CHAPTER II
THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Elemental Sulphur Fertilizers

Sulphur is essential for protein synthesis and the formation of chlorophyll. Sulphur is required in the development of leaves, stems, and flowers and must be present for good nodule development on bean roots. Sulphur deficiency symptoms vary between crops. The deficiency symptoms may begin as early as the one leaf stage. with the newest leaves turning yellowish green with dark vein coloration. Flowers and leaves are small and pale. Under mild sulphur deficiency, there may be good vegetative growth, but flowers and pods will be underdeveloped.

An elemental sulphur fertilizer is a kind of sulphur fertilizer. It is slow release fertilizers, containing high sulphur contents. They are not popular in a widely used (but growing). However. these circumstances may change recognized a need to find methods of adding sulphur to a widely used fertilizers urea and triple superphosphate. This would probably involve mixtures of the fertilizers with sulphur.

Elemental sulfur has been oxidized to sulfate before it can be taken up by plants. The oxidation rate depends on the surface area of the particles of sulphur available to be used by oxidizing micro-organisms in the soil. For the rapid oxidation requires fine sulphur particle size (e.g. with 1–2 µm particles in slurry, oxidation is practically instantaneous, (Bettany and Janzen, 1984). However, very fine particles of sulphur are difficult to use and to apply as a fertilizer, it damages to the eyes and lungs, and it easy to loss by wind or loss by water (Hilal, Abdel-Fattah and Korkor, 1990). But. the most seriously, fine particles of sulphur represent a fire and explosive hazard (Rothbaum and Groom, 1961).

The rate of oxidation is determined by the activity of the sulphur-oxidising microorganism in soil, which influenced by (a) soil properties especially soil aeration and temperature which oxidation rate increase with increasing temperature and (b) fertilizer properties, with oxidation rate increase with decreasing sulphur particle size.

2.2 Sulphur Bentonite Mixture

Mixture of sulphur and bentonite clay and bentonite clay offer a method of applying sulphur in high concentration (e.g. 70–90% S) of fine to moderately-fine particle size in a safe-handling (dust-free) product. Sulphur bentonite mixtures can be prepared as dry mixes of ground sulphur and clay which are then granulated or as wet mixes of molten sulphur and bentonite clay. The latter mixes may be granulated or flaked or prilled by one of several methods. When wetted the bentonite take up water and the clay disperses (i.e. the prill breaks down) to release the sulphur for oxidation

Most commercially available sulphur bentonites are prepared as wet mixes 90% sulphur and about 10% bentonite. In wet mix products, the sulphur forms the structure of the prill, the expanding bentonite clay is mixed within it, when wetted the bentonite expand and fractures the sulphur surrounding it. The extent of the shattering of the sulphur depends on the bentonite used, the proportion of bentonite in the mixture, and the homogeneity of the mixing. Sodium bentonite swells to 14 times its volume when wetted, while calcium bentonite swells 1–2 times its volume.

The rapid dispersion of prills, resulting fineness of sulphur particle size and rate of pasture plant uptake sulfate increase as the bentonite content of mixture is increased. For example, the prills with 40% bentonite were 90% dispersed within 4 minutes of wetting, whereas those with 15% bentonite were about 55% dispersed after 1 hour. Results from analyses of the 10% bentonite prills (Figure 2.1; broken line) indicate that at this bentonite content the evenness of mixing of bentonite within the prills is variable and may have a large effect on their measured rate of dispersion. The dispersion of the 5% bentonite product was very slow reaching only 10% after 8 days immersion. The 5% bentonite product would appear to have little value as a practical sulphur fertilizer (Bosswell *et al.*, 1988).
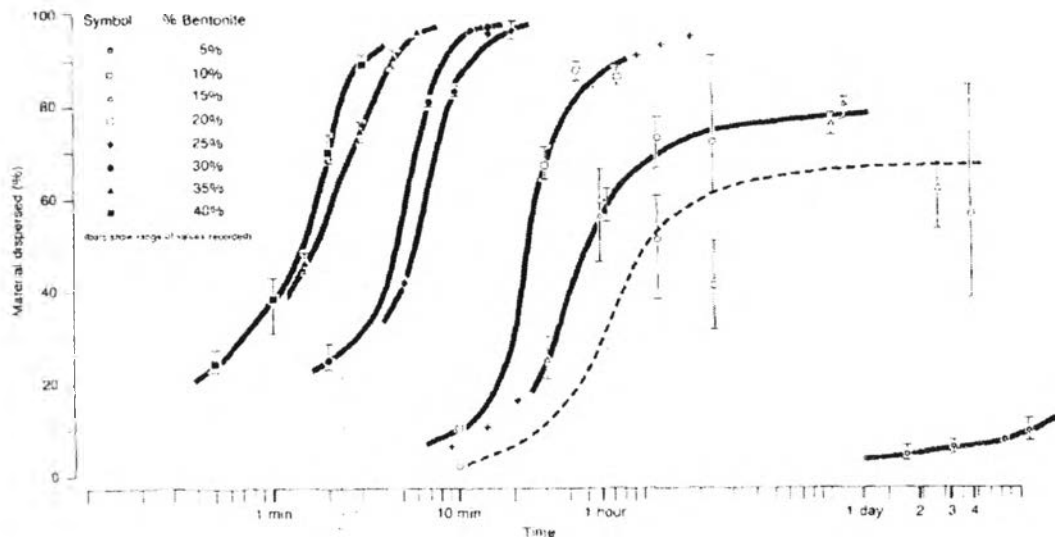
Figure 2.1 Effect of bentonite content on the rate of dispersion of prills in water, Bosswell *et al.*, 1988.

The particle size of Sulphur distribution after dispersion in water, When the content of bentonite increased from 5 to 40 wt%, the particle size of sulphur tend to decrease from 5 to 40 wt% of bentonite, respectively (Figure 2.2).
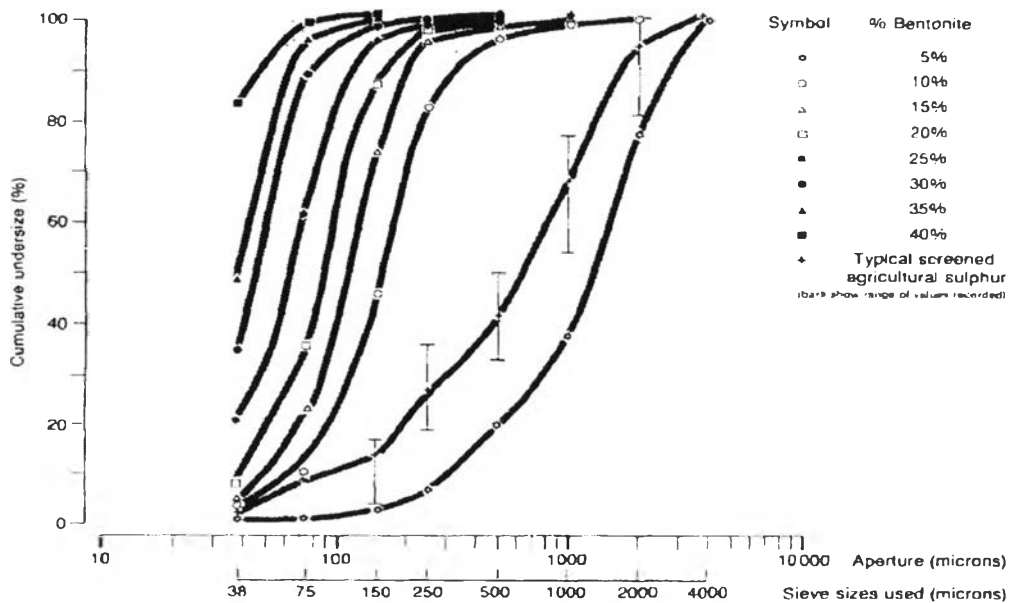

Figure 2.2 Sulphur particle size distribution after dispersion in water, Bosswell *et al.*, 1988.

2.3 Effect of Different Forms of Sulphur Fertilizers to Crop's Yield

Zhao *et al.* (2000) compared the different forms of sulphur fertilizer between sulphur bentonite and micronized sulphur. The result showed that the sulfate content of the soil in first and second harvest were greater in micronized sulphur more than sulphur bentonite because micronized sulphur has smaller particle size, easy to disperse and has maximize surface area for oxidation. In contrast, the sulphur bentonite prills were still visible on the soil surface at least 2 months after application. The expected swelling of bentonite upon water absorption was not sufficient to shatter and disperse sulphur in the prills. The dispersal of sulphur bentonite prills was poor and the external physical force was necessary to ensure dispersal, the sulphur bentonite prills were still too large for rapid oxidation, but the increasing the proportion of bentonite improved dispersal of sulphur and more rapid release of available sulfate.

2.4 Process for Forming Prill for Sulphur and Bentonite

A process for prilling a mixture of sulphur and bentonite to produce a water-degradable prill includes adding dry bentonite in powdered into a molten sulphur at a temperature to provide a molten sulphur-bentonite mixture (above the melting point of sulphur and below 140°C) (Rosso and Les Veaux, 1950). The mixture forming into a droplet form, for quenching solution, water cannot be used because the sulphur bentonite does not pelletize in water but rather degrade, providing a quenching solution of either sodium chloride, sodium sulphate, potassium chloride or potassium sulphate at a temperature low enough to solidify the sulphur-bentonite mixture, dipping the droplet into the quenching solution, passing the droplets through the quenching solution for a time and at a temperature of the quenching solution sufficient to anneal the droplets into prills, then removing the annealed prills from the quenching solution and drying the prills to a specified temperature and moisture content (Zaharko, 1986).

For some another commercial process, they mixed molten sulphur and bentonite with continuous and through mixing at an elevated temperature between

115–140°C, pouring the uniform mixture onto a moving wet stainless steel belt, allowing the mixture to cool to a thickness of one-quarter to one-half inch, curing the cooled mixture, comminuting the mixture and screening and separating the granules to have a specified particle size (Caldwell *et al.*, 1979).

2.5 Clay Minerals

Clay minerals, or phyllosilicate, consist of silicate layer held together by weak ionic force. Generally, it can be classified into many types according to differences in structures and composition. Owing to their chemical composition and crystal structure, they are divided into four main groups which are illite, smectite, vermiculite, and kaolite. Among these, the one that is found to be useful in the field of polymer composites is a group of expandable clay known as smectite clay.

Smectite clay is a group of clay mainly composed of montmorillonite (MMT) that is a naturally occurring 2:1 phyllosilicate, which has layered and crystalline structure. Montmorillonite, which is the main constituent of bentonites, is a mainly species of smectite clay. The structure of MMT is made of several stacked layers, with a layer thickness around 0.96 nm and a lateral dimension of 100–200 nm (Lertwimolnum and Vergnes, 2005). Its crystal lattice consists of a central octahedral sheet of alumina fused between two external silica tetrahedral sheets (in such a way that the oxygen from the octahedral sheet also belong to the silica tetrahedral), as shown in Figure 2.3. These layers organize themselves in a parallel fashion to form stacks with a regular gap between them, called interlayer or gallery (Manias *et al.*, 2001). Moreover, the stacks of clay layer are held tight together by Van der Waals forces.

Isomorphic substitution within the layers (for example, Al^{3+} replaced by Mg^{2+} or Fe^{2+}, or Mg^{2+} replaced by Li^{1+}) generates negative charges that are counter-balanced by alkali and alkaline earth cations situated inside the galleries. This type of layered silicate is characterized by a moderate surface charge known as the cation exchange capacity (CEC), and generally expressed as mequiv/100 gm. This charge is not locally constant, but varies from layer to layer, and must be considered as an

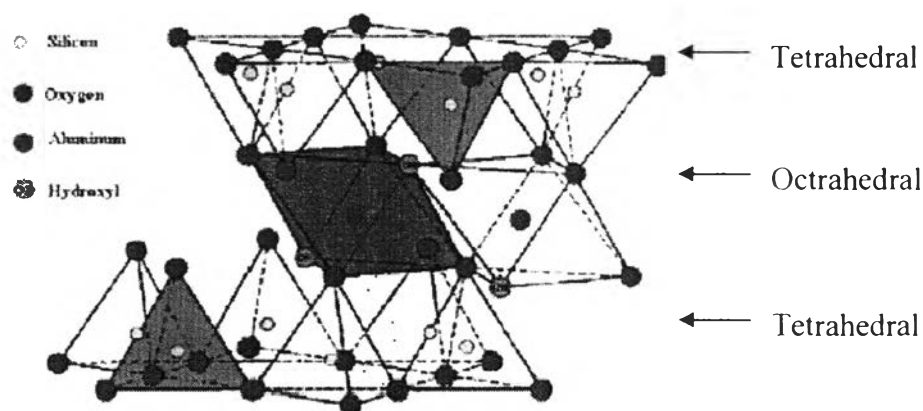average value over the whole crystal (Manias *et al.*, 2001; Sinha Ray Okamoto., 2003).

Figure 2.3 Structure of montmorillonite (Morlat *et al.*, 2004).

Bentonite is a clay generated frequently from the alteration of volcanic ash, consisting predominantly of smectite minerals, usually montmorillonite. Depending on the nature of their genesis, bentonite contains a variety of accessory minerals in addition to montmorillonite. These minerals may include quartz, feldspar, calcite, gypsum, and other metal oxide. The presence of these minerals can impact the industrial value of a deposit, reducing or increasing its value depending on the application.

2.6 Organoclay

Jin-Ho *et al.* (1997) prepared organoclay complexes exhibiting hydrophilic as well as organo-philic natures by using several kinds of quanternary alkylammonium cations with different molecular structure and functional groups, tearyldimethyl ammonium chloride (DMDS), methyltriethanoldipalmitylester-ammonium methyl-sulfate (DCEM), monostearyltrimethylammonium chloride (ODEM), and methyl-triethanolpalmitylesterammonium methylsulfate (DHMC), were incorporated into interlayer spaces. X-ray diffraction patterns for the dried organo-clay complexes. Upon intercalation, the basal spacing of DHMC-M expanded up to 66 Å, indicating the incorporation of large surfactant molecules. On the basic

of X-ray diffraction patterns and infrared spectra, the interlayer packing structures were proposed, as shown in Figure 2.4. Among them, the formation of a regular interstratified structure for DHMC molecules (Figure 2.4d) might be due to the coexistence of DCEM molecules in the starting material as a competing guest species.
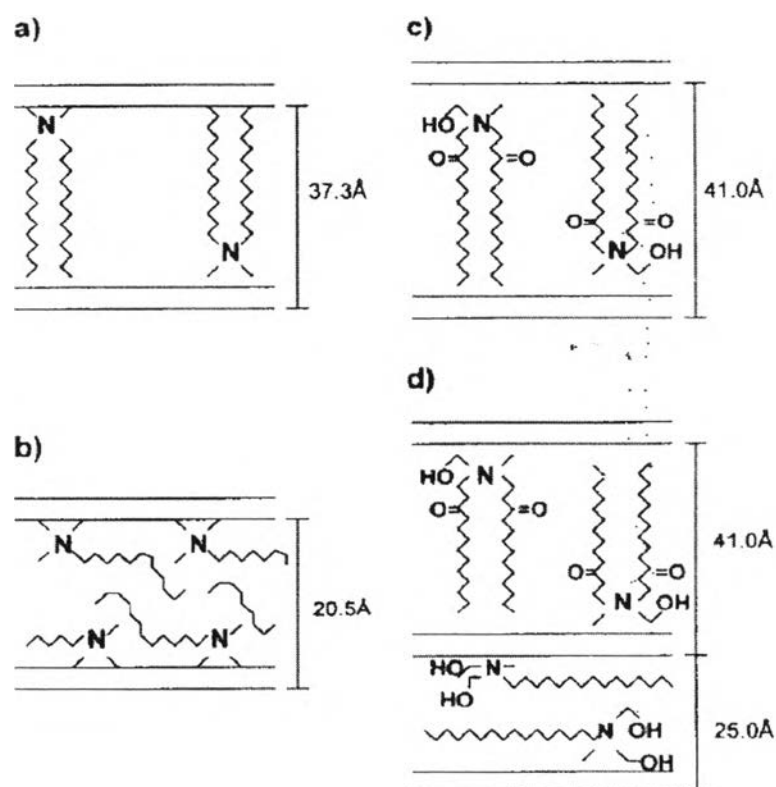

Figure 2.4 Schematic diagrams of the possible interlayer structure of each quaternary alkylammonium derivative: (a) DMDS-M, (b) ODTM-M, (c) DCEM-M and (d) DHMC-M (Jin-Ho *et al.* 1997).

2.7 Porous Clay Heterostructure (PCH)

A variety of ordered mesoporous materials have been synthesized by surfactant-templated methods. Porous clay heterostructure (PCH) is a recent class of solid porous materials formed by the intercalation of surfactant within the intragalleries of clays. Various types of expandable clay could be employed such as

hectorite, vermiculite, synthetic saponite and montmirillonite for the synthesized of these highly porous clays.

Polverejan et al., (2000) prepared porous clay heterostructure from synthetic saponite clay with targeted layer charge densities in the range of x = 1.2–1.7 e⁻ units per $Q^{+}_x[Mg_6](Si_{8-x}Al_x)O_{20}(OH)_4$ unit cell. The total acidity (0,64–0.77 mmol/g) increased with the saponite layer charge density (x), indicating that the acidity is correlated with the number of portons balancing the clay layer charge after calination. The BET surface areas of 800–920 m^2/g and pore volume of 0.3–0.44 cm^3/g were obtained. These materials showed the unique pore structure in the supermicropore to small mesopore rang about 1.5–2.3 nm, as can be seen in TEM image (Figure 2.5) and the thermal stability is up to at least 750°C.
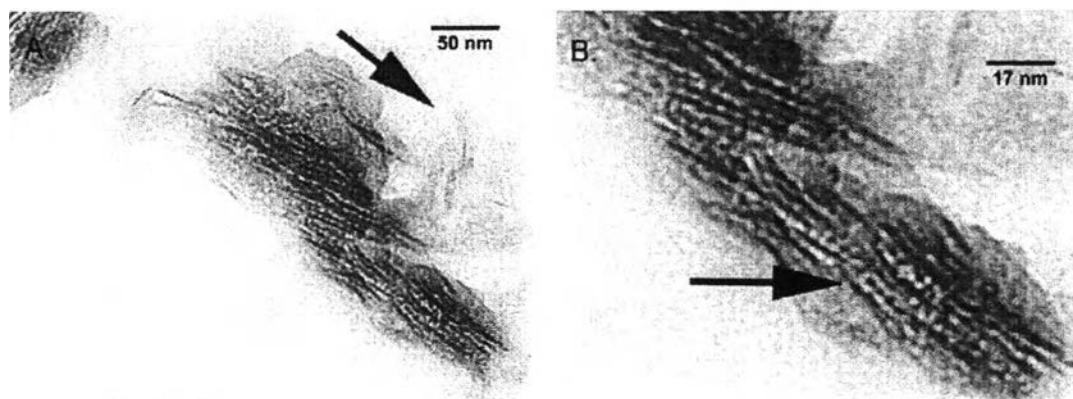

Figure 2.5 TEM of saponite heterostructure image, Polverejan et al,. (2000).

Polverejan et al., (2002) prepared the post synthesis grafting of aluminum into the meso structured intra gallery silica framework of a PCH precursor derived adsorption, from asynthetic saponite clay. Elemental analyses, powder X-ray diffraction, N_2 adsorption and [27]AlMAS NMR spectroscopy were used to characterize the products, which designated Al-SAP/PCH. Depending on the choice of aluminum reagent ($AlCl_3$ or $NaAlO_2$), the Al-SAP/PCH derivatives exhibited basal spacings of 32–34.8 Å, BET surface areas of 623–906 m^2/g, pore volumes of 0.32–0.45 cm^2/g, and pore sizes in the large micropore to small mesopore range (14–25 Å). The formation of porous clay heterostructure is presented in Figure 2.6.
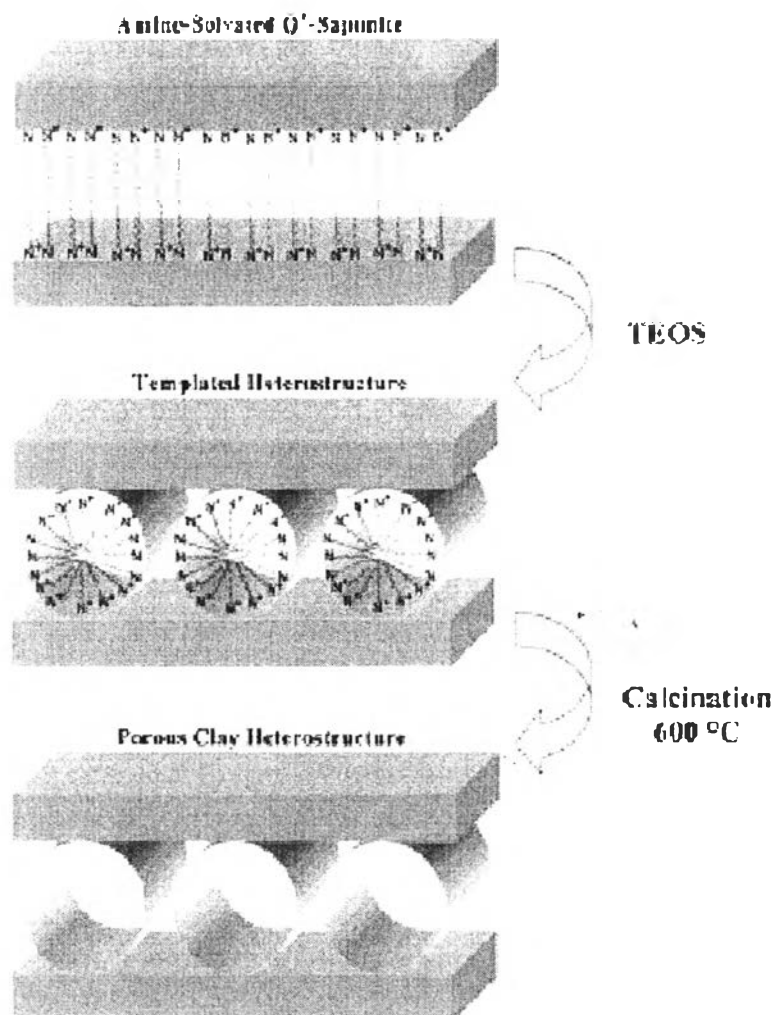
Figure 2.6 Schematic representation of porous clay hetero structure (PCH) formation (Polverejan *et al.*, 2002).

The PCH's surface area is higher than that of oraganoclay, making it suitable for easily modified by functional group and higher surface area for scavenging system. The previous work (Prakobna *et al.,* 2007) showed the dramatically enhanced surface area of PCH compared to bentonite and successfully attached the surface of PCH with methyl group. These modified PCH exhibited the increasing of ethylene adsorption. The continuous work (Srithammaraj *et al.,* 2008) involved the modification of PCH's surface by thiol group to enhance the conductive properties of these PCH. In 2009, a PCH surface was modified by Fe ions and then

blended with polylactide for low oxygen gas permeability in food packaging (Mattayan *et al.*, 2009).