.650	0.961 ab	0.117
Altered Fly Ash	1.474	0.259 abc	0.354
Control	1.114	0.025 bc	0.280
Altered Fly Ash + CaCl ₂	0.690	0.443 c	0.273
Control + CaCl ₂	0.507	0.732 c	0.231
Mordenite + CaCl ₂	0.057	3.260 d	0.709
Mordenite	0.037	3.406 d	0.337

Day 26			
Treatment	Mean mg NH ⁴⁺	Log Mean mg NH ⁴⁺	Standard Error
Unaltered Fly Ash + CaCl ₂	2.669	0.953 a	0.171
Unaltered Fly Ash	1.963	0.667 a	0.083
Control	0.903	0.154 ab	0.220
Altered Fly Ash	0.808	0.221 ab	0.090
Altered Fly Ash + CaCl ₂	0.566	0.666 b	0.318
Control + CaCl ₂	0.331	1.116 b	0.103
Mordenite	0.058	3.114 c	0.503
Mordenite + CaCl ₂	0.031	4.288 c	0.909

Day 27			
Treatment	Mean mg NH ⁴⁺	Log Mean mg NH ⁴⁺	Standard Error
Unaltered Fly Ash + CaCl ₂	3.126	1.044 a	0.306
Unaltered Fly Ash	1.866	0.594 ab	0.171
Altered Fly Ash	0.911	0.110 abc	0.131
Control	0.791	0.374 abc	0.379
Altered Fly Ash + CaCl ₂	0.571	0.612 bc	0.229
Control + CaCl ₂	0.333	1.393 cd	0.541
Mordenite + CaCl ₂	0.056	2.817 d	0.872
Mordenite	0.014	5.447 e	1.132

Day 28			
Treatment	Mean mg NH ⁴⁺	Log Mean mg NH ⁴⁺	Standard Error
Unaltered Fly Ash + CaCl ₂	3.559	1.143 a	0.346
Unaltered Fly Ash	2.026	0.649 ab	0.239
Control	1.069	0.015 bc	0.280
Altered Fly Ash	0.909	0.106 bc	0.102
Altered Fly Ash + CaCl ₂	0.526	0.706 cd	0.251
Control + CaCl ₂	0.294	1.321 d	0.311
Mordenite + CaCl ₂	0.053	3.036 e	0.312
Mordenite	0.011	4.211 f	0.394

Day 29			
Treatment	Mean mg NH ⁴⁺	Log Mean mg NH ⁴⁺	Standard Error
Unaltered Fly Ash + CaCl ₂	2.616	0.900 a	0.247
Unaltered Fly Ash	2.269	0.725 ab	0.297
Altered Fly Ash	0.958	0.080 ab	0.193
Altered Fly Ash + CaCl ₂	0.773	0.322 ab	0.267
Control	0.831	0.524 b	0.624
Control + CaCl ₂	0.153	2.256 c	0.596
Mordenite + CaCl ₂	0.069	2.983 c	0.623
Mordenite	0.046	3.368 c	0.619

Day 30			
Treatment	Mean mg NH ⁴⁺	Log Mean mg NH ⁴⁺	Standard Error
Unaltered Fly Ash + CaCl ₂	4.648	1.378 a	0.385
Unaltered Fly Ash	2.541	0.898 a	0.898
Altered Fly Ash	1.138	0.111 b	0.132
Altered Fly Ash + CaCl ₂	0.996	0.045 b	0.211
Control + CaCl ₂	0.905	0.114 b	0.122
Control	0.890	0.140 b	0.150
Mordenite + CaCl ₂	0.095	2.467 c	0.321
Mordenite	0.072	2.778 c	0.369

Day 31			
Treatment	Mean mg NH ⁴⁺	Log Mean mg NH ⁴⁺	Standard Error
Unaltered Fly Ash + CaCl ₂	3.491	1.222 a	0.167
Unaltered Fly Ash	2.524	0.881 a	0.215
Altered Fly Ash	0.842	0.183 b	0.107
Control	0.606	0.537 b	0.195
Altered Fly Ash + CaCl ₂	0.551	0.623 b	0.167
Control + CaCl ₂	0.511	0.672 b	0.009
Mordenite	0.038	2.865 c	0.131
Mordenite + CaCl ₂	0.047	3.103 c	0.226

Day 32			
Treatment	Mean mg NH ⁴⁺	Log Mean mg NH ⁴⁺	Standard Error
Unaltered Fly Ash + CaCl ₂	3.192	1.126 a	0.188
Unaltered Fly Ash	2.525	0.901 ab	0.163
Altered Fly Ash	0.935	0.069 bc	0.040
Control	0.784	0.280 c	0.218
Altered Fly Ash + CaCl ₂	0.540	0.835 c	0.511
Control + CaCl ₂	0.464	0.856 c	0.309
Mordenite + CaCl ₂	0.081	2.969 d	0.790
Mordenite	0.027	3.638 d	0.162

Day 33			
Treatment	Mean mg NH ⁴⁺	Log Mean mg NH ⁴⁺	Standard Error
Unaltered Fly Ash + CaCl ₂	4.449	1.318 a	0.424
Unaltered Fly Ash	2.782	0.989 ab	0.188
Altered Fly Ash	1.169	0.128 abc	0.167
Control	0.954	0.064 bc	0.134
Altered Fly Ash + CaCl ₂	0.666	0.538 c	0.351
Control + CaCl ₂	0.510	0.723 c	0.233
Mordenite + CaCl ₂	0.060	2.991 d	0.441
Mordenite	0.082	3.047 d	0.899

Day 34			
Treatment	Mean mg NH ⁴⁺	Log Mean mg NH ⁴⁺	Standard Error
Unaltered Fly Ash + CaCl ₂	7.987	1.525 a	0.782
Unaltered Fly Ash	2.474	0.836 ab	0.264
Altered Fly Ash	2.234	0.782 ab	0.150
Altered Fly Ash + CaCl ₂	1.758	0.536 ab	0.193
Control	1.490	0.382 ab	0.127
Control + CaCl ₂	1.038	0.026 b	0.104
Mordenite + CaCl ₂	0.178	2.135 c	0.967
Mordenite	0.078	2.714 c	0.385

Day 36			
Treatment	Mean mg NH ⁴⁺	Log Mean mg NH ⁴⁺	Standard Error
Unaltered Fly Ash + CaCl ₂	10.633	2.148 a	0.436
Unaltered Fly Ash	6.060	1.762 a	0.196
Control	1.905	0.612 b	0.185
Altered Fly Ash	1.703	0.521 bc	0.104
Altered Fly Ash + CaCl ₂	1.092	0.066 bc	0.145
Control + CaCl ₂	0.810	0.275 c	0.267
Mordenite + CaCl ₂	0.240	1.522 d	0.319
Mordenite	0.154	2.006 d	0.364

Day 38			
Treatment	Mean mg NH ⁴⁺	Log Mean mg NH ⁴⁺	Standard Error
Unaltered Fly Ash + CaCl ₂	6.305	1.791 a	0.234
Unaltered Fly Ash	4.945	1.284 a	0.545
Altered Fly Ash	2.230	0.783 ab	0.141
Altered Fly Ash + CaCl ₂	0.853	0.173 bc	0.119
Control + CaCl ₂	0.903	0.286 c	0.456
Control	0.755	0.298 c	0.071
Mordenite + CaCl ₂	0.291	1.544 d	0.552
Mordenite	0.099	2.318 d	0.074

Day 40			
Treatment	Mean mg NH ⁴⁺	Log Mean mg NH ⁴⁺	Standard Error
Unaltered Fly Ash	10.732	1.839 a	0.714
Unaltered Fly Ash + CaCl ₂	6.372	1.760 a	0.324
Altered Fly Ash	4.379	1.229 ab	0.491
Control	1.869	0.486 ab	0.382
Altered Fly Ash + CaCl ₂	4.509	0.404 ab	0.086
Control + CaCl ₂	1.227	0.182 b	0.156
Mordenite + CaCl ₂	0.380	1.672 c	0.900
Mordenite	0.141	2.107 c	0.370