CHAPTER II

BACKGROUND AND LITERATURE REVIEW

2.1 Thailand's Agriculture

Agriculture has long been an important sector of the Thai economy despite the rapid growth of other sectors in recent years. In 1988, agriculture contributed about 17 per cent of the GNP and 34 per cent of all exports, while providing full of part-time employment for more than half of the country's labor force. Figure 1 shows the agricultural planted area of Thailand by region during 1961-1995. Of the total land area of 51 million hectares, about 20 million hectares are used for agricultural purposes and employ a labor force of about 17 million.
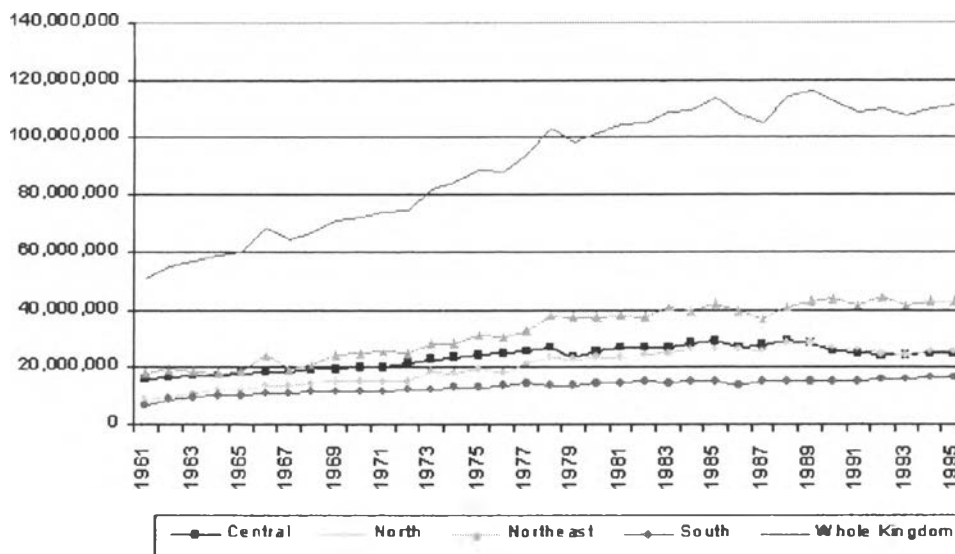

Figure 1 Thailand: Agricultural Planted Area, by Region, 1961-1995 (rai)[1]
(data from http://www.thaieconwatch.com/articles/j98_2/j98_2_f4.htm)

Today agricultural products account for the bulk of Thailand's foreign exchange earnings and are produced in such large quantities that the country ranks as the world's number one supplier in many commodities. Agriculture has also provided

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[1] One rai is approximately 0.16 hectares.

the springboard for the rapid development of Argo- processing industries with their favorable bias towards labor-intensive production and foreign exchange earnings.

In order to improve the standard of quality of farm products and to ensure that supply will be able to meet the ever-rising demand, many factors have been studied such as new production technologies. Fertilizer is one of the most important factors of production in agriculture. Fertilizer can be broadly categorized into 2 types. The first one is organic fertilizer such as compost, animal manure, green manure, and biofertilizer. The second one is chemical fertilizer, which has played a vital role in raising agricultural productivity.

After a downturn in 1997/98 (referred to 1997) due to the economic crisis and El-Nino-related drought, fertilizer consumption in Thailand recovered strongly in 1998/99 (referred to 1998) and reached a new record level of 1.7 million tons nutrients (Fig. 2). A similar trend could be observed in fertilizer imports, which grew by 8.4 per cent during the same period.
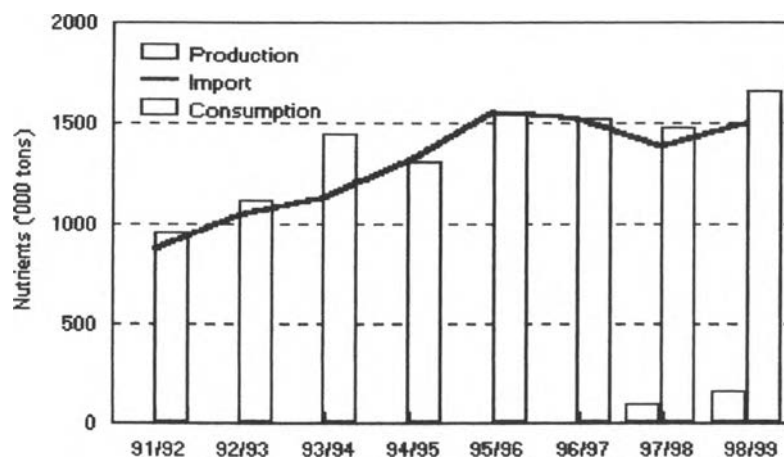

Figure 2 Fertilizer trends in Thailand (data from http://www.fadinap/Thailand/index.htm).

The recovery of fertilizer use could be attributed to improved weather conditions, higher prices of agricultural products partly due to the Thai devaluation and strong export demand, renewed government support for agriculture as the driver

of economic growth, and increased local fertilizer production due to the commissioning of several new NPK plants.

The situation changed very dramatically in 1999 as prices of agricultural products, particularly, rice and tapioca fell significantly due to over production from the previous year and low prices on the international market. This occurred while prices of imported agricultural inputs, such as fertilizers and pesticides, soared as a result of the Baht devaluation. Consequently, Thai farmers and farm cooperatives suffered huge losses and became heavily indebted. This situation sparked huge farmer rallies in the streets of Bangkok calling on the government to raise prices of rice and cassava. The government responded by increasing available funds to purchase agricultural products at relatively higher prices and easing repayment terms of farmer loans. For the period between 2001 and 2003, chemical fertilizer use was estimated to increase at an average of about 2.1 percent a year. From 3.50 million tons this year, total consumption should go up to 3.55 million tons in 2002 and 3.65 million tons in 2003.

Being largely imported, fertilizer is a major liability to the country's foreign reserve. The government has encouraged and supported the development of the domestic fertilizer production sector. However, this effort has been constrained by the lack of raw materials. Until recently, domestic production capacity had been limited to blending of NP and NPK fertilizers. The following fertilizer plants were commissioned during 1998 and 1999:

- Thai Central Chemical Public Co. (TCCC) fourth unit located in Ayutthaya province capable of producing up to 350,000 tons per year NPK became operational in May 1998 bringing the company's nameplate capacity for NP/NPK compound fertilizers to 1.2 million tons per year.

- Thai Fertilizer Company's (TFC) two 330,000 tons per year NPK plants began the production in March 1997 and were opened officially in May 1998. Additional 400,000 tons per year plant at the site was expected to be commissioned sometime in 1999 bringing the company's capacity to 1 million tons per year.

- National Fertilizer Corporation (NFC) brought its 1 million ton per year NPK plant on stream in 1998. NFC would initially import phosphoric acid

awaiting the completion of construction of its acid plant. Production began in January 1998, but output was minimal in the first half of the year, owing to the lack of finance to procure fertilizer raw materials.

Although chemical fertilizers have brought great benefits to Asian agriculture, they have also brought a number of problems, which are tending to become more serious over the years. Overuse of fertilizer is a problem in many industrialized countries in Asia, particularly with regard to nitrates and phosphates (http://www.agnet.org/library/article/ac1994f.html). Some studies have suggested that between a fifth and a half of the chemical fertilizer being applied by farmers is unnecessary. Not only is the fertilizer overuse wasteful, but also it can result in the contamination of both crops and water resources with nitrates and other residues. Furthermore, quite apart from the pollution problems, the overuse of fertilizers means higher costs for farmers and wasted resources. Soil testing and plant diagnosis make it possible for farmers to assess the nutrient status of the soil and crop, and apply fertilizers only when there is a deficiency to be corrected. This solves the problem of overuse, and means that crops benefit from a balanced fertilizer regime. In countries where fertilizer applications are very low because of economic constraints, soil and plant testing can help farmers improve the timing and quantity of their fertilizer applications, to make sure that they bring the maximum benefit in terms of crop yield.

It is essential for healthy agricultural industry in Thailand to realize/understand the need/use of new technology in order to increase their productivity. One of the promising technologies for effective use of plant fertilizers is the use of natural adsorbents such as clay and zeolite to selectively adsorb plant nutrients and release at appropriate amount.

2.2 Clinoptilolite

Recently, zeolites have been considered as a potential mineral group in a wide variety of agricultural processes. The unique ion exchange, dehydration-rehydration, and adsorption properties of materials promise to contribute significantly to many years of agricultural and aquaculture technology.

Zeolites are crystalline, hydrated aluminosilicates of alkali and earth metals that posses infinite, three-dimensional crystal structures (Mumpton, 1999). They were discovered in 1756 by Freherr Axel Fredrick Cronsted, a Swedish mineralogist, who named them from the Greek words meaning "boiling stone" in allusion to their peculiar frothing characteristics when heated before the mineralogist's blowpipe. More than 50 natural species of zeolites have been identified and more than 100 species having no natural counterparts have been synthesized in the laboratory. The applications and potential applications of both synthetic and natural zeolites depend on their fundamental physical and chemical properties. These properties are in turn related directly to the chemical composition and crystal structure of individual species.

Among those natural zeolites, clinoptilolite with the formula

$$(Na, K, Ca)_{2-3}Al_3(Al, Si)_2Si_{13}O_{36}-12H_2O$$

is an abundant natural zeolite found in igneous, sedimentary, and metamorphic deposits (Kithome *et al.*, 1998). It is very closely related to heulandite and is currently disused itself as if may just be a variety of heulandite. It differs from heulandite significantly only in its enrichment in potassium and slightly more silica and it is argued that a separate mineral is not needed. Clinoptilolite is widely used among zeolite industries, mineral collectors and mineralogists. The framework structure of clinoptilolite consists of interlinked four- and five-tetrahedral rings, creating a layer. Between these layers are open eight- and 10-tetrahedral ring channels having approximate dimensions of 7.9×10^{-8} by 3.5×10^{-8} m and 4.4×10^{-8} by 3.0×10^{-8} m, respectively (Vaughan, 1978). These rings form the ion sieving channels in clinoptilolite. Negative charge of the clinoptilolite framework, which comes from tetrahedrally coordinated aluminum, has been neutralized by monovalent cations, chiefly by Na(I) and K(I) (Tomazovic *et al.*, 1996). There are deposits of clinoptilolite containing predominantly divalent cations such as Ca(II) and Mg(II).

2.2.1 Relevant Properties of Clinoptilolite

2.2.1.1 Chemical composition

Major chemicals that contained in clinoptilolite are SiO_2, Al_2O_3, Fe_2O_3, K_2O, Na_2O, CaO, TiO_2, and MnO (Hernandez *et al.*, 2000).

2.2.1.2 Adsorption properties

Under normal conditions, the large cavities and entry channels of clinoptilolite and other zeolites are filled with water molecules forming hydrated spheres around the exchangeable cations (Mumpton, 1999). Once the water is removed, molecules having diameters small enough to fit through the entry channels are readily adsorbed on the inner surface of the vacant central cavities. Molecules those are too large to pass through the entry channels are excluded. This is the well-known "molecular sieving" property of most crystalline zeolites. The inner surface area available for adsorption ranges up to several hundred square meters per gram. According to their ability to separate gas molecules on the basis of size and shape, the unusual charge distribution within a dehydrated void volume allows many species with permanent dipole moments to be adsorbed with a selectivity unlike that of almost all other sorbents. Thus, polar molecules are preferential adsorbed over nonpolar molecules. Due to their adsorption properties, many natural zeolites are used in cleaning process, for example, removing carbon dioxide and other contaminants from natural gas and methane streams to upgrade products. These properties may find application in agricultural technology.

2.2.1.3 Ion exchange properties

The exchangeable cations of clinoptilolite and other zeolites are also only loosely bonded to the tetrahedral framework and can be removed or exchanged from the framework structure easily by washing with a strong solution of another element (Mumpton, 1999).

- Cation Exchange Capacity

Cation exchange capacity is basically a function of the degree of substitution of aluminum for silicon in the zeolite framework: the greater the substitution, the greater the charge deficiency of the structure, and the greater the number of alkali or alkaline earth atoms required for electrical neutrality. The average

alkaline earth atoms required for electrical neutrality. The average exchange capacity of clinoptilolite is 1.3 mg eqv./g and the full cation capacity is in a range of 1.9 - 2.4 mg eqv./g (http://www.gtamart.com/mart/products/zeolite/)

1. Major Exchangeable Cations:

   Rb, Li, K, NH₄, Na, Ag, Cd, Pb, Zn, Ba, Sr, Cu, Hg, Fe, Co, Al, Cr, Mg (Selectivity of these cations is a function of hydrates molecular size and relative concentrations)

2. Primary Absorbing Gases:

   CO, CO_2, SO_2, H_2S, C_2H_6, C_2H_2, CH_3OH, CH_3NH_2, CH_3Cl, H_3Br

   • Cation selectivity

   In contrast to most noncrystalline ion exchangers, the framework of a crystalline zeolite dictates its selectivity toward competing ions. The cation selectivity of clinoptilolite is described as follows (Mumpton, 1999):

   Cesium > Rubidium > Potassium > Ammonium >

   Barium > Strontium > Sodium

   Calcium > Iron > Aluminum > Magnesium > Lithium

2.2.2 Selective Adsorption of Fertilizers by Natural Zeolite

The use of clinoptilolite in agriculture had been studied for decades. Pepper *et al.* (1982) studied the growth of Tifgreen Bermuda grass (cynodon dactylon) on washed mortar sand amended with 10% clinoptilolite. They found that clinoptilolite can reduce leaching losses of both NH_4^+ and NO_3^-. It shows that clinoptilolite has high affinity for the ammonium ion (Ferguson and Pepper, 1987). Biomass production and nitrogen use efficiency increased with clinoptilolite. In addition, clinoptilolite appears to delay nitrification and act as a slow release fertilizer (Pepper *et al.*, 1982). Barbarick and Pirela (1984) reported that the channels of clinoptilolite, which act as a reservoir of NH_4^+, may also reduce ammonia toxicity that results from over-application of urea-based fertilizers. It could be concluded that clinoptilolite may have promise for use as a soil amendment

because it can reduce NH_4^+ losses from the soil mix and allow increased plant N fertilizer-use efficiency. Petrovic (1993) stated that clinoptilolite does increase the water-holding capacity and nitrogen-holding capacity of a green when used as an amendment.

Owing to its high cation exchange capacity and molecular sieving property, clinoptilolite has been utilized effectively for terrestrial agriculture, where clinoptilolite is first saturated with ammonium and then incorporated into crop soils. In this way it acts as a slow-release fertilizer, with plants able to extract the sequestered ammonia from the clinoptilolite. For adsorbents to be effective in increasing N-use efficiency, they must be able to trap large amounts of NH_4^+ and release this N slowly during the growing season when applied to soil. Rapid release of the adsorbed NH_4^+ would increase the potential for N loss when applied to soil, and too slow a rate of release would limit the short-term benefits to the crop (Kithome *et al.*, 1998). Ferguson and Pepper (1987) stated that clinoptilolite has the potential to physically protect NH_4^+ from nitrification by microbes, and may reduce volatilization losses resulting in increased plant fertilizer-N use efficiency. In addition, clinoptilolite can prevent both ammonium and nitrate toxicity by disrupting the bacterial vitrification process. Coupled with its ion exchange properties which allow a controlled release of micronutrients, such as iron, zinc, copper, maganese, and cobalt, the ability of clinoptilolite to absorbed excess moisture makes it an attractive addition to chemical fertilizers to prevent caking and hardening during storage (Mumpton, 1999).

Allen *et al.* (1996) indicated that clinoptilolite (CL) and phosphate rock (PR) may be used to obtain a controlled release of NH_4^+, P^+, and K^+ in a synthetic soil. Nutrient release in CL-PR systems occurs through dissolution and cation-exchange reaction (Allen *et al.*, 1996). They used a continuous-flow thin-disk technique in their study. The power-function model indicates that initial release rates and cumulative nutrient release in CL-PR mixtures are increased by using a higher CL/PR ratio and by using a more reactive PR. Nutrient release rates are also affected by changes in the proportion of NH_4^+ and K^+ occupying CL exchange sites and reflected ion-selectivity characteristics of CL.

important plant nutrient N in its NH_4^+ form at various pH values and initial NH_4^+ concentrations. They found that amounts of NH_4^+ sorbed increased with increasing pH and initial NH_4^+ concentration. Desorption completed faster for lower initial NH_4^+ concentration. The Elovich model is employed to describe the behavior of adsorption and desorption. The model indicates that NH_4^+ adsorption and desorption by clinoptilolite are diffusion controlled.

Dwairi (1997) evaluated the exchange properties of the natural phillipsite tuff in the NH_4^+-Na^+ system. The exchange isotherms at 18, 35, and 50°C show that phillipsite exchanges NH_4^+ preferably over Na^+ at all temperatures. However, the selectivity coefficient for NH_4^+ decreases with decreasing temperature.

Ko *et al.* (1996) developed a mathematical model that described the controlled release of urea from rosin-coated urea granules and investigated the release mechanism. They observed two classes of release pattern from single-pellet release experiments including: (1) immediate and relatively rapid release through a few holes or many microscopic pores originally present in the coating, and (2) little or no release for an extended period of time followed by a sudden, rapid release through the holes formed in the coating. They found that individual granules could not give sustained release of urea by itself.

Not only for controlled release of fertilizer that clinoptilolite has been used, but also the filter in water treatment process. Rozic *et al.* (2000) investigated the removal of nitrogen in the form of ammonium ions from aqueous solutions using natural zeolite, natural clay, and alkaline and acid modified clay. They found that both zeolites and clays had limited sorption capacities. The acid modification of the clay decreased the efficiency of ammoniacal nitrogen removal.

Clinoptilolite is also used in catalytic application. Hernandez *et al.* (2000) performed a series of comparative sorption studies between a natural zeolite and its homologous synthetic or modified form. Unlike synthetic materials, natural clinoptilolites have a limited crystallinity thus indicating a certain degree of contamination of the structure with other minerals or amorphous glassy material. The presence of cations or minerals blocking the pore channels of a zeolite and the limited extent of its crystalline structure, drastically reduces its sorption activity by diminishing the microporous volume accessible to the adsorbate. Acid treatment of a

high-silica natural clinoptilolite increases an improvement of an adsorbent. A distinctive characteristic of modified clinoptilolite is the irreversible adsorption of nitrogen at pore entrances that gives origin to low-pressure hysteresis.

Clinoptilolites are also used as animal feed supplements, floor drying material, cat litter, soil enhancement material, air treatment and purification media, and other industrial and environmental application. However, ion metals and ammonia adsorption are two of the important properties of clinoptilolite.

Clinoptilolite have the advantages of low cost and high tolerance to changing temperatures and chemical conditions. Ion exchange does not affect significantly parameters of the unit cell of clinoptilolite (Tomazovic *et al.*, 1996). Furthermore, clinoptilolite is renewable, since regeneration can be simply accomplished through heating or immersion in a salt solution. And since clinoptilolite is natural, inert, and does not degrade, they have no associated environmental risks (Bart *et al.*, 2002).

2.2.3 Related Kinetic Models

There are several models that have been used to describe adsorption and desorption of ions from soils and soil minerals. The kinetic models used to describe NH_4^+ or K^+ adsorption and desorption by/from clinoptilolite are listed in Table 2.1-2.2.

Table 2.1 Various kinetics models to describe nutrients (NH_4^+ or K^+) adsorbed on the clinoptilolite sample (Allen *et al.*, 1995; Galadima and Silvertooth, 1998; Kithome, 1998; Sanjay and Chahal, 2002)

First-order equation	$\ln (1-F_a) = k\ t$
Modified Freundlich equation	$\ln X_t = \ln k + \ln C_o + (1/m) \ln t$
Parabolic diffusion	$F_a = a + R\ t^{1/2}$
Elovich equation	$X_t = a + b \ln t$

Table 2.2 Various kinetics models to describe nutrients (NH_4^+ or K^+) desorbed on the clinoptilolite sample (Allen *et al.*, 1995; Galadima and Silvertooth, 1998; Kithome, 1998; Sanjay and Chahal, 2002)

Zero-order equation	$X_t = -k\,t + X_o$
First-order equation	$\ln(X_t / X_o) = k\,t$
Second order	$1 / Xt = k\,t + 1 / Xo$
Modified Freundlich equation	$\log X_t = \log k + \log C_o + (1/m)\log t$
Parabolic diffusion	$F_d = a + R\,t^{1/2}$
Elovich equation	$Xt = a + b \ln t$
Power function	$\ln Xt = \ln a + b \ln t$

Where F_a : the fraction of NH_4^+ or K^+ adsorbed (X_t / X_{eq})

F_d : the fraction of NH_4^+ or K^+ released (X_t / X_{eq})

X_t : the total amount of NH_4^+ or K^+ adsorbed on the zeolite at time t per unit weight of zeolite

X_o : the total amount of NH_4^+ or K^+ desorbed on the zeolite at time t_o per unit weight of zeolite

X_{eq} : the total amount of NH_4^+ or K^+ adsorbed on the zeolite at equilibrium per unit weight of zeolite

C_o : the initial NH_4^+ or K^+ concentration

t : the reaction time

k : the apparent adsorption rate coefficient

R : the overall diffusion constant

a, b, m : constant

Allen *et al.* (1995) used zero-order model to describe kinetics in soils and clay minerals. First-order kinetic equation has been applied broadly to cation and anion sorption in soils (Allen *et al.*, 1995; Kithome *et al.*, 1998; Alireza and Mahmoud, 2002). Second-order model has also used to adequately describe reactions in soils and soil minerals (Griffin and Jurinak, 1974; Kuo and Lotse, 1972; Jardine and Zelazny, 1986). The Modified Freundlich equation involved the energy

of adsorption and surface saturation (Bache and Williams, 1971; Kithome *et al.*, 1998). When the adsorption fitted the Freundlich equation, the energy of adsorption decreased exponentially with increasing surface saturation. This may be explained by interactions between the molecules (Kithome *et al.*, 1998). At low surface saturation the adsorbed molecules tended to locate themselves, thus the minimum potential energy was obtained. The distance between the adsorbed molecules decreased with increasing ion adsorption, while the total potential energy of the adsorbed molecules increased.

The parabolic diffusion model has been widely used to describe diffusion-controlled phenomena in soil constituents and release of ions in soils and soil minerals (Sparks, 1989). This process is a transport of the adsorbing ion through the liquid associated with less accessible exchange sites of the adsorbent. In addition, the conformity to the parabolic diffusion model suggested that intraparticle diffusion or surface diffusion might be rate limiting (Jardine and Sparks, 1984). This diffusional process involves the movement of the adsorbing ion along the walls of the less accessible spaces of the adsorbent (Kithome *et al.*, 1998). Allen *et al.* (1995) found the good conformity of NH_4, K, and P release to the parabolic diffusion model. This indicated that NH_4, K, and P release were diffusion-controlled transport processes, with the rate-limiting step being the movement of nutrients through a diffusion layer to reactive sites (Allen *et al.*, 1995).

The Elovich model has been employed to describe the kinetics of ion adsorption and desorption on soils and soil mineral (Sparks and Jardine, 1984; Peryea *et al.*, 1985). It was first developed to describe the kinetics of chemisorption of gases on solid surfaces (Sparks, 1986). The Elovich model was found adequately described the K release kinetics of sonoran soils of Arizona (Galadima and Silvertooth, 1998).

The power-function model, which is known as the two-constant rate equation, is modified from the Freundlich equation. It has been applied effectively to describe K release in soils (Havlin and Westfall, 1985). Allen *et al.* (1995) reported that the power-function model provided an excellent description of nutrient release from clinoptilolite-phosphate rock mixtures.