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APPENDICES

Appendix A Introduction of Sulphur

Elemental Sulphur

Sulphur or Sulfur is the chemical element that has the atomic number 16 and the standard atomic weight 32.07. It is denoted with the symbol S. There are a large number of allotropes of sulphur. The most common form found in nature is yellow orthorhombic crystalline α -sulphur, which contains puckered rings of S₈, as it is thermodynamically stable at ordinary temperatures.

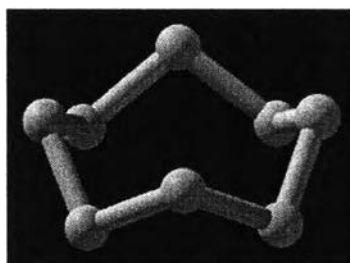


Figure A1 Structure of Cyclooctasulphur (α -sulphur), S₈.

Sulphur is vital to modern life as one of the most versatile and essential raw materials. It exists in food and medicine, which is a building block of life for plants and animals, and is used in most manufacturing and industrial worldwide. Elemental sulphur sources mostly obtained from the natural gas processing, or were recovered from the refining of high-sulphur crude oil and heavy oil, through hydrodesulfurization. An additional small amount of sulphur production, recovered from the smelting of metallic sulphides and the roasting of zinc-sulphide concentrates, was in the form of sulphuric acid and liquefied sulphur dioxide.

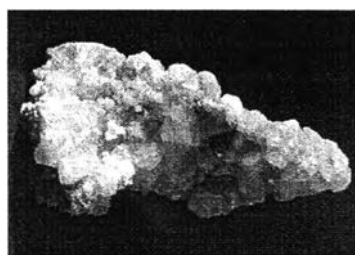


Figure A2 Crystalline Elemental Sulphur.

The Characteristics and Properties of Sulphur

At room temperature, sulphur is a soft, bright-yellow solid. Elemental sulphur has only a faint odor, similar to that of matches. The odor associated with rotten eggs is due to hydrogen sulphide and organic sulphur compounds rather than elemental sulphur. Sulphur burns with a blue flame that emits sulphur dioxide, notable for its peculiar suffocating odor due to dissolving in the mucosa to form dilute sulphurous acid. Sulphur itself is insoluble in water, but soluble in carbon disulfide.

Table A1 Physical Properties of Elemental Sulphur

Properties	
Phase	Solid
Density (α -sulphur)	2.07 g·cm ⁻³
Liquid density @ melting point	1.819 g·cm ⁻³
Melting point	115.21 °C
Boiling point	444.6 °C
Specific heat capacity @ 25 °C	22.75 J·mol ⁻¹ ·K ⁻¹

Common oxidation states of sulphur include -2, +2, +4 and +6. Sulphur forms stable compounds with all elements except the noble gases. Sulphur in the solid state ordinarily exists as cyclic crown-shaped S₈ molecules. The crystallography of sulphur is complex. Depending on the specific conditions, the sulphur allotropes form several distinct crystal structures, with rhombic and monoclinic S₈ best known.

A noteworthy property of sulphur is that its viscosity in its molten state, unlike most other liquids, increases above temperatures of 200 °C due to the formation of polymers. The molten sulphur assumes a dark red color above this temperature. At higher temperatures, however, the viscosity is decreased as depolymerization occurs. Amorphous or "plastic" sulphur can be produced through the rapid cooling of molten sulphur. X-ray crystallography studies show that the

amorphous form may have a helical structure with eight atoms per turn. This form is metastable at room temperature and gradually reverts back to crystalline form. This process happens within a matter of hours to days but can be rapidly catalyzed. Sulphur phase diagram is shown in Figure A3.

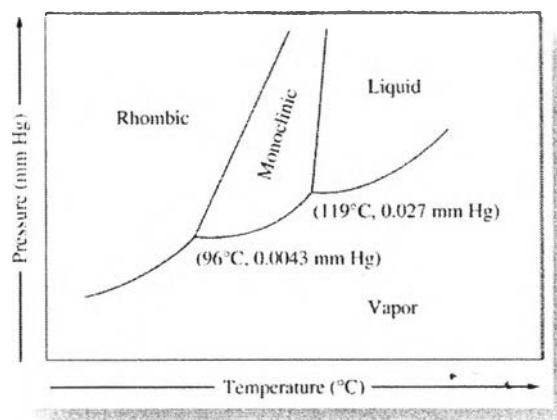


Figure A3 Sulphur Phase Diagram.

Sulphur Derived from Oil Refinery Process

The Claus process is the most significant gas desulfurizing process, recovering elemental sulphur from gaseous hydrogen sulphide found in raw natural gas and from the by-product gases containing hydrogen sulphide derived from refining crude oil and other industrial processes. The by-product gases mainly originate from physical and chemical gas treatment units in refineries, natural gas processing plants and gasification or synthesis gas plants. These by-product gases may also contain hydrogen cyanide, hydrocarbons, sulphur dioxide or ammonia. A schematic process flow diagram of a basic 3-bed Claus unit is shown in Figure 4.

Hydrogen sulphide produced, for example, in the hydro-desulfurization of refinery naphthas and other petroleum oils, is converted to sulphur in Claus plants. The H_2S gas is reacted with the O_2 and converted into SO_2 . Then, the H_2S and SO_2 are converted into S. The overall main reaction equation is:

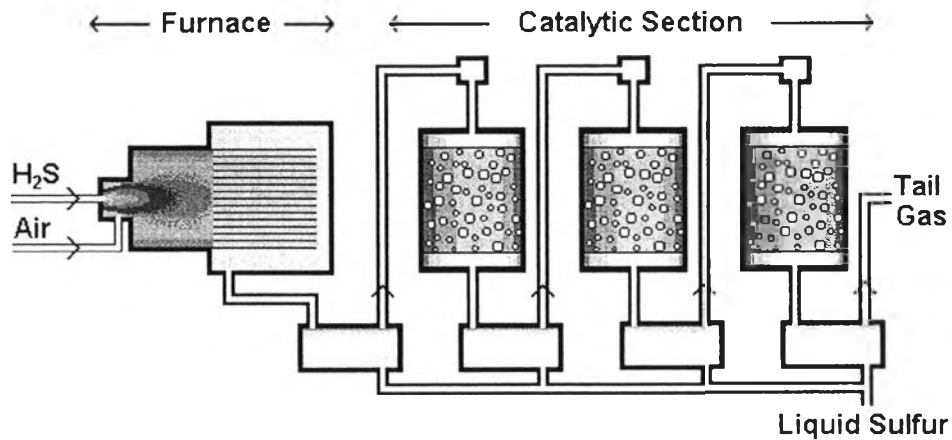
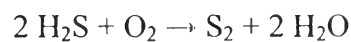


Figure A4 Schematic Flow Diagram of Sulphur Production by the Claus Process.



The Claus technology can be divided into two process steps, thermal and catalytic.

Sulphur Specification

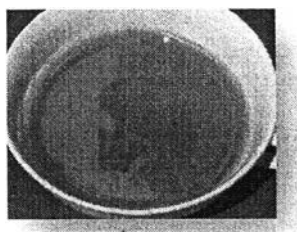
Sulphur has become a basic necessity in many industries, most importantly, the chemical industry. The most important industrial uses of sulphur are:

- Chemical Industry - manufacturing of compounds like sulphuric acid, sulphate
- Food Industry
- Pharmaceutical Industry
- Agricultural Industry
- Tyre and Rubber Industry
- Paper and Cellulose Industry
- Pigments, Colorants and Paint Manufacturing Industry
- Detergent Manufacturing Industry
- Metallurgical Industry
- Etc.

Sulphur specification was varied by the sulphur product form and the application used. From an observation, the sulphur purity was specified in the range

from the minimum 99.5 to 99.99%, with least amount of organic and mineral matter, and low moisture content. The sulphur product and specification from companies were presented as follows:

Molten Sulphur (Liquid Sulphur)



Example:

Properties	
Application	Chemical industries-sulphuric acid production
Purity of sulphur	99.99%
Moisture content	<0.017%
Mineral matter	<0.005%
Organic matter	<0.005%
Acidity	<0.0003%

source: Thai Oil Public Co., Ltd.- laboratory test report

Powder Sulphur



HS Code: 2503 Sulphur of all kinds (other than sublimed or precipitated sulphur, colloidal sulphur)

Purity of sulphur 99.5-99.9%

Example:

Properties (dusting sulphur)	
Application	Chemical industries Match industry Explosive industry Fungicide - powdery mildew
Color and appearance	Bright yellow powder
Purity of sulphur	99.5% minimum
Ash	0.2% maximum
Moisture	0.1% maximum
Acidity	0.003% maximum
Mineral matter	Arsenic, Selenium and Tellurium Commercially Free
Application	Rubber tires Vulcanization Latex industries
Color and appearance	Bright Yellow Powder
Purity of sulphur	99.8% minimum
Ash	0.1% maximum
Moisture	0.1% maximum
Acidity	0.003% maximum
Mineral matter	Arsenic, Selenium and Tellurium Commercially Free

source: Fast Track Trading Co., <http://www.fasttrackt.com/specifications.html>

Lump Sulphur



HS Code: 2503 Sulphur of all kinds (other than sublimed or precipitated sulphur, colloidal sulphur)

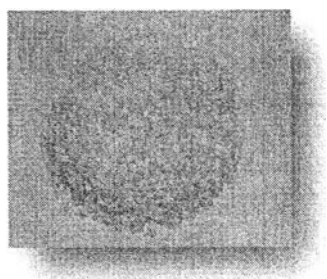
Purity of sulphur 99.5-99.9%

Example:

Properties (broken lump sulphur)	
Application	Chemical industries Detergent & sulphonation Sulphuric acid production Sugar refineries
Color and appearance	Bright yellow sulphur lumps
Purity of sulphur	99.8% minimum
Ash	0.5% maximum
Moisture	0.1% maximum
Acidity	0.003% maximum
Mineral matter	Arsenic, Selenium and Tellurium Commercially Free

source: Fast Track Trading Co., <http://www.fasttrackt.com/specifications.html>

Granular Sulphur



HS Code: 2503 Sulphur of all kinds (other than sublimed or precipitated sulphur, colloidal sulphur)

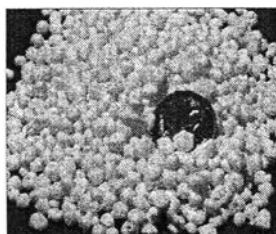
Purity of sulphur 99.5-99.9%

Example:

Properties (sugar industry sulphur)	
Application	Sugar industry
Color and appearance	Bright Yellow Sulphur (Granule)
Purity of sulphur	99.5% minimum
Ash	0.05% maximum
Hydrocarbon	0.05% maximum
Acidity	0.002% maximum
Mineral matter	Arsenic, Selenium and Tellurium Commercially Free

source: Fast Track Trading Co., <http://www.fasttrackt.com/specifications.html>

Prilled Sulphur



HS Code: 2503 Sulphur of all kinds (other than sublimed or precipitated sulphur, colloidal sulphur)

Purity of sulphur 99.5-99.9%

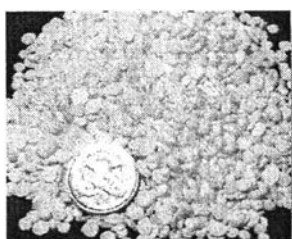
Example:

Properties (domestic grade)	
Application	Agricultural industry Food industry Sugar refineries
Purity of sulphur	99.8% minimum
Carbon	0.1% maximum
Ash	0.1% maximum
Moisture	5% maximum

Properties (domestic grade)	
Mineral matter	Arsenic, Selenium and Tellurium less than 20 ppm
Application	Agricultural industry Food industry Sugar refineries
Purity of sulphur	99.9% minimum
Carbon	0.05% maximum
Ash	0.05% maximum
Moisture	0.5% maximum
Mineral matter	Arsenic, Selenium and Tellurium Commercially Free

source: Devco Australia Holdings Pty Ltd, <http://www.sulphur.com.au>

Pastelle Sulphur



HS Code: 2802 Sulphur, sublimed or precipitated; colloidal sulphur

Purity of sulphur 99.8% minimum

Example:

Properties	
Application	Chemical industries Detergent & sulphonation Sulphuric acid production Sugar refineries
Color and appearance	Bright Yellow Pastilles (Dust free)
Purity of sulphur	99.8% minimum

Properties	
Ash	0.1% maximum
Moisture	0.1% maximum
Acidity	0.003% maximum
Mineral matter	Arsenic, Selenium and Tellurium Commercially Free

source: *Fast Track Trading Co.*, <http://www.fasttrackt.com/specifications.html>

Appendix B Specification of Bentonite (Mac-Gel F4/R)

F4/R is an activated Bentonite, processed from high content of specially selected montmorillonite. F4/R is very suitable and superior characteristic for all kinds of foundry applications (CEC =100).

Table A3 Chemical Properties (On dry basis at 105°C)

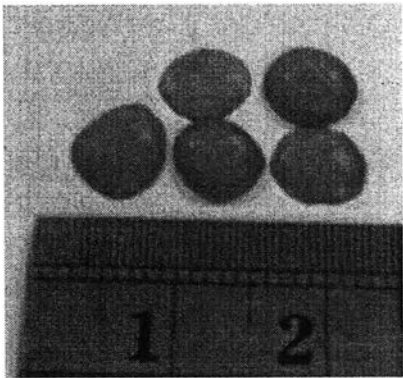
Chemical	Content (% wt)
SiO ₂	55.0-60.0
Al ₂ O ₃	16.0-20.0
Fe ₂ O ₃	7.0-10.0
Na ₂ O	2.5-3.5
LOI	9.0-12.0
MgO	2.0-3.0
CaO	2.0-3.0
K ₂ O	0.1-0.5
TiO ₂	0.3-0.6

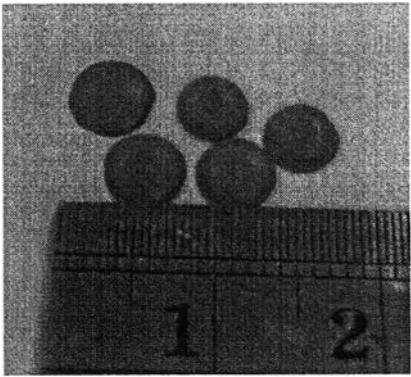
Table A4 Physical properties

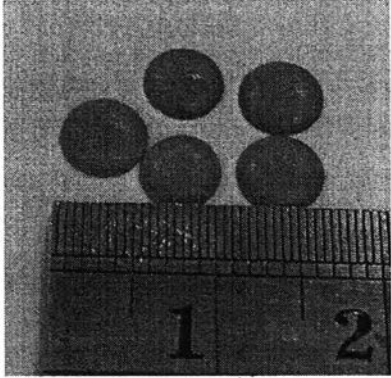
Physical properties	Property	
Moisture content	12	% max
5% Suspension, pH	10.00-11.50	
Swelling	25	ml per 2 g of clay, Min.
Liquid Limit	600	%, min.
ml of methylene Blue	45	ml per 0.5 g of clay, Min.
Dry particle size	80	% pass 200 mesh, Min.
Montmorillonite Content	80	%, Min.
Green Compressive Strength	9.0	N/cm ² , min

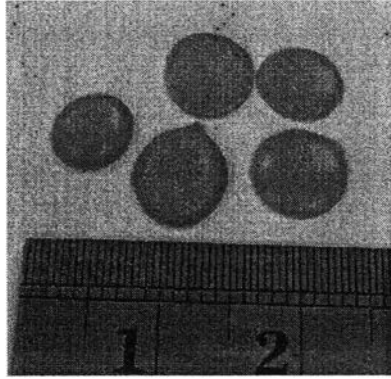
source: Thai-Nippon Chemical Industrial Co., Ltd.

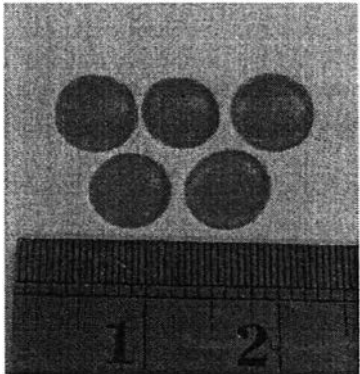
Appendix C The Prepared Sulphur bentonite fertilizers

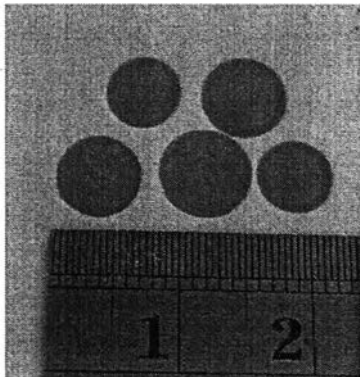
Sulphur bentonite (B10)	
Formular Prill	90% sulphur, 10% bentonite 
Sulphur content	91.74 % wt
Dispersion rate	0.70 % wt / min
*Conversion to sulfate after 45days curing	35.52 mg S ₀₄ -S/kg of soil

Sulphur bentonite (B20)	
Formular Prill	80% sulphur, 20% bentonite 
Sulphur content	81.62 % wt
Dispersion rate	5.70 % wt / min
*Conversion to sulfate after 45days curing	58.49 mg S ₀₄ -S/kg of soil

Sulphur bentonite (B30)	
Formular Prill	80% sulphur, 20% bentonite 
Sulphur content	71.95 % wt
Dispersion rate	1.08 % wt / min
*Conversion to sulfate after 45days curing	30.40 mg SO ₄ -S/kg of soil

Sulphur-PCH (PCH7)	
Formular Prill	93% sulphur, 7% PCH 
Sulphur content	93.90 % wt
Dispersion rate	N/A
*Conversion to sulfate after 45days curing	1.99 mg SO ₄ -S/kg of soil

Sulphur-PCH (PCH10)	
Formular	90% sulphur, 10% PCH
Prill	
Sulphur content	91.63 % wt
Dispersion rate	N/A
*Conversion to sulfate after 45days curing	0.45 mg S ₀₄ -S/kg of soil

Sulphur-PCH (PCH12)	
Formular	88% sulphur, 12% PCH
Prill	
Sulphur content	88.75 % wt
Dispersion rate	N/A
*Conversion to sulfate after 45days curing	0.54 mg S ₀₄ -S/kg of soil

* Conversion to sulfate base on 500 mg of sulphur fertilizer per 3 kg of soil

Appendix D Soil Planted Soybean Plantation

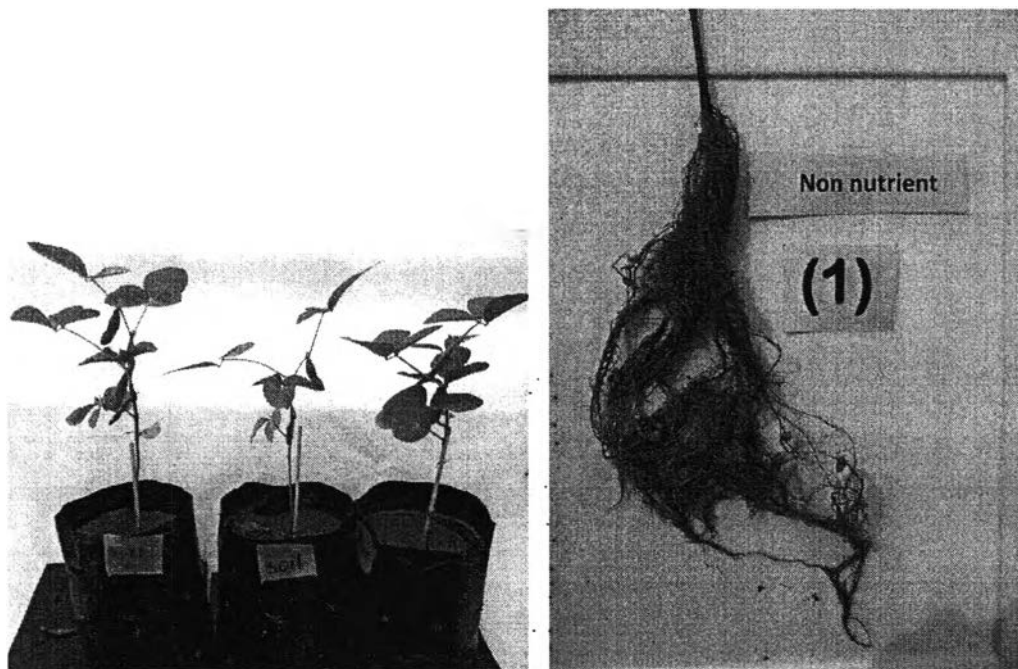


Figure D1 Non nutrient treatment.

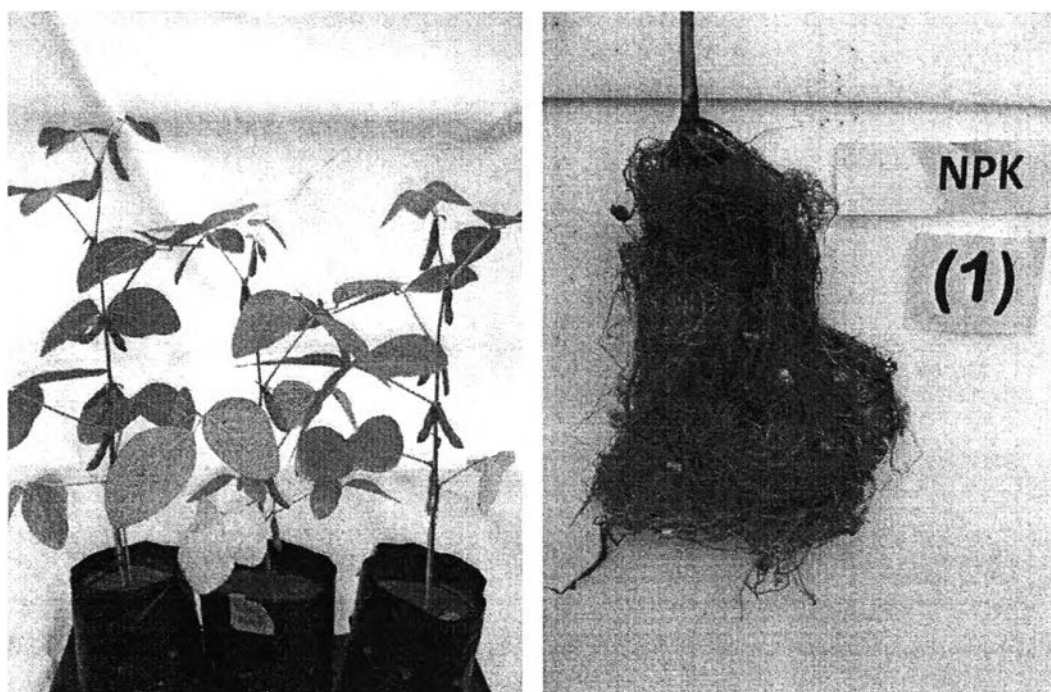


Figure D2 NPK treatment.

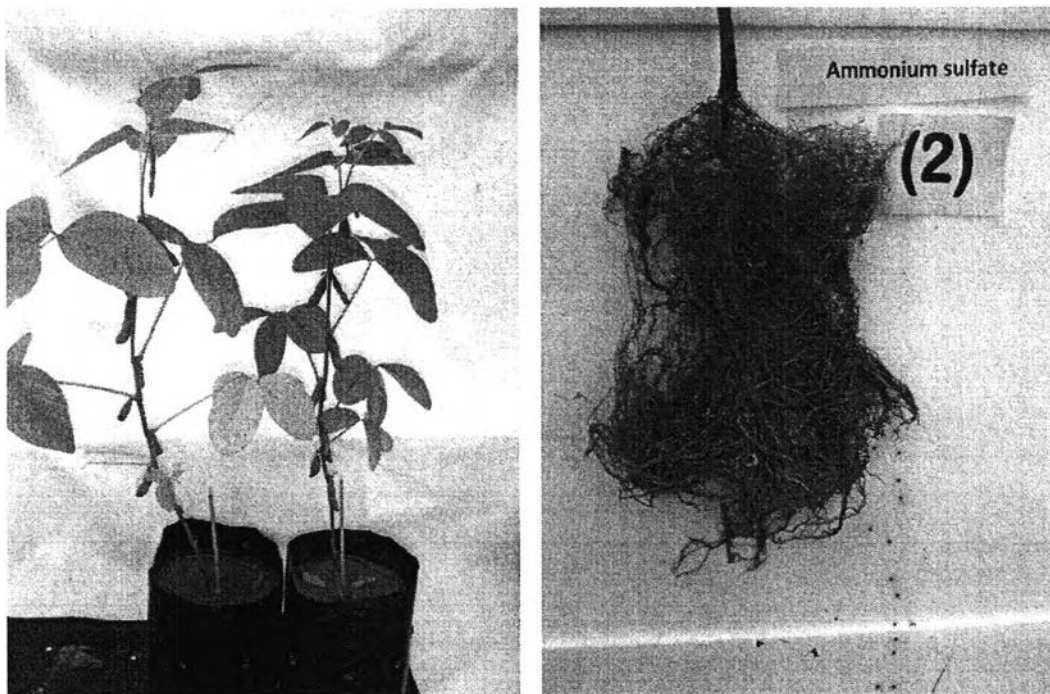


Figure D3 Ammonium sulfate treatment.



Figure D4 Sulphur bentonite (B10) treatment.

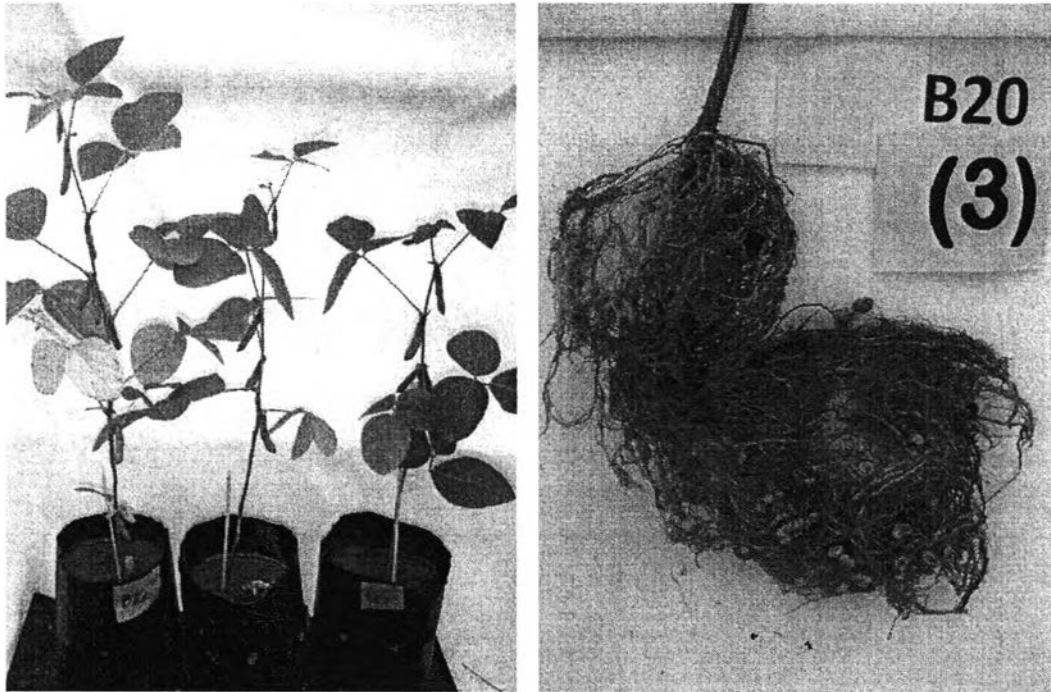


Figure D5 Sulphur bentonite (B20) treatment.

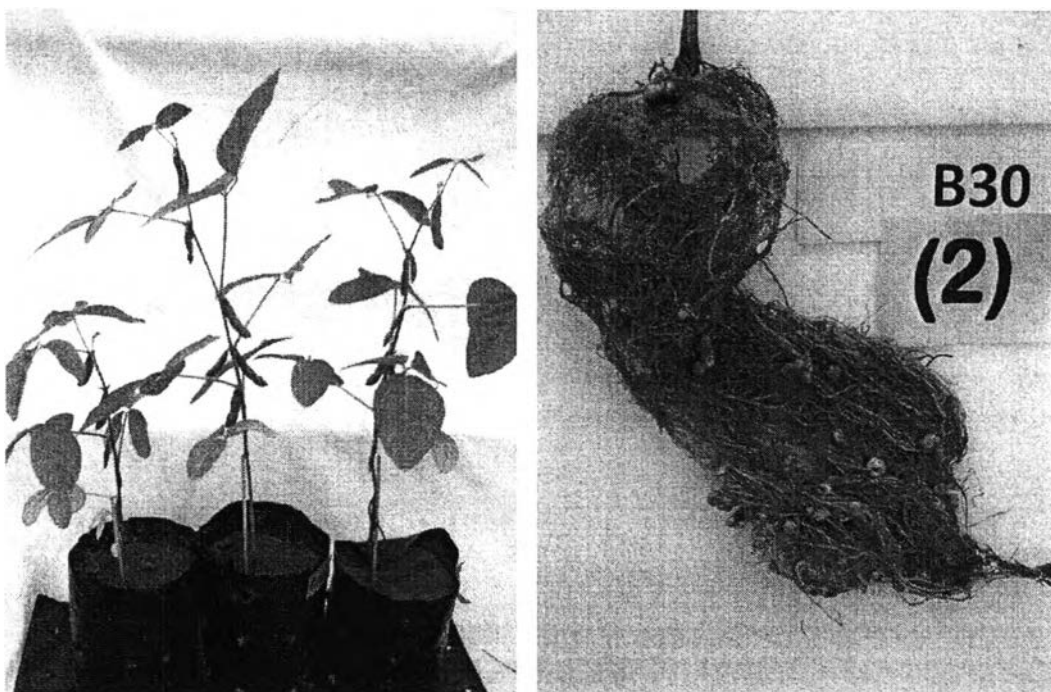


Figure D6 Sulphur bentonite (B30) treatment.

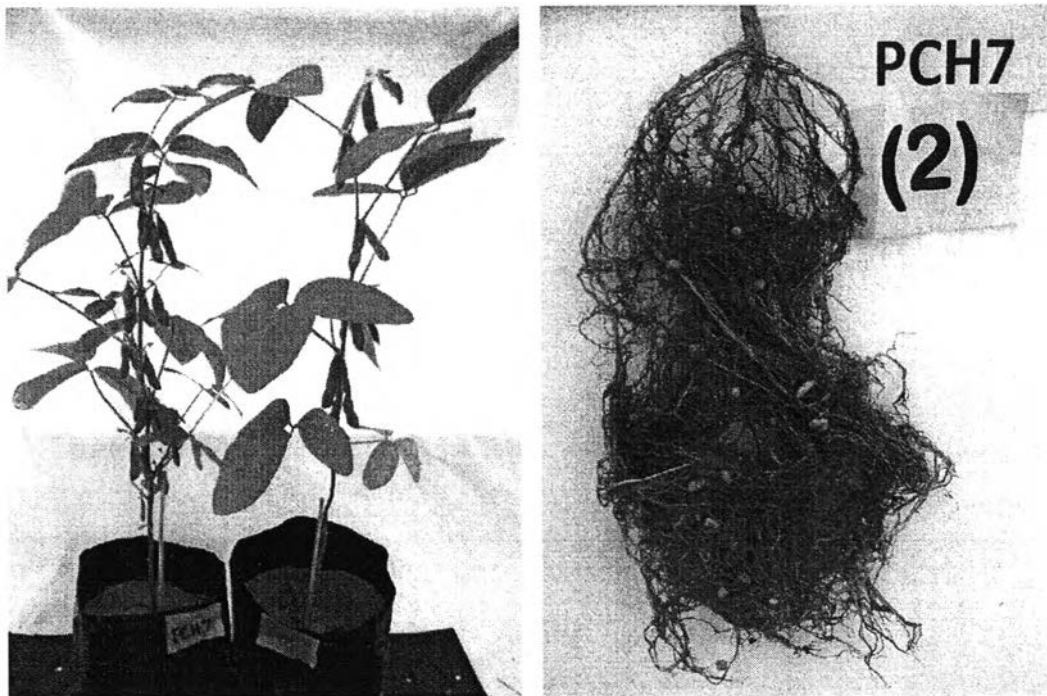


Figure D7 Sulphur-PCH (PCH7) treatment.

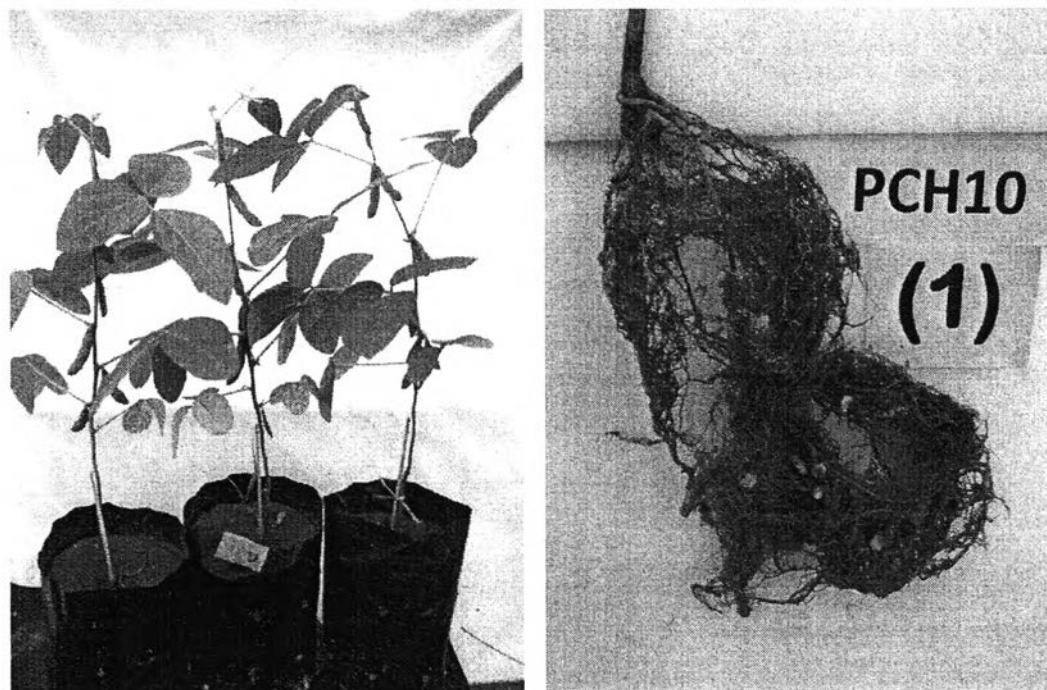


Figure D7 Sulphur-PCH (PCH10) treatment.

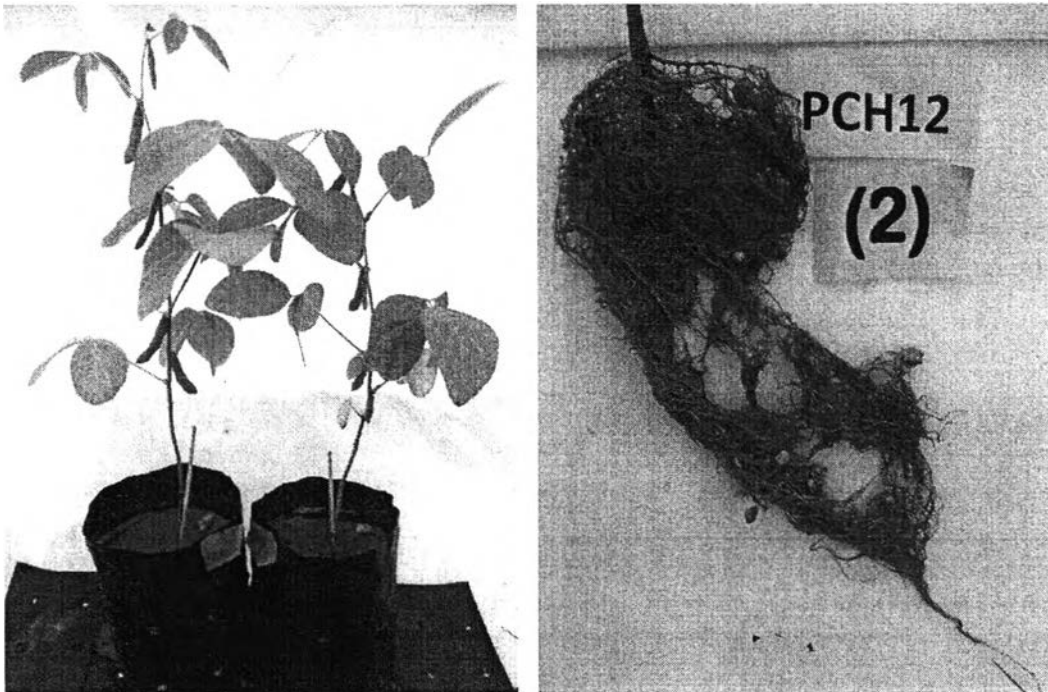


Figure D7 Sulphur-PCH (PCH12) treatment.

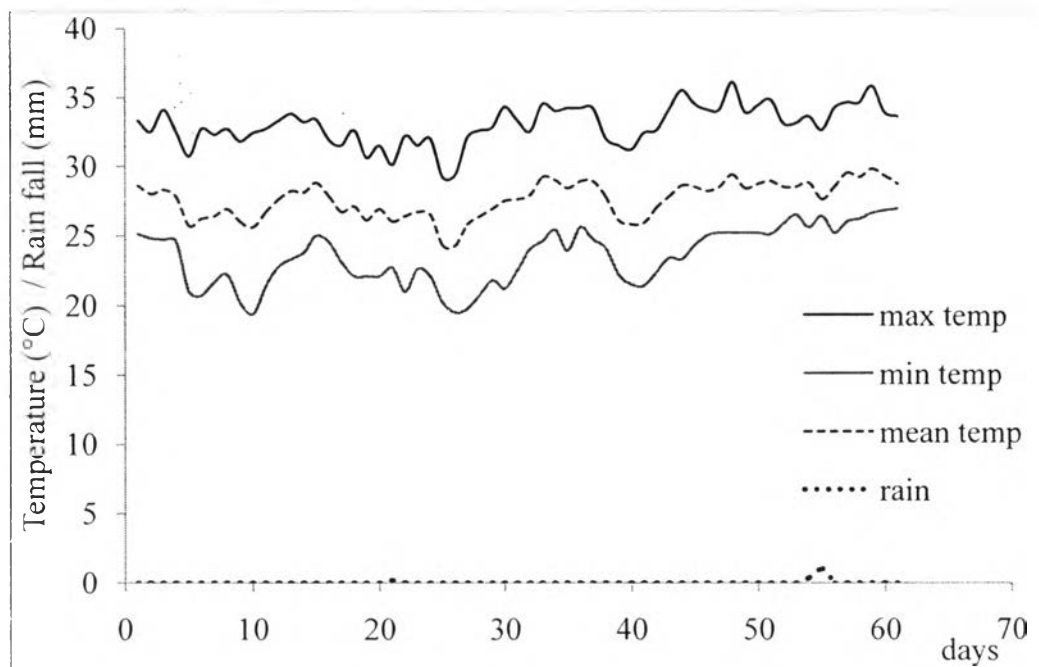


Figure D8 Temperature and rain fall during plantation from 23/10/2010 to 21/2/2011.

source: Thai Meteorological Department

Appendix E Water Planted Soybean Plantation

Sand preparation

Sandy was sieved pass 1 mm sieves, It was treated with 0.25 N of HCl for 24 hr. After that it was washed with deionised water many times until sand pH approximately 5. The treated sand was neutralized by using 0.1 N NaOH until sand pH approximately 6.5. It was air dried for 5 days or until it completely dry.

Free sulphur nutrient solution

Non sulphur nutrient solution was prepared in a 20L of gallon for watering soybean in the growing season. The solution was prepared from free sulphur fertilizer, it composed of:

KH_2PO_4	1 mM
KCl	50 μM
MgCl_2	25 μM
CaCl_2	25 μM
H_3BO_3	25 μM
MnCl_2	2 μM
ZnCl_2	2 μM
CuCl_2	0.5 μM .

source: Riley, N.G., *et al.*, 2000 and Mechteld, M.A., *et al.*, 1998

Planting method

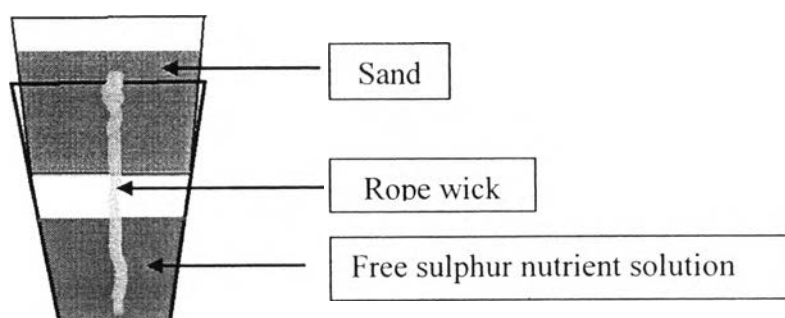


Figure E1 Water planted soybean plantation method.

Table E1 The 11 treatments of water planted soybean plantation

Sample	Non- Rhizobium	Nitrogen	Rhizobium
Non-sulphur	x	x	x
Sulphur			x
Sulfate fertilizer			x
B10			x
B20			x
B30			x
PCH7			x
PCH10			x
PCH12			x

Water Planted soybean plantation results

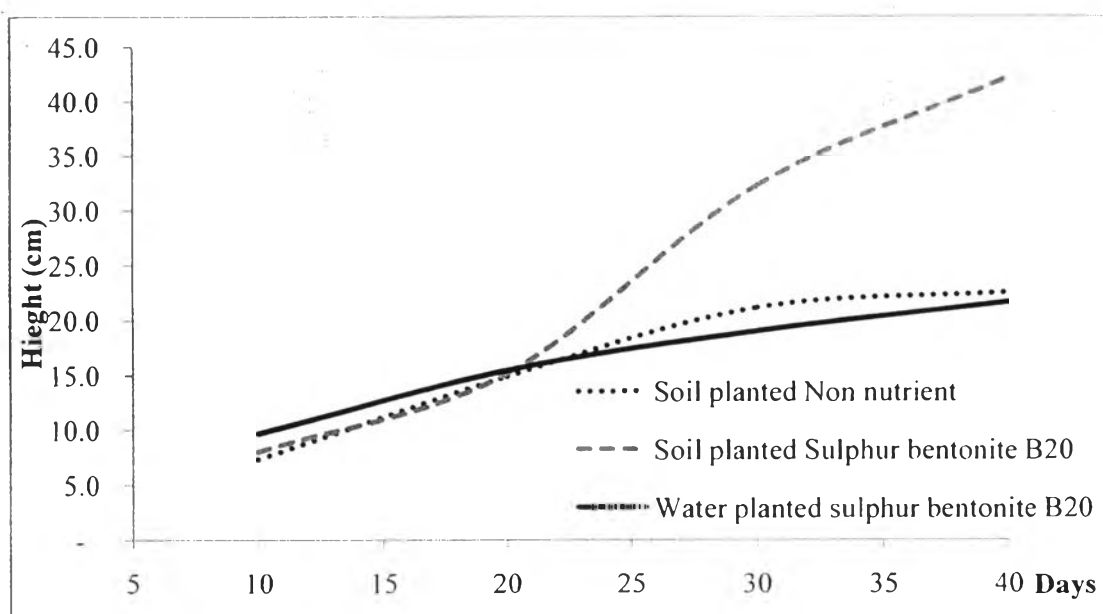


Figure E2 Comparison the growth rate of soybean of soil planted non nutrient, Soil planted sulphur bentonite B20 and water planted sulphur bentonite B20.

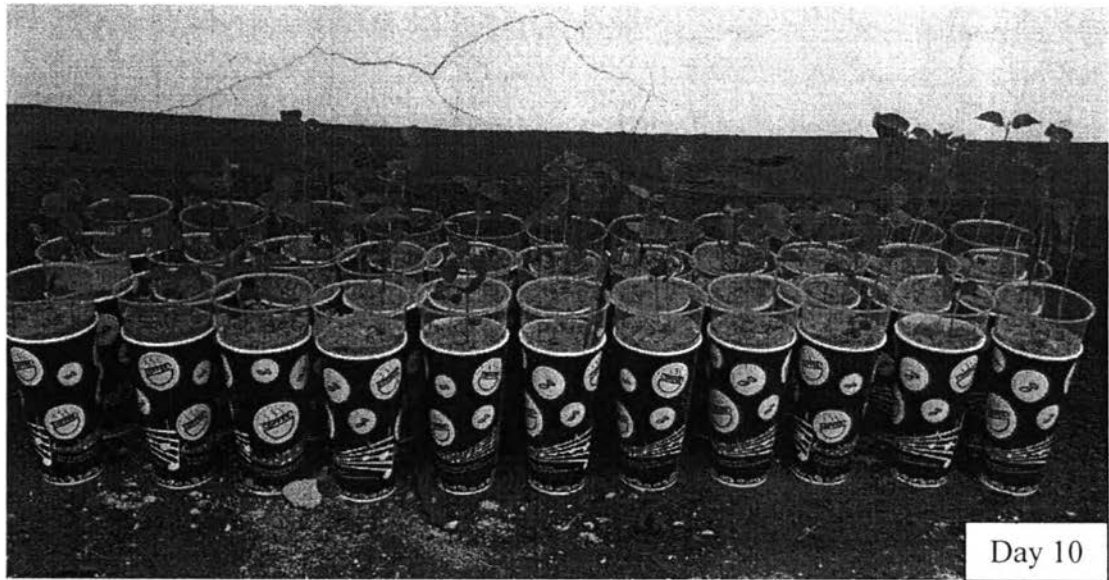


Figure E3 Water planted soybean plantation.

CIRRICULUM VITAE

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Proceedings:

1. Nuntawat, S.; Luengnaruemitchai, A.; Manuspiya, H.: and Magaraphan, R. (2011, January 5-7) Synthesis of Sulphur Bentonite as an Effective Liquid Sulphur Derivative. Proceedings of the PACCON2011, Bangkok, Thailand.
2. Nuntawat, S.; Luengnaruemitchai, A.; Manuspiya, H.: and Magaraphan, R. (2011, April 26) Sulphur Bentonite as an Effective Liquid Sulphur Derivative. Proceedings of the 2nd Research Symposium on Petroleum, Petrochemicals, and Advanced Materials and the 17th PPC Symposium on Petroleum, Petrochemicals, and Polymers, Bangkok, Thailand.

