



## CHAPTER V

### SYNTHESIS OF SULPHUR BENTONITE FERTILIZER

#### 5.1 Abstract

Bentonite clay was modified to organoclay and porous clay heterostructure (PCH), respectively. Each clay was mixed with liquid sulphur to obtain elemental sulphur fertilizer: sulphur bentonite, sulphur-organoclay, and sulphur-PCH, with content of clays 10–30 wt%. Mixture was mixed at 140–150°C for 2 h. After that the mixture formed the structure of the prill by dipping pass through the hold with 2 mm diameter and continuously dipped on the cooling plate, the droplets were quickly cooled on a cooling plate. The pelletizing process was successfully produced sulphur bentonite with bentonite contents of 10, 20, and 30 wt%. In the case of sulphur-PCH, the formulas were successfully synthesized only for contents of PCH in the range of 7 to 12 wt%.

The sulphur bentonite was characterized by using scanning electron microscope (SEM). When the bentonite content increased from 10 to 30 wt%, the bentonite phase was clearly observed. The dispersion of bentonite and PCH in the sulphur matrix was relatively uniform and free from aggregation. In the case of sulphur-PCH, SEM micrographs were different because a portion of sulphur matrix going inside pore and void of PCH and some of a sulphur portion remain coated on the surface of PCH. The evident of SEM-EDX images and the density map showed the combination of silicon and sulphur.

#### 5.2 Introduction

The world demand of sulphur for agricultural use has grown rapidly in recent years, as farmers seek to replace the sulphur that was previously deposited as 'free nutrient' from the atmosphere. Every year, 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 (Scherer, 2001). So the sulphur fertilizers are required

for soil supplement. Elemental sulphur, although available in large quantities, cannot be used as a nutrient mainly because it is not soluble in water. A granule of elemental sulphur, therefore, takes a very long time before it actually releases into the soil (Riley *et al.*, 2000). The solution for this problem is to combine elemental sulphur with bentonite, a type of clay that increases its volume by a factor of 3 to 5 when it comes into contact with water. For preparing sulphur bentonite, a molten sulphur has been mixed with bentonite to form a safe and easy to apply product. The principle is that when the clay absorbs water and swells, it makes the prill fracture and disperses into small particles of sulphur (Boswell *et al.*, 1988).

### 5.3 Experimental

#### 5.3.1 Materials

Sulphur (99.99%) was collected from a Thai oil plant from Thai Oil Co., Ltd. Na-Bentonite, (Mac-Gel® GRADE SAC), was obtained from Thai Nippon Chemical Industry Co., Ltd. The cation exchange capacity (CEC) of bentonite is 100 mmol/100g of clay. PCH and Organoclay prepared from modification of bentonite.

#### 5.3.2 Preparation of Sulphur Bentonite Fertilizer

There were 3 formulas of sulphur bentonite: (1) bentonite+sulphur (BS<sup>o</sup>), (2) organoclay+sulphur (OS<sup>o</sup>), (3) PCH+sulphur (PCHS<sup>o</sup>). The synthesis of organoclay and PCH was described in chapter IV of this report. Each formula was divided into 3 compositions of clay: 10, 20, 30 % of clay (w/w).

Clays and sulphur mixture was stirred by a mixing stirrer in a mixing chamber at 140°C (Caldwell, 1979) for 2 h. Then a droplet of the mixture was formed immediately, the droplets of mixture were dipped on a stainless steel plate to obtain sulphur bentonite fertilizer.

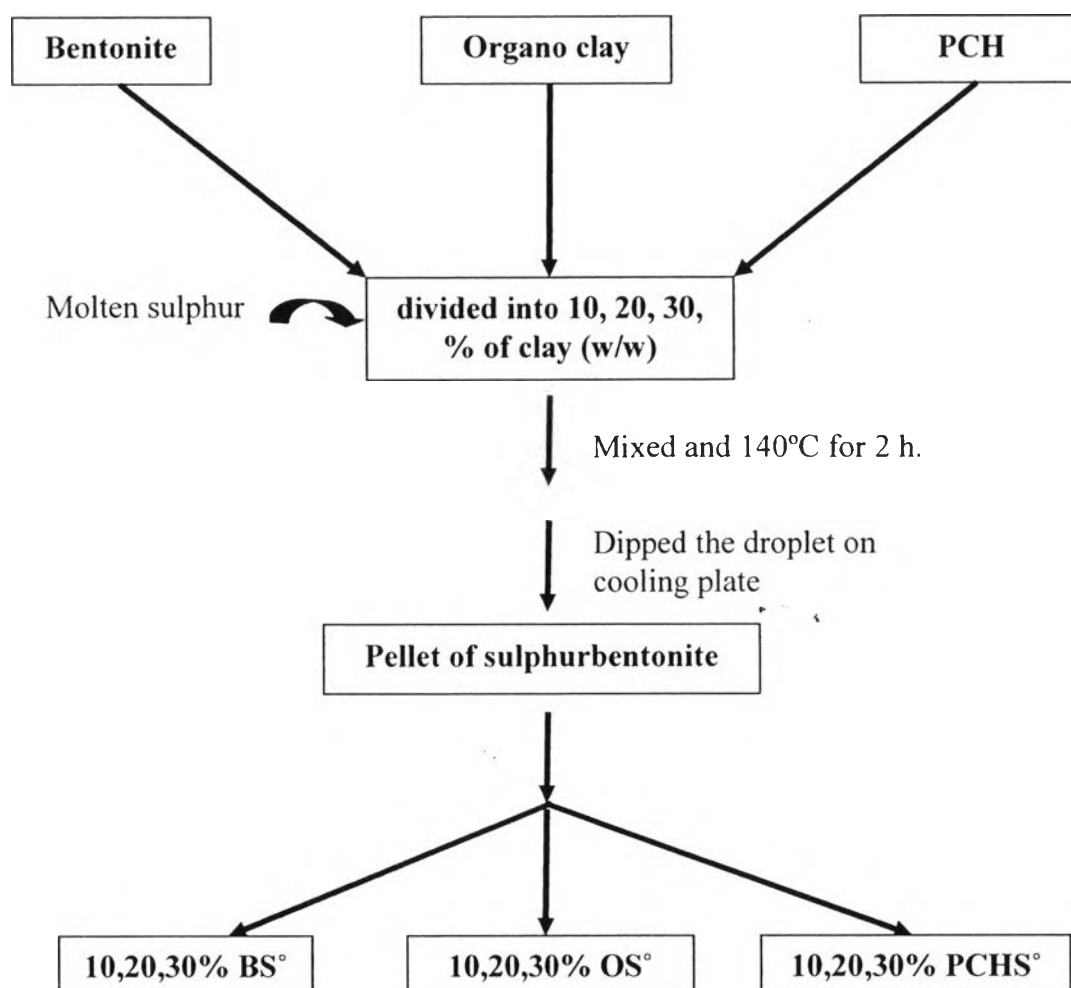


Figure 5.1 Preparation procedure of sulphur bentonite fertilizer.

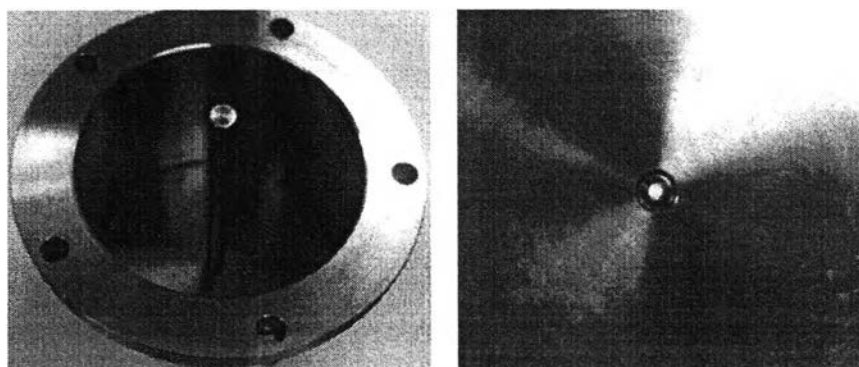
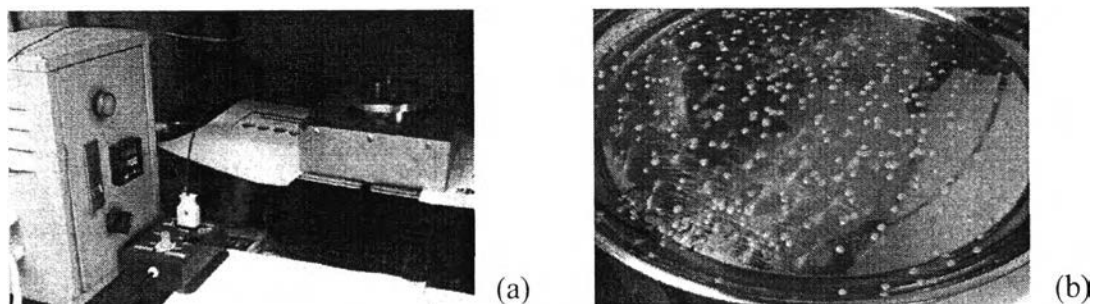


Figure 5.2 Mixing chamber perforated with hole diameter of 2 mm.



**Figure 5.3** Mixing chamber with temperature controller set (a) and forming sulphur bentonite prills on stainless steel plate (b).

### 5.3.3 Characterization

X-ray diffraction patterns were measured on a Rigaku Model Dmax 2002 diffractometer with Ni-filtered Cu  $K_{\alpha}$  radiation operated at 40 kV and 30 mA. The powder samples were observed on the  $2\theta$  range of 2–10 degree with a scan speed of 2 degree/min and a scan step of 0.02 degree.

Scanning electron microscopy (SEM) and Energy-dispersive x-ray spectroscopy (EDX) were performed on Hitachi S-4800 model. The specimens were coated with platinum under vacuum to make them electrically conductive.

## 5.4 Results and Discussion

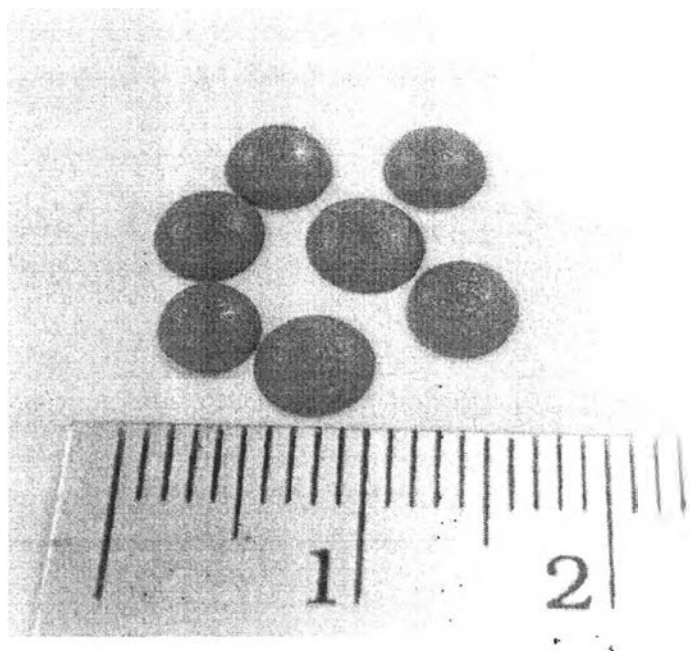
### 5.4.1 Formulation of Sulphur Bentonite Prills

Sulphur and bentonite were mixed in the chamber at 140°C until fully homogenous, after that the mixture was allowed to flow pass through the hole with 2 mm. diameter and continuously dipped on the cooling plate. The mixture was rapidly cooled by the room temperature to form a prill shape on a stainless steel plate. The size of prills depended on viscosity of mixture, bentonite content, and temperature during mixing process. The higher viscosity of mixture, the smaller size of prill was obtained. Due to the limitation of viscosity, high bentonite content caused high viscosity of mixture. Exaggerate high viscosity of mixture could not flow pass through the perforated hole. The bentonite content did not affect to viscosity as much

as PCH did, because PCH had high surface area, pore volume, and low density. When content of PCH was higher than 13 wt%, the mixture could not flow by itself. Consequently, 3 formulas of sulphur-bentonite (10, 20, 30 wt% bentonite) and 3 formulas of sulphur-PCH (7, 10, 12 wt% PCH) were obtained. Formation of sulphur and organoclay was not successful due to the changing of mixture's color from brown to black and it release smell during formulation at 140–150°C. This is due to the presence of CTAB in the inter gallery of organoclay, which was slowly degraded after mixing for 5 minutes. Therefore, organoclay was not suitable for making sulphur bentonite fertilizer.

**Table 5.1** Formulation of sulphur bentonite prill

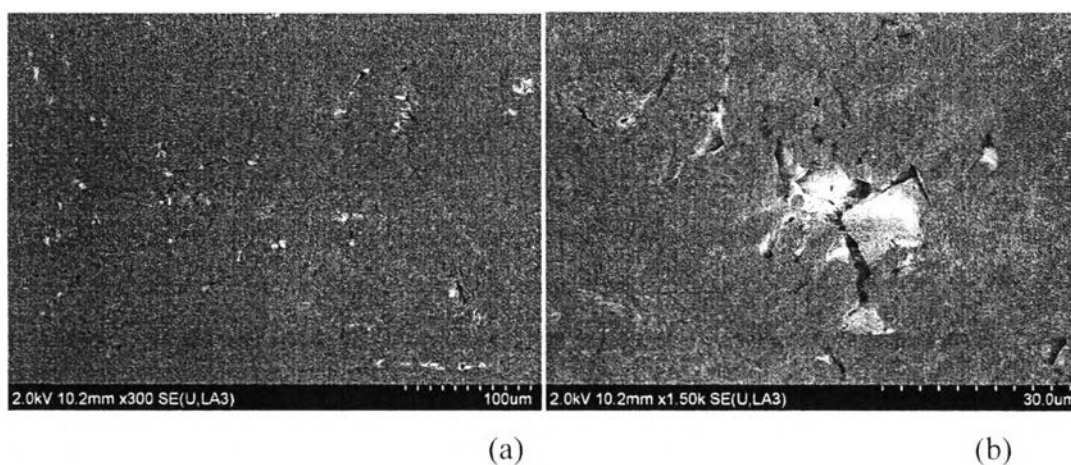
Clay	Clay's content (wt%)	Prill	Color	Note
Bentonite	10	✓	brown	
	20	✓	brown	
	30	✓	brown	
Organoclay	10	✓	black	Released smell
	20	✓	black	
	30	✓	black	
PCH	7	✓	brown	
	10	✓	brown	
	12	✓	brown	
	20	x	brown	

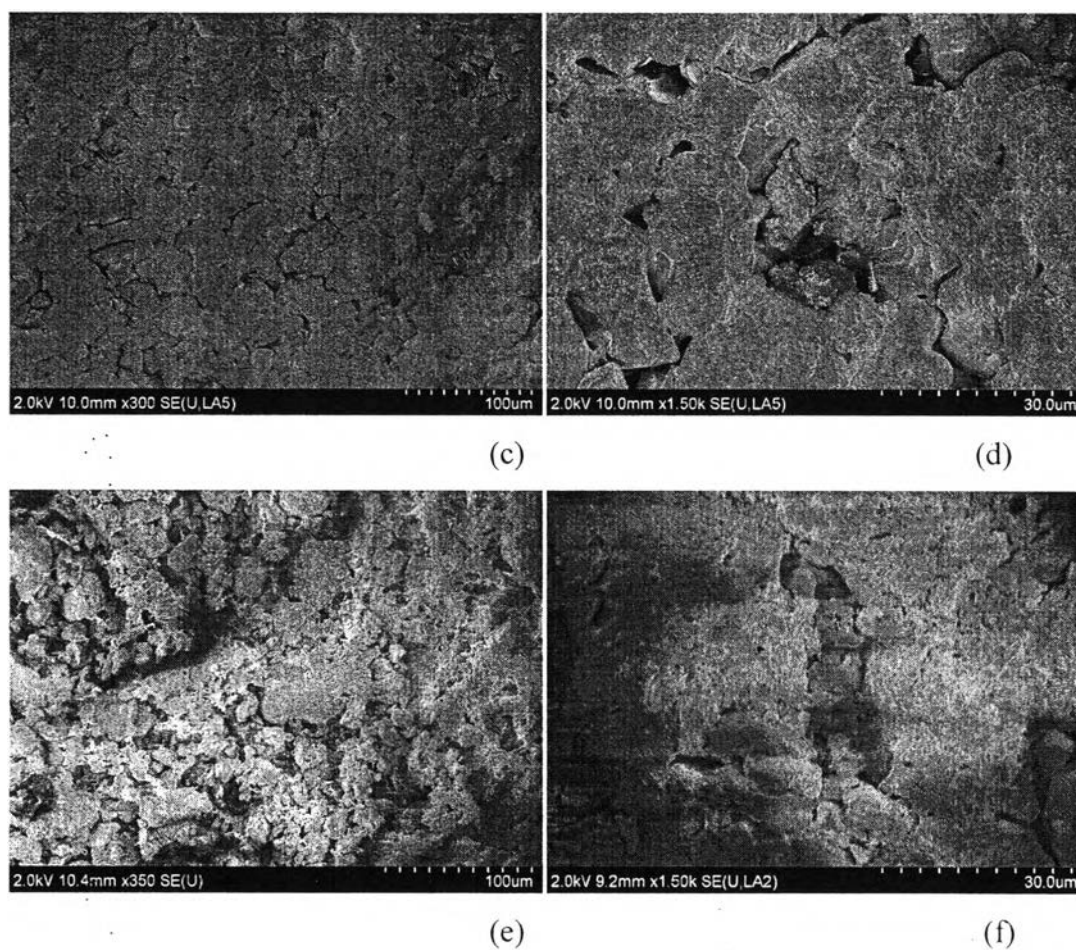


**Figure 5.4** Sulphur bentonite prill, 30 wt% of bentonite content.

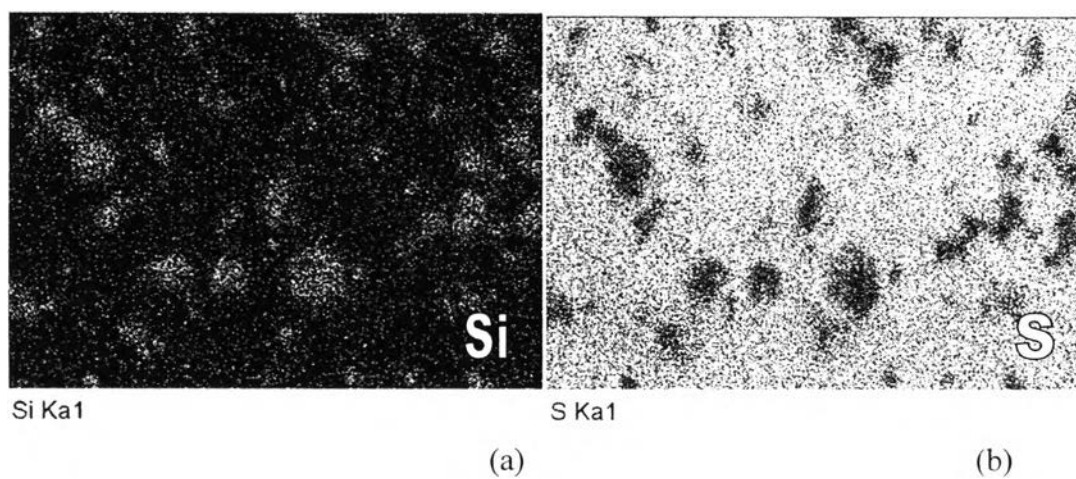
#### 5.4.2 Prill Structure

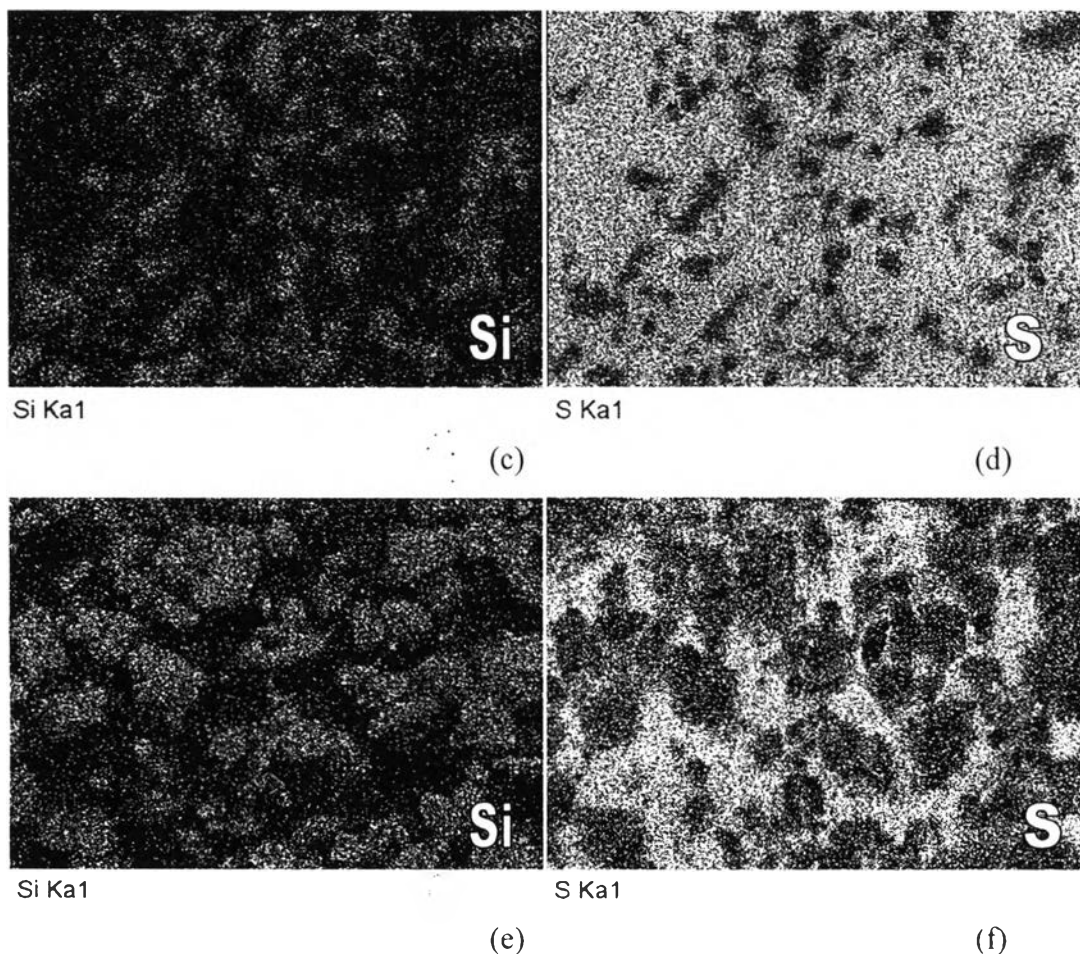
Sulphur formed the matrix of the prill and the amount of bentonite was held within it. When bentonite content increased from 10 to 30 wt% (Figure 5.5 (a)-(f)), the bentonite phase was clearly observed. From the evident of SEM-EDX images (Figure 5.6 (a)-(f)), almost all of our evidence suggests that the dispersion of bentonite and PCH in the sulphur matrix was relatively uniform and free from aggregation. Sulphur matrix and bentonite was clearly separated and sulphur matrix just covered around the bentonite particle.





**Figure 5.5** SEM images of (a) and (b) sulphur bentonite (10 wt% of bentonite), (c) and (d) sulphur bentonite (20 wt% of bentonite), (e) and (f) sulphur bentonite (30 wt% of bentonite) with magnification x300 and x1500, respectively.

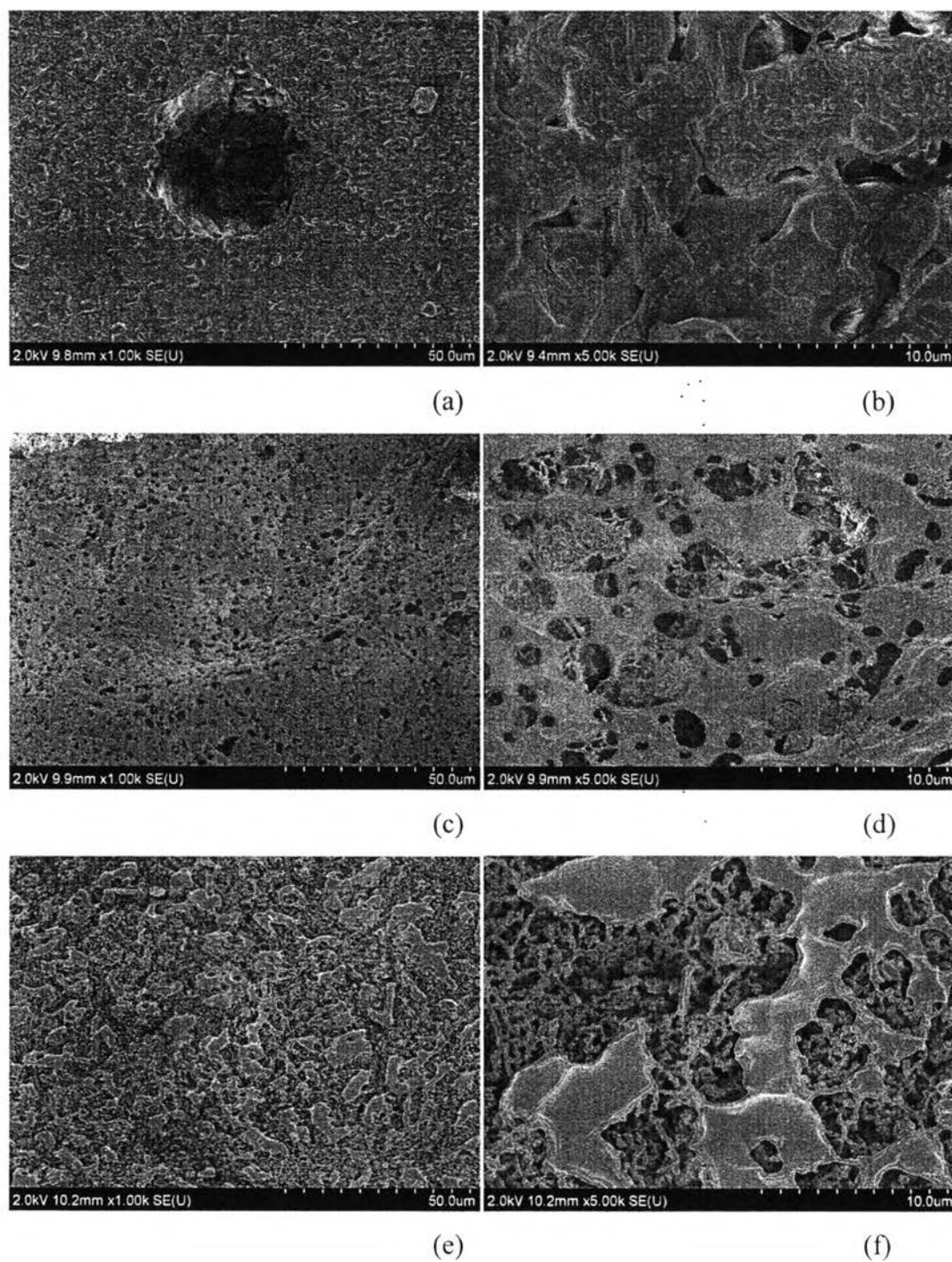




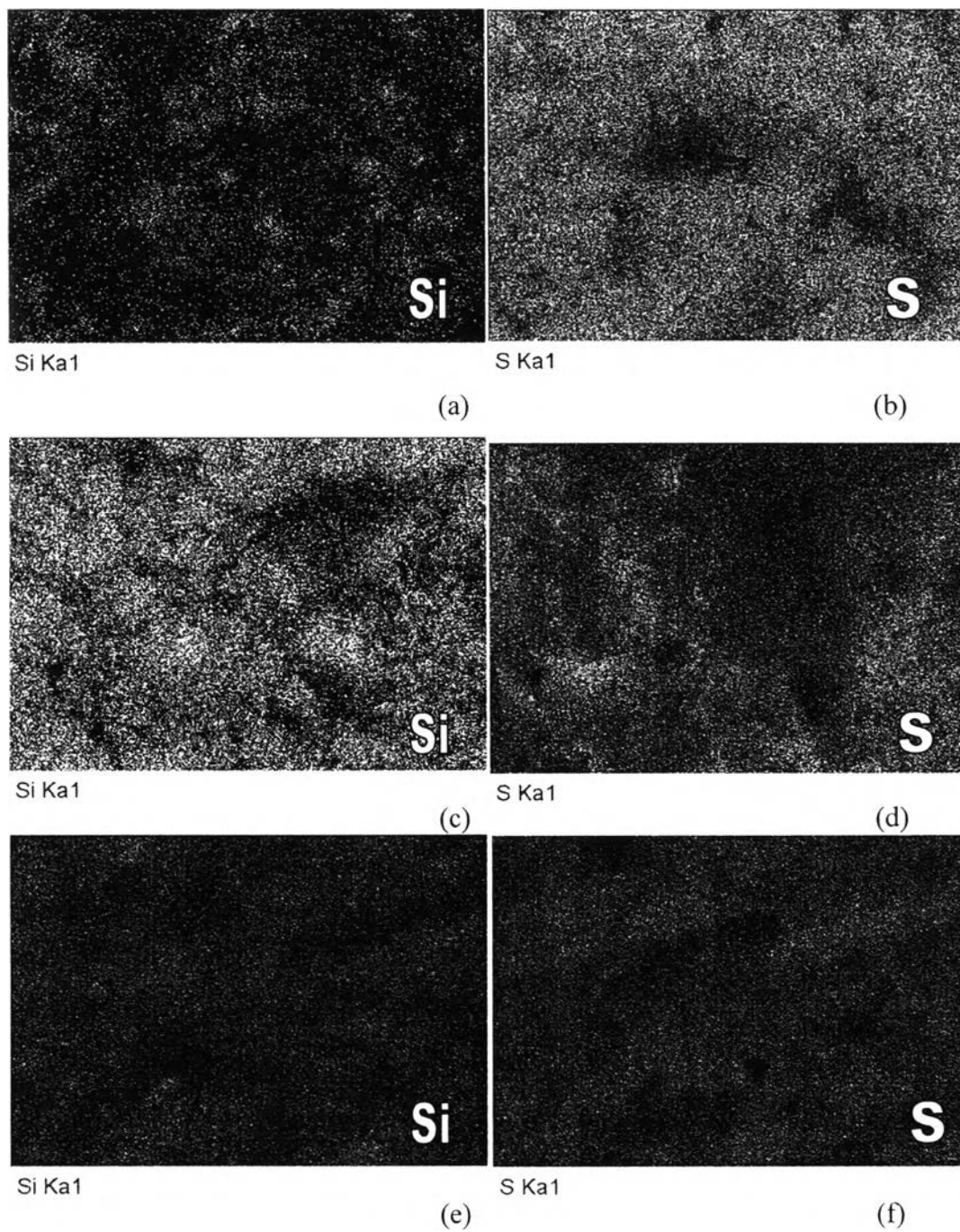
**Figure 5.6** EDX density map of sulphur bentonite prill showed silicon (left) and sulphur (right) , which contain (a) and (b) 10 wt% of bentonite, (c) and (d) 20 wt% of bentonite, (e) and (f) 30 wt% of bentonite with magnification x700.

In the case of Sulphur-PCH, micrographs were different and a portion of sulphur matrix was inside the pore and void of PCH. The other portion of the remaining covered on the surface of PCH (Figure 5.7 (a)-(f)). The evident of SEM-EDX images (Figure 5.8 (a)-(f)), represents the density map showing the combination of Si and S.





**Figure 5.7** SEM image of (a) and (b) sulphur-PCH (10 wt% of PCH), (c) and (d) sulphur-PCH (20 wt% of PCH), (e) and (f) sulphur-PCH (30 wt% of PCH) with magnification x300 and x1500, respectively.



**Figure 5.8** EDX density map of sulphur-PCH prill showed silicon (left) and sulphur (right) , which contain (a) and (b) 10 wt% of PCH, (c) and (d) 20 wt% of PCH, (e) and (f) 30 wt% of PCH with magnification x700.

## 5.5 Conclusion

The pelletizing process was limited by bentonite contents, pore volume of clay, and viscosity of mixture. This work successfully prepared novel sulphur bentonite fertilizer and sulphur-PCH fertilizer in pellet form. While, the sulphur-organoclay was not successfully prepared because of the degradation of existing surfactant. Consequently, 3 formulas of sulphur-bentonite (10, 20, 30 wt% bentonite) and 3 formulas of sulphur-PCH (7, 10, 12 wt% PCH) were obtained. Fertilizers derived by sulphur bentonite and sulphur-PCH require testing the physical properties, the dispersibility and the control release of sulphur in the next works.

## 5.6 Acknowledgements

The author would like to thank The petroleum and petrochemical college, Chulalongkorn University, The National Excellence Center for Petroleum, Petrochemicals, and Advance Materials for research funding. In addition, the authors wish to thank Thai-Niponchemical Co., Ltd. for supporting bentonite clay and Thairoil for supporting liquid sulphur sample.

## 5.7 References

- Boswell, C.C., Owers, W.R., Swanney, B., and Rothbaum, H.P. (1988). Sulfur/sodium bentonite mixtures as sulfur fertilizers. 1. The effects of S/Na-bentonite ratios on the rate of dispersion and particle size distribution of elemental sulfur dispersed from laboratory-produced prills. Fertilizer Research, 15, 13–31.
- Caldwell, B.L. (1979). Process for pelletizing a sulphur-bentonite clay mixture and the product formed thereby. U.S. Patent 4,133,669, filed April 20, 1977, and issued January 9, 1979.
- Riley, N.G., Zhao, F.J., and McGrath, S.P. (2000). Availability of different forms of sulphur fertilisers to wheat and oilseed rape. Plant and Soil, 222, 139–147.

Scherer, H.M (2001). Sulphur in crop production—invited paper. European Journal of Agronomy, 14, 81-111.