CHAPTER VI
THE EFFICIENCY OF SULPHUR BENTONITE FERTILIZER

6.1 Abstract

The prepared sulphur bentonite and sulphur-PCH fertilizer were tested the efficiency in fertilization, sulphur content, dispersibility in water, oxidation to sulphate, soybean plantation, and sulphur uptake.The measured sulfur contents weredetermined by loss on ignition, it was formed that the measure sulphur contents are close agreement to nominal contents.The dispersion rate was determined by immersion sulphur bentonite prill in water and measuring weight loss of sulphur bentonite prill. The rate dispersion in water of sulphur bentonite in water increased when the bentonite content was increased from 10 to 20 wt% and then decreased when the bentonite content was increased from 20 to 30 wt%. The sulphur-PCH prills did not swell in water although it was immersed in water several days, it is still in prill form.The oxidation to sulphate was studied by curing each sulphur fertilizers in sand. After 45 days, the incubated soil was collected and determined the water soluble sulphate in soil. The results showed the good oxidation of sulphur bentonite fertilizer. Soybean was tested the efficiency of each sulphur fertilizer. The soybeans were harvested 60 days after planting, soybeans that uptake sulphur bentonite had significantly higher average height, weight, products, and sulphur uptake than sulphur-PCH.

keywords : Sulphur bentonite, Soybean plantation, Oxidation of sulphur, Sulphur uptake

6.2 Introduction

After crop is harvested, a portion of the available sulphur is depleted and a portion is returned to soil as residue and converted into organic matter. But in the cropping system, it tends to remove more sulphur than being replaced. So the sulphur fertilizers are required for soil supplement. There are various chemical and physical forms of sulphur fertilizer such as sulphate fertilizes (example ammonium sulphate and potassium sulphate) and another one is elemental sulphur in different physical forms. For the sulphate fertilizer, it provides an immediate source of sulphate to the plant, but sulphate is easy to leaching loss. For the elemental sulphur fertilizer that contains high concentration of 70 to 100 wt% sulphur and greatly physical characteristic. Element sulphur must be biologically oxidized to sulphate before it can be taken up by plant. Release of an available sulphate form sulphur pills depends on 2; process 1) physical dispersion of the pill and 2) oxidation to sulphate. The benefits of elemental sulphur are a continual releasing of sulphate during the growth season and minimal sulphate leaching loses. However, the oxidation process depends on soil moisture, temperature, bacteria activity, time, and particle size. The particle size of sulphur is the most important factor, especially the small particle sizes are easily dispersed and oxidized. However finely divided sulphur is hazardous as it can form explosive mixtures with air. To avoid explosions limitations are placed on the proportion of fine particles permitted in screened agricultural sulphur intended for aerial application (20% < 150 microns is the recommended maximum) (Duncan, 1983). According to the reasons above, Sulphur bentonite is the intelligent choice for solving the oxidation rate, small particle size and explosion for the actual uses.

6.3 Experimental

6.3.1 Materials

Sulphur fertilizers used in this experiment were sulphur bentonite (B10, B20, B30) and sulphur-PCH (PCH7, PCH10, PCH12). The preparation of sulphur bentonite and sulphur-PCH were mentioned in previous chapter 5. Hydrochloric acid (HCl) 37 wt% and acetic acid gracial (CH_3COOH) were supplied by Carlo Erba.Sodium Hydroxide (NaOH), Ammonium acetate (CH_3COONH_4), Barium chloride ($BaCl_2.2H_2O$) and Potassium sulphate (K_2SO_4) were supplied by Ajax Fine Chem.Potassium phosphate (0-52-34) and urea (46-0-0) were supplied by Viking,and activated carbon was supplied by Fluka.

6.3.2 Sulphur Content

The sulphur content was determined by loss on ignition.Sulphur bentonite fertilizer was weight approximately 200 mg on the known weight crucible. The sample was placed into TruSpec® sulphur Module furnace at 1350°C for 5 minutes, sulphur was completely burn up. After that the crucible was removed from the oven and then was cooled at room temperature for 10 minutes or until the temperature of crucible was equal to the room temperature. The sample in the crucible was reweighted again. The lost weight was the weight of sulphur.

6.3.3 Dispersion in Water

Small colander of approximately 10 cm diameter and 7 cm height were made from stainless steel mesh of about 1 mm aperture. For prill of each sulphur/bentonite ratio dispersion tests were carried out simultaneously in 12 colanders (3 replicates, 4 times interval) (Boswell*et al.*, 1988). One gram of prill was weighed into each oven dried colander and the cells were placed in a tray of water at 25°C at 2 minutes intervals. After time interval l, the first colander was removed and the material carefully and quickly washed with 100 ml of water to flush from the colander those particles dispersed to dimensions less than 1 mm. The other two replicates for the time interval were similarly removed and rinsed at 2 minutes intervals. After washing, the cells and the retained particles were oven-dried for 5h at 85°C and reweighed. The time intervals chosen ranged widely from 2 minutes up to 35 minutes depending on the bentonite content; but for each mixture the four times used covered a wide dispersal range.

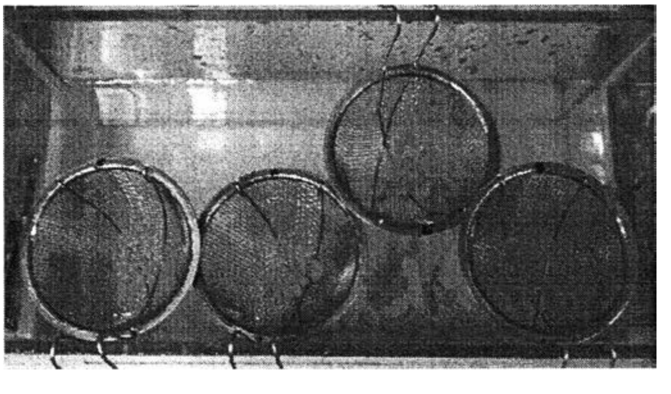

Figure 6.1 Dispersion test of sulphur bentonite in water.

6.3.4 Purification and pH Adjustment of Sand

Sandy-soil was sieved pass 1 mm sieves, after that it was washed with distilled water many times until soil pH approximately 6.5 by neutralizing soil using 0.1 N HCl or 0.1 N NaOH. The soil was determined sulphur content in soil by using TruSpec®sulphurModule before and after washed with distilled water. Treated soil was air-dried for 5 days or until it completely dried.

6.3.5 Oxidation of Sulphur Fertilizers

The equivalent of 2.5 kg air-dried soil was weighed and placed in a 3-litre black plastic bag with drainage holes. There were 8 treatments of sulphur fertilizer: (1) control (no sulphur), (2) elemental sulphur, (3–5) sulphur bentonite 10, 20, 30 wt% of bentonite content respectively, (6–8) sulphur-PCH 7, 10, 12%wt of PCH content, respectively. The quantities of sulphur fertilizer were weighted base on 500 mg of sulphur content. Each sulphur fertilizer was put on the surface of soil, and each pot was watered 250 ml per day until day 45. 20 grams of soil sample was collected by digging down 2 inches deep, after that soil samples were oven-dried at 60°C for 24 h.

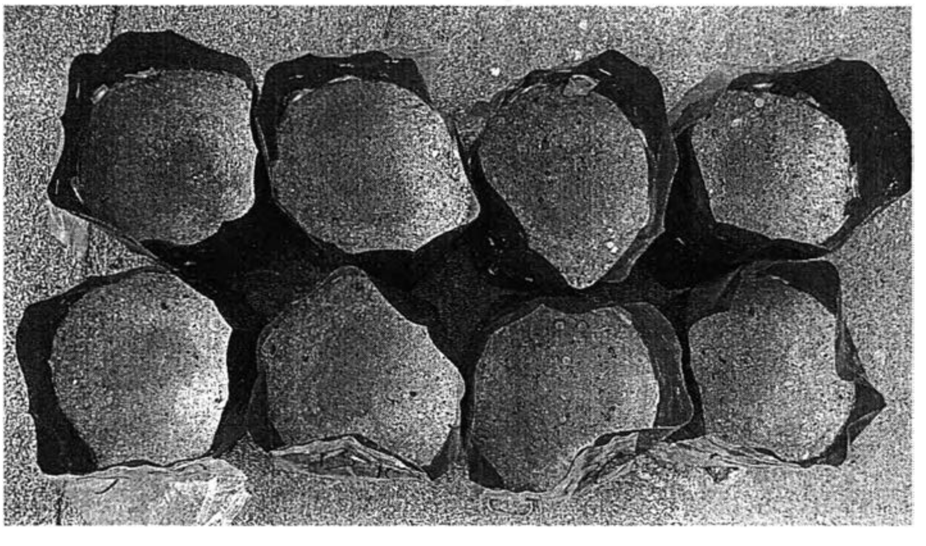

Figure 6.2 Oxidation test of sulphur fertilizers.

The water soluble sulphate in soil was determined by the extraction of sulphate from soil (Jones*et al.*, 1972). 10 g of oven-dried was put in an erlenmeyer flask, then add 25 ml of acidified ammonium acetate extractant (dissolve 39 g of NH_4OAc in 1 L of 0.25 M acetic acid) and shake by using reciprocating shaker at 200 oscillation per minute for 30 minutes. Sample was added 0.25 g of activated charcoal and shake for 3 minutes, after that sample was filtered pass though a filter paper (Whatman N0.1). 10 ml of the filtrate from the extraction process was pipette into 50 ml Erlenmeyer flask, added 1 ml of acid solution (6 M of HCl acid). The solution was swirled, and then added 0.5 g of $BaCl_2.2H_2O$ crystal. Within the time interval of 3 to 8 minutes, the absorbance using UV spectrophotometer at a wavelength of 420 nm was recovered. The sulphate concentration of unknown solution was estimated from the sulphate standard curve. The calculation based on 10 g sample of soil, 25 ml of extracting solution, and a 10 ml aliquot (Schulte *et al.*, 1988).

$$\text{mg } SO_4\text{-S/kg of soil} = (mg\ S/L \times 0.025\ L)/0.010\ kg\ soil = \text{mg S/L} \times 2.5$$

6.3.6 Soybean Plantation

The equivalent of 2.5 kg air-dried soil was weighed and placed in a 3-litre black plastic bag with drainage holes. There were 9 treatments of sulphur fertilizers: (1) control (non nutrient), (2) NPK fertilizer only, (3) NPK plus ammonium sulphate, (4–6) NPK plus sulphur bentonite 10, 20, 30 wt% of bentonite content, respectively, (7–9) NPK plus sulphur-PCH 7, 10, 12 wt% of PCH content, respectively. Each treatment was planted 3 pods per treatment. The quantities of sulphur fertilizer were weighted base on 200 mg of sulphur content, the sulphur fertilizer was put on the soil surface. Each pot excepted control treatment (non nutrient) received a NPK fertilizer dressing of 240 mg potassium phosphate (KH_2PO_4) and 162 mg of urea ($(NH_2)_2CO$) (Riley, N.G.,*et al.*, 2000). All treatments and nutrient quantities are listed in Table 6.1.

Table 6.1 The soybean planted treatment

Treatment	Sulphur (g)	Urea (g)	K_3PO_4(g)
Non nutrient	-	-	-
NPK	-	0.162	0.240
NPK+$(NH_4)_3SO_4$	0.300	0.162	0.240
NPK+B10	0.222	0.162	0.240
NPK+B20	0.250	0.162	0.240
NPK+B30	0.286	0.162	0.240
NPK+PCH7	0.215	0.162	0.240
NPK+PCH10	0.222	0.162	0.240
NPK+PCH12	0.227	0.162	0.240

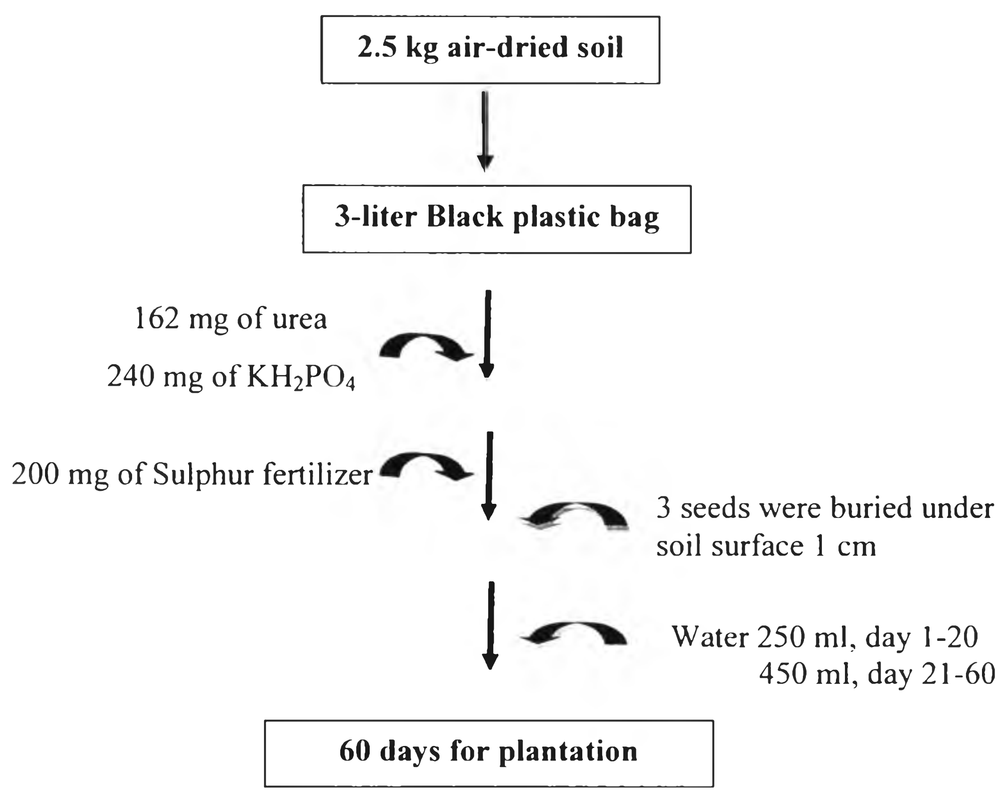

Figure 6.3 Diagram of soybean plantation.

Each pod, 3 seeds of soybean were buried under soil surface depth 1 cm. Pots were arranged orderly on benches under nylon net house with controlled environmental conditions: day/night time, day/night temperature of Bangkok during December 2010 to February 2011. The pots were watered with water to the soil surface to allow the fertilizers to percolate though the soil. Height, amount of leaves, and seeds data were collected every 10 days. The plants were harvested at maturity (60 days after planting) by removing sand and washing with deionised water until roots completely clean. Soybeans (shoot and root) were separated into leaves, stem, root, and seeds. All soybean parts were oven dried at 80°C for 72 h to remove moisture, after that each dried part were weight and collected dry weight data.

6.3.7 Sulphur Uptake of Soybean

Each part of soybean including of leaves, root, stem and seeds were oven dried in oven. After that the analyzed samples were cut, pulverized, and ground to pass a No. 100 (150 micron) sieve, respectively. The prepared samples were determined sulphur content by using TruSpec® sulphur Module. The sulphur uptake of each part was calculated thesulphur content of each part and dried weight.

6.3.8 Characterization

UV/VIS Spectrophotometer was recorded on a UV/vis spectrophotometer UV-1800 (Shimadzu) scanning in photometric mode at a wavelength of 420 nm at room temperature. Experiments were performed in a liquid cuvette.

CHNS Analyzer was recorded on TruSpec® sulphur Module for determination of sulphur content in material. This instrument was operated at 1,350°C and the high heat resistant crucible was required.

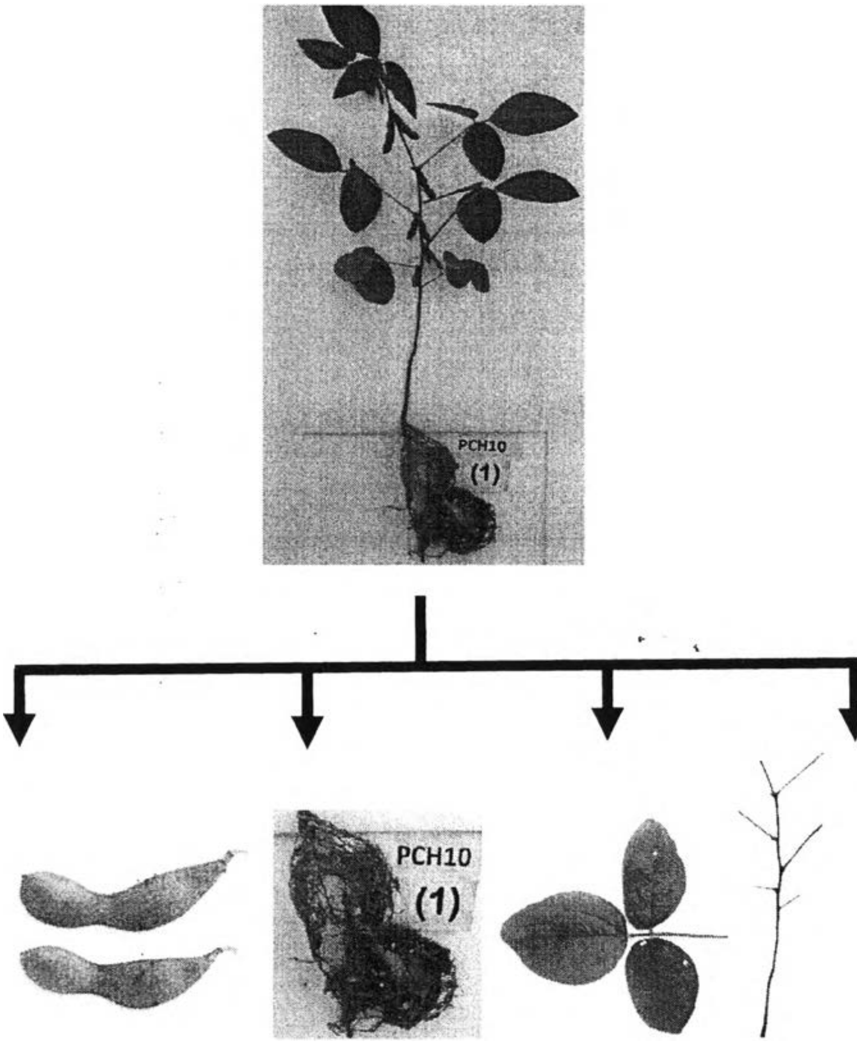

Figure 6.4 Diagram of separation of soybean into seeds, root, leaves, and stem.

6.4 Results and Discussion

6.4.1 Sulphur Content Results

The measured sulfur contents were close to the nominal contents but all the measured sulphur content had higher value than stated sulphur content because the small amount of analyzed sample was used. So, the moisture in air and weighing may affect the measured sulphur content.

Table 6.2 Sulphur content of sulphur bentonite fertilizers

sample	Stated clay content (wt%)	Measured sulphur content (wt%)
B10	10	90.74
B20	20	81.62
B30	30	71.95
PCH7	7	93.90
PCH10	10	91.63
PCH12	12	88.75

6.4.2 Rate of Dispersion in Water

The dispersion rate of sulphur bentonite in water increased when the bentonite content was increased from 10 to 20 wt% because of bentonite has good swelling property. On the other hand, the dispersion rate in water decreased when bentonite content increased from 20 to 30 wt% because of the adhesion property of bentonite clay (Figure 6.5).

Sulphur-PCH did not swell in water although it was immersed in water several days, it is still in original prill form (Figure 6.6 (b)). The reason of this problems were the loss of swelling property of PCH, the structure of PCH was changed from the ordered structure of layer to disordered structure. Another reason is shown in SEM micrographs of sulphur-PCH (Figure 5.7 (a)-(f)), the sulphur matrix going inside pore and void of PCH and another portion remain coated on surface of PCH. This decreased the opportunity of the contacting between clay surface and water.

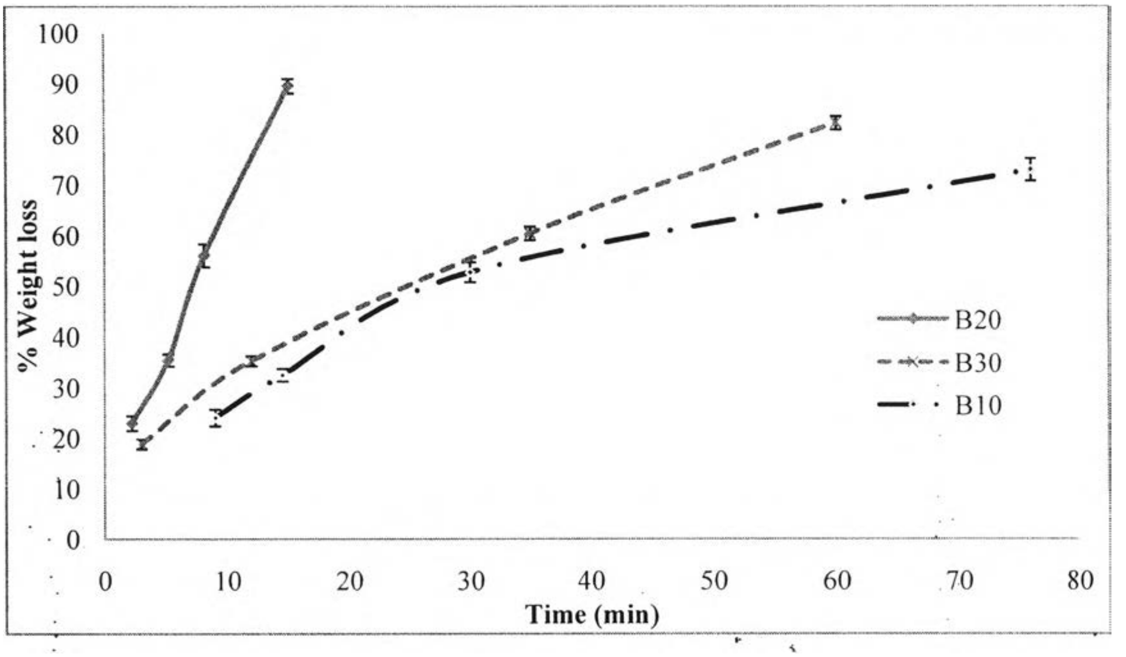

Figure 6.5 Effect of bentonite content on the rate of dispersion of prill in water (% material < 1 mm).

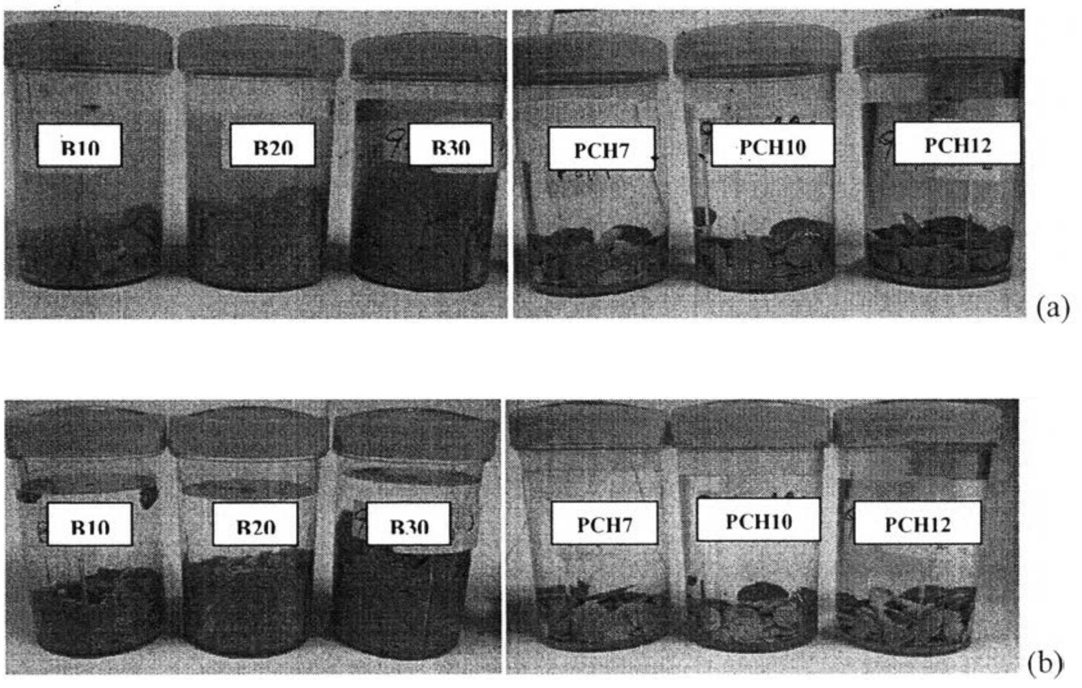

Figure 6.6 Dispersion of Sulphur bentonite, B10, B20, B30 and sulphur-PCH, PCH7, PCH10, PCH12 in water, (a) after 1 h, (b) after 1 day.

6.4.3 The Oxidation of Sulphur Fertilizers

After 45 days, the sulphur incubated soils were collected to determine the water soluble sulphate in soil. The results showed that the sulphur bentonite has significant effect on the oxidation of sulphur to sulphate more than elemental sulphur, because sulphur bentonite can swell and release a small particle of sulphur. From many studies of oxidation rate of sulphur show that the rapid oxidation was affected by the small particle of sulphur, so the sulphur bentonite B20 would be releasing a suitable particle size for oxidation. The sulphur-PCH's prills did not swell and release small particle size of sulphur, so the oxidation of sulphur to sulphate did not significantly change when compared with No-sulphur soil.

Table 6.2 The water soluble sulphate in sulphur incubated soils

Treatment	Extracted sulphate solution concentration (ppm)	mg SO_4-S/kg of soil
Soil (No sulphur)	10.210	25.525
Elemental sulphur (S^0)	13.232	33.080
Sulphur bentonite (B10)	24.417	61.043
Sulphur bentonite (B20)	33.606	84.015
Sulphur bentonite (B30)	22.369	55.923
Sulphur-PCH (PCH7)	11.004	27.510
Sulphur-PCH (PCH10)	10.392	25.980
Sulphur-PCH (PCH12)	10.425	26.063

6.4.4 The Results of Soil Planted Soybean Plantation

Soybean which consumed N, P, K nutrients has normally grown, greenish leaves, and strong stem. In the other hand, Non nutrient soybean showed strongly unhealthy symtoms, pale leaves, scrubby stem, comparing with NPK consumed soybean. According to the height of soybeans, sulphur bentonite affected to the growth of soybean similar to ammonium sulphate fertilization. Based on growth rate, sulphur bentonite B20 affected to a well growth of initial interval but the final interval ammonium sulphate has more srtongly affect to the growth rate (Figure 6.8). Considering the dried weight, soybean which consumed NPK base had a similar weight. Soybean which consumed sulphur bentonite has a significant affect on the weight of root, leaves, stem, and seeds. As for sulphur-PCH fertilization almost did not affect to each part of soybean.

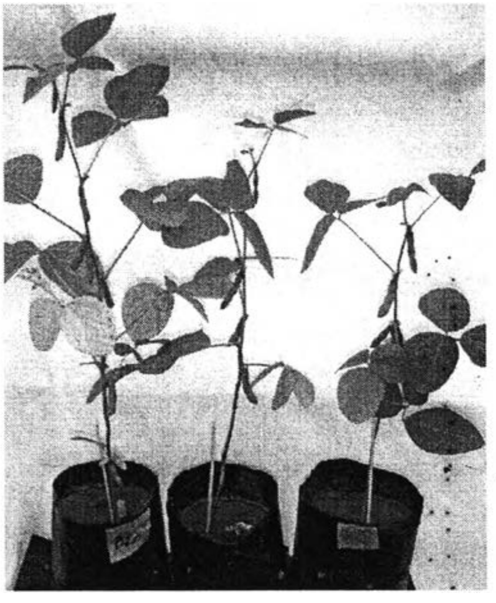

Figure 6.7 The observation of soybean plantation (B20).

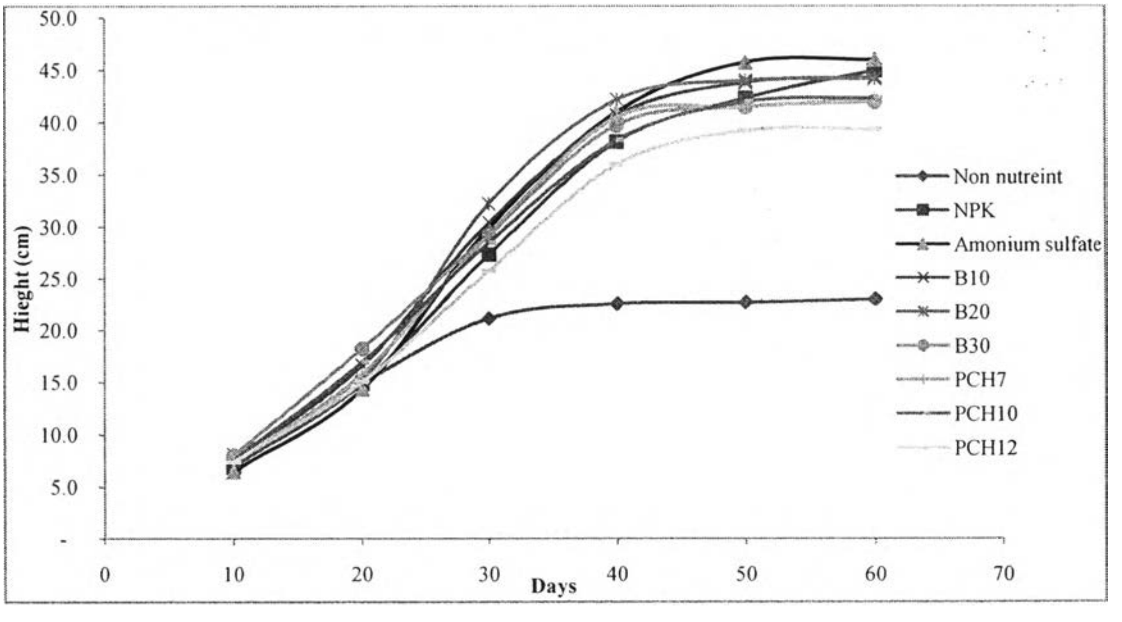

Figure 6.8 Effect of sulphur fertilizers on the growing rate of soybean.

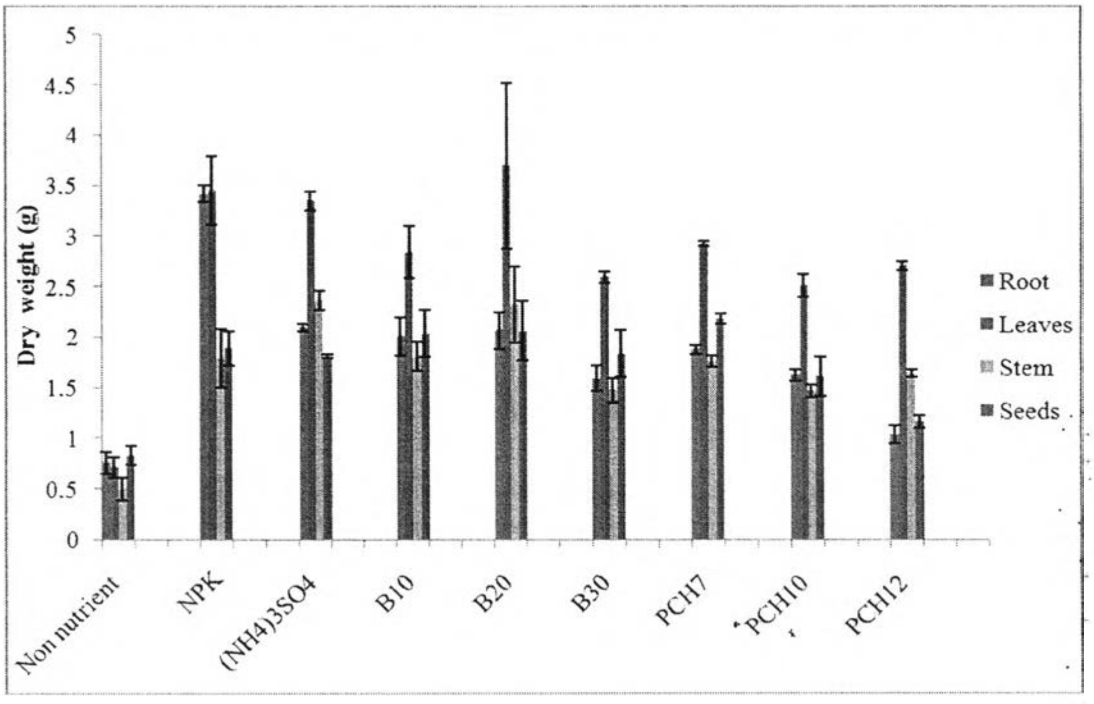

Figure 6.9 Effect of sulphur fertilizers on the dried weight of soybean.

6.4.5 Sulphur uptake results

Sulphur bentonite B10, B20, B30 affected a good responsibility of stem and leaves. Soybean could uptake sulphate from sulphur bentonite as the same quantity as ammonium sulphate fertilizer. As for the soybean which uptake sulphur-PCH had low uptaking quantity of sulphur.

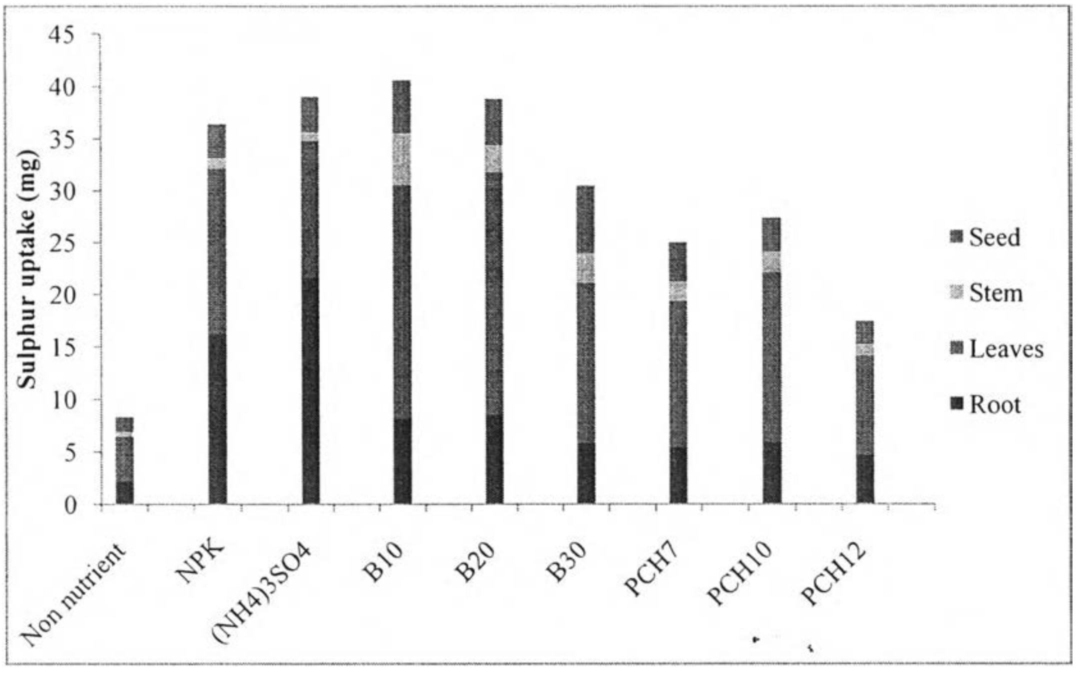

Figure 6.10 Effect of sulphur fertilizers on the sulphur uptake of soybean.

6.5 Conclusions

According to all experiments, sulphur bentonite fertilizers showed a higher performance than sulphur-PCH because sulphur-PCH released a small amount of small particle size of sulphur. Even though the sulphur fertilizer did not strongly affect to the growth of soybean as N, P, K did, it can be used as an effective source to fully improve the abundance of stems, leaves, seeds, and root of soybean. Soybean did not show the sulphur deficiency symptom because the planted soil remained some quantity of sulphur from tap water.

6.6 Acknowledgements

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6.7 References

Boswell. C.C., Owers, W.R., Swanney, B., and Rothbaum, H.P. (1988). Sulfur/sodiumbentonite mixtures as sulfur fertilizers. 1. Theeffects of S/Na-bentonite ratios on the rate of dispersion andparticle size distribution of elemental sulfur dispersed fromlaboratory-produced prills. Fertilizer Research, 15, 13–31.

Duncan, A.A., (1983) The application of fertilisers containing elemental sulphur. In Gregg PEHand Syers JK, eds. Proceedings of the Technical Workshop on Sulphur in New ZealandAgriculture, pp 176-180. Massey University, N.Z.

Jones, L. H. P., D. W. Cowling, and D. R.Leckyer. (1972). Plant-available and extractable sulfur in soils of England andWales.Soil Science, 114, 104–114.

Riley, N.G., Zhao, F.J., and McGrath, S.P. (2000). Availability of different forms of sulphurfertilisers to wheat and oilseedrape. Plant and Soil, 222, 139–147.

Schulte, E.E., and Kalju Elk.(1988).Recommended sulphate-S test. p. 17-20. InW.C. Dahnke (ed.). Recommendedchemical soil test procedures for the NorthCentral Region.North Dakota Agric. Exp.Stn. Bull. 499.