HYDROGEN SULFIDE ADSORPTION BY POLYETHYLENE FOAM

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การดูดซับแก๊สไฮโดรเจนซัลไฟด์โดยใช้โฟมพอลิเอทีลีน

ทศพล ทองคำ

ปริญญานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตร
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Title	Hydrogen Sulfide Adsorption by Polyethylene Foam
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Field of Study	Petrochemical Engineering
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Abstract

Hydrogen sulfide gas (H_2S) can causes a number of problems whether environmentally hazardous, corrosive, or toxic gas. In this study, the characterizations and performances for hydrogen sulfide gas removal in bio gas storage was evaluated using ferric oxide-polyethylene foam (Fe_2O_3-PE foam). To accomplish this, the simulating hydrogen sulfide gas was produced by reaction of ferric sulfide and hydrochloric acid. This gas was generated and passed through Fe_2O_3-PE foams which were prepared in different ratio of mixing (40%, 50% and 60% weight/weight of Fe_2O_3-PE foam). The system for this study was designed as a close system at ambient temperature and pressure. The remaining hydrogen sulfide content gas was recorded for each polymer foam types at different amount foam loading. From the experiment results, Fe_2O_3-PE foam with expansion ratio of 2.6 – 3.1 times could be applied to remove H_2S gas. As expected, high loading of Fe_2O_3 as 50-60% revealed drastically removal of H_2S gas.

Keyword: H_2S removal, Polyethylene foam

เรื่อง	การดูดซับแก๊สไฮโดรเจนซัลไฟด์โดยใช้โฟมพอลิเอทีลีน
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บทคัดย่อ

ก๊าซไฮโดรเจนซัลไฟด์ (H_2S) สมารถทำให้เกิดผลกระทบได้หลายอย่าง ไม่ว่าจะเป็นก๊าซที่เป็นอันตรายต่อสิ่งแวดล้อม มีความกัดกร่อนสูง หรือเป็นพิษต่อสิ่งแวดล้อม จึงได้ทำการศึกษาลักษณะและประสิทธิภาพ ในการกำจัดแก๊สไฮโดรเจนซัลไฟด์ในก๊าซชีวภาพ โดยใช้โฟมผสม พอลิเอทิลีน-เฟอร์ริกออกไซด์ (Fe_2O_3-PE foam) เพื่อให้บรรลุจุดมุ่งหมายนี้ แก๊สไฮโดรเจนซัลไฟด์จะถูกจำลองได้เกิดขึ้นจากปฏิกิริยาของเฟอร์ริกซัลไฟด์ และกรดไฮโดรคลอริก ก๊าซนี้ถูกสร้างขึ้นและถูกส่งผ่านโฟม Fe_2O_3-PE ที่เตรียมในอัตราส่วนของการผสม ที่แตกต่างกัน (40%, 50% และ 60% โดยน้ำหนักของโฟม Fe_2O_3-PE) ระบบการศึกษานี้ได้รับการออกแบบให้เป็นระบบแบบปิดที่อุณหภูมิและความดันบรรยากาศ ปริมาณก๊าซไฮโดรเจนซัลไฟด์ที่เหลือถูกบันทึกไว้สำหรับแต่ละโฟมพอลิเมอร์ชนิดต่างๆ จากผลการทดลองพบว่าโฟม Fe_2O_3-PE มีอัตราการขยายตัว 2.6 - 3.1 เท่าและสามารถลดไฮโดรเจนซัลไฟด์ได้ และตามที่คาดไว้ปริมาณของการผสม Fe_2O_3 ที่ 50-60% แสดงให้เห็นว่ามีการลดแก๊สไฮโดรเจนซัลไฟด์ได้อย่างมาก

คำสำคัญ: การกำจัดแก๊สไฮโดรเจนซัลไฟด์, พอลิเอทิลีนโฟม

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Thodsapon Thongkam

Table of Contents

Table of Contents (CONT.)

List of Figures

List of Tables

CHAPTER I
INTRODUCTION

1.1 Significant and background

Discharged waste water from various industries has different compositions which depend on industrial type. For example, waste water from still mill contains heavy metal or toxic substances waste water from chemical plant. Thus they have several methods for waste water treatment such as precipitation, filtration, adsorption or ion-exchange which is selected and applied for specific source. Waste water sources are regularly controlled by industrial supervisor for ineffective to environment which means higher expenditure. Some of industrial can use discharged waste water as benefit which use as energy source. Mentioned industrials are generally operating about food, ranch, manure, agriculture or harvesting that regularly has fermentation system for biogas generation.

Biogas is one of renewable energy that can be generated by anaerobic digestion of biodegradable materials. The ordinary methods of biogas production are landfill or gas covering storage for waste water. This biogas is widely used as energy source for electricity production in power plant. Main composition in biogas is methane gas approximately 50-70% and other compositions such as carbon dioxide, nitrogen, hydrogen, oxygen and hydrogen sulfide [1]. The significant problem of using biogas is tiny amount of hydrogen sulfide gas can damages equipment for production line [2, 3].

Hydrogen sulfide gas (H_2S) can cause several problems such as high corrosive, air pollutant and also health risk that must be considered. H_2S must be treated and removed as least 4 parts per million volumes (ppmv) [4]. As well as, high content of H_2S in feed bio gas steam means low energy gain for power generation [5]. For H_2S removal from waste water, adsorption process is widely used which high effectiveness and economical expenses. They have several studies and report that H_2S can be reduced from the system by reaction of ferric oxide (Fe_2O_3) inside adsorbents and converted to ferric sulfide (FeS). The reaction can also be regenerated to Fe_2O_3 for reusing when exposed to oxygen or air.

Nowadays, commercial Fe_2O_3 adsorbent such as iron sponge, Media-G2, CG-4, activated carbon [6] were created as very uniform pore size and high pore volume inside and it normally be placed in a pack column. Polymer foam such as polyethylene foam is one of good Fe_2O_3 adsorbent by many suitable properties which not only high pore volume and pore size uniformity but also stable in high acid/base condition [7] and economical cost. The withstanding of extreme condition properties of polymer foam were suitable for our work because of it will be floated on waste water source at high temperature and acidity as well.

In this study, hydrogen sulfide gas reduction from waste water is main objective which achieved by using polyethylene foam with ferric oxide inside. For experiment, polyethylene beads and ferric oxide powder were perfectly compounded at mixing ratio 40% wt/wt, 50% wt/wt and 60% wt/wt. After that, they are transformed to Fe_2O_3-PE compounded foam by soaking carbon dioxide gas as physical foaming process. The H_2S removal effectiveness was investigated by using gas detector at ambient conditions in close system batch experiment. Fe_2O_3-PE compounded foam characteristic results were analyzed by scanning electron microscope (SEM) technique.

1.2 Objectives

1.2.1 To study polymeric foam processing and equipment
1.2.2 To study polymeric properties of Fe_2O_3-PE compounded foam
1.2.3 To study hydrogen sulfide removal and it relevant reactions

1.3 Scopes of work

1.3.1 Find suitable ratio of mixing between polyethylene beads and ferric oxide powder for polymer foaming process
1.3.2 Apply in laboratory scales of high H_2S content removal

1.4 Expected outputs

1.4.1 High pore volume and uniform of pore size
1.4.2 Considerable adsorption performances

CHAPTER II
THEORY AND LITERATURE REVIEW

2.1 Introduction of hydrogen sulfide

Hydrogen sulfide (H_2S) can be mainly generated from natural source or industrial which almost released from refining and coal gasification process. Tiny amount of this gas can cause several health effects by exposure and highly damages to equipment, pipe lines or catalysts in manufacturing. Therefore, treatment processes must require for meeting environment regulation (concentration must be less than 4 ppm [4]) before releasing. Moreover, H_2S can combines to rain and formed as acid rain thus several sulfur removal processes are developed and applied. The suitable method allow for many factors e.g., gas composition, volume, pressure, and temperature. For large scale of H_2S removal process set front of Claus process which can removes H_2S from gaseous phase and changes to harmless form. For small scale removal, Claus process is not proper used because of high operation cost and plenty of complex procedures. The suitable H_2S removal ways for small scale include of adsorption, absorption, or biological method. The adsorption by adsorbents method is widely used because high effective and simply operation.

2.1.1 Hydrogen sulfide properties

Characteristics of H_2S are colorless, extremely toxic and flammable. Identification bad odor same as rotten eggs. H_2S can cause several symptoms such as headache, cough, eye irritation, insomnia by exposure small doses. Human can be fatal in five minutes by 1,000 ppm exposure [8]. H_2S gas can slightly dissolved in water and its solution is highly corrosive (pH value around 4.5) for entire equipment, production pipe lines and also damage to using catalysts as well.

2.1.2 Hydrogen sulfide content in bio gas

In biogas generation from fermentation process mainly produce methane gas as major energy source which small content of H_2S concentration approximately 0-3%v/v.

2.2 Typical methods for hydrogen sulfide removal

The sampling way for remove in aqueous systems such as estuaries, aquaculture ponds is precipitation of hydrogen sulfide with dissolve metal like iron, zinc, copper but we focus on H_2S removal in gaseous phase in this study that can generally be removed by two main technics that are H_2S adsorption and liquid H_2S removal processes.

2.2.1 Hydrogen sulfide adsorption processes

This method is widely used because simply operation that is occurs by contracting between adsorbents and hydrogen sulfide constituent. In many industrial, gases steam with hydrogen sulfide constituent was passed to adsorbents tower. So adsorbent type selecting is importance to evaluate eventually saturated of adsorbent media. Adsorbent tower generally consists of two vessels; one of them is operating while other is offline for regeneration. Absorption processes can classify for physical absorption and chemical absorption.

H_2S removal by chemical absorption generally is accomplished by using metal oxides such as ferric oxide, zinc oxide, barium oxide, zirconium oxide, etc [9]. These metal oxides reactions have been studied and widely used. Some of it reactions are shown below.

$$CaO\ (s) + H_2S\ (g) \rightarrow CaS\ (s) + H_2O\ (l) \quad (2.1)$$

$$ZnO\ (s) + H_2S\ (g) \rightarrow ZnS\ (s) + H_2O\ (l) \quad (2.2)$$

However, suitable operation conditions should be considered; ZnO reactions is proper for operation temperate lower than 100°C and CaO reactions for approximately 250-500°C. The best choice of metal oxide for H_2S removal at room temperature operation is ferric oxide (Fe_2O_3) reactions that are going to describe in next topic.

For physical H_2S adsorption requires proper physical properties, high surface area and also high pore volume are desired. Outstanding adsorbent for physical adsorption is set front of molecular sieves (zeolites) which high surface area and pore size. It can be generated in natural or synthesized by silicates/aluminate.

2.2.2 Liquid hydrogen sulfide removal processes

H_2S can be removed from gas steams into aqueous solution by contacting between each other by stripping process with high performance. However, element sulfur after process must be considered. Other method is biological treatment by using bacteria results in 99-100% efficiency of H_2S removal.

2.2.2.1 Stripping process

Water is commonly used in stripping process in industrial because of its commercial prices and easy source. Although H2S is slightly dissolved into water (0.4 %wt/wt at 20°C) but it is still available process.

$$H_2S\ (g) \rightarrow H_2S\ (aq) \leftrightarrow H^+ + HS^- \qquad (2.3)$$

H_2S in aqueous phase can be form as H^+ and HS^-. Absorption efficiency can increase by reducing of these two mentioned ions.

2.2.2.2 Biological treatment

Some of bacteria specie has ability can reduce H2S from system by oxidation reaction. These bacteria are coated into film as intermedia to form bio-filter. H_2S is absorbed into mentioned layer than oxidized in aerobic conditions. High efficiency of hydrogen sulfide removal around 99% was obtained by using this method.

$$H_2S\ (g) + 2O_2\ (g) \xrightarrow{\text{bacteria}} H_2SO_4\ (aq) \qquad (2.4)$$

Another biological treatment occurs in anaerobic system with light requirement. This treatment method can reduce H2S in system up to 100% [10]
by reaction below.

$$2H_2S\ (g) + CO_2\ (g) \xrightarrow[\text{bacteria}]{\text{light}} 2S + (CHO) + H_2O\ (l) \qquad (2.5)$$

2.3 Introduction of ferric oxide

(a) (b)

Figure 2.1 (a) Alpha phase ferric (III) oxide and (b) gramma phase ferric (III) oxide

Ferric oxide or iron (III) oxide is inorganic compound. They have three main types. First, ferric (III) oxide (Fe_2O_3) is generally known as "rust" or hematite mineral which used as feed stock for iron steel production by equation (2.5). Second, ferric (II) oxide (FeO) is rarely found in nature. Last one, ferric (II,III) oxide (Fe_3O_4) found in magnetite mineral.

$$Fe_2O_3\,(s) + 3CO\,(g) \rightarrow 2Fe\,(s) + 3CO_2\,(g) \qquad (2.6)$$

Fe_2O_3 can be distinguished into various polymorph which dominate types are α-Fe_2O_3 and γ-Fe_2O_3. The α-Fe_2O_3 type is easier found in nature than γ-Fe_2O_3 because of γ-Fe_2O_3 must be covered α-Fe_2O_3 at high temperature or deriving from maghemite mineral. Fe_2O_3 can also be prepared by series chemical reactions below.

$$4Fe\,(s) + 3O_2\,(g) + 2H_2O\,(l) \rightarrow 4Fe(O)OH\,(s) \qquad (2.7)$$

$$2Fe(O)OH\,(s) \rightarrow Fe_2O_3\,(s) + H_2O\,(l) \qquad (2.8)$$

Because of ferric oxide can form in many ways, so they have different colors. For example, typical Fe_2O_3 is red iron which can turn to black as Fe_3O_4 at high temperature or iron hydroxide ($Fe(OH)_3$) in nature has yellow iron.

2.3.1 Hydrogen sulfide removal by ferric (III) oxide

Sulfur removal by ferric (III) oxide (Fe_2O_3) has been developed since 19th Century [10]. The reaction suitably carried out at room temperature that was acceptable for using in many industries. Sulfur in gas stream will react with Fe_2O_3 which can observes by color changing of from either red or yellow to black color of FeS.

The reaction of sulfur removal using iron oxide adsorption [10,11] is:

$$H_2S\,(g) + \frac{1}{3}Fe_2O_3\,(s) \rightarrow \frac{1}{3}Fe_2S_3\,(s) + H_2O\,(l) \qquad (2.9)$$

$$\Delta H = -22\ \text{kJ} \qquad (\text{at } 25°C \text{ and } 1\ \text{atm})$$

The spent Fe_2O_3 can be regenerate by exposing to oxygen or air. However, adsorption performance will decrease in regeneration process because of sulfide element can clogged in pores of adsorbent. Moreover, Fe_2O_3 can be decompose into FeS_2 or Fe_8S_9 which are difficult for regeneration

The regeneration reaction is:

$$\frac{1}{3}Fe_2S_3\ (s) + \frac{1}{2}O_2\ (g) \rightarrow \frac{1}{3}Fe_2O_3\ (s) + S\ (s) \qquad (2.10)$$

$\Delta H = -198$ kJ (at 25°C and 1 atm)

2.4 Chemical equilibrium

The chemical equilibrium state occurred in reversible reaction which can preceded both the forward and backward directions. Most reactions are theoretically reversible in a closed system but some can be considered to be irreversible if they heavily favor the formation of reactants or products. In this work Fe_2O_3 and H_2S reaction can be considered as reversible reaction because of the reaction occurs in a batch closed system.

Initially, the vial contains only hydrogen sulfide gas (H_2S) and ferric (III) oxide (Fe_2O_3). When the reaction occurred, Fe_2O_3 was turned to black color of ferric (II) sulfide (FeS). The concentration of FeS was increased while concentration of H_2S and Fe_2O_3 were decreased until it reaches the equilibrium concentration. When the concentrations of those compositions remain constant, the reaction has reached equilibrium state. The concentration of all the different reaction species at equilibrium can defines by a quantity called equilibrium constant K_c. The equilibrium constant value can help us to understand whether the reaction tends to have a higher concentration of products or reactants at equilibrium.

The value of K_c in this reaction can find by using relationship:

$$K_c = \frac{[H_2S][Fe_2O_3]^{1/3}}{[Fe_2S_3]^{1/3}} \qquad (2.11)$$

And it also find by using relationship below:

$$K_c \equiv \exp\left(\frac{-\Delta G^\circ}{RT}\right) \qquad (2.12)$$

Where,

$$\Delta G^\circ = \sum_i \nu_i \Delta G^\circ{}_i$$

$$= \tfrac{1}{3}(-166900) + (-237129) - (-33560) - \tfrac{1}{3}(-742200)$$

$$= -11802.3 \text{ J/mol}$$

Where, $\Delta G^\circ{}_{H_2S}$ (g) = -33560 J/mol

$\Delta G^\circ{}_{Fe_2O_3}$(s) = -742200 J/mol

$\Delta G^\circ{}_{Fe_2S_3}$(s) = -166900 J/mol

$\Delta G^\circ{}_{H_2O}$ (l) = -237129 J/mol

From equation (2.12):

$$K_C \equiv \exp\left(\frac{-\Delta G^\circ}{RT}\right)$$

$$\equiv \exp\left(-\frac{(-11802.333)}{8.314(298.15)}\right) \equiv 116.9$$

The value of K_c shows that the reaction is not strongly forward reaction. Therefore, amount of each component for reaching equilibrium state can find according this equilibrium constant value.

2.5 Introduction of polyethylene

Polyethylene (PE) is one of thermoplastic polymer which is hugely produced for many million tons of worldwide production each year. There are plenty of polyethylene applications such as grocery bag, drain pipe, plastic wrap, etc. PE is made from polymerization of ethylene monomers where are typically derives from ethylene gas. This ethylene gas is major constituent of natural gas or can be distillated from petroleum plant. Double bond of ethylene is broken to be single bond by polymerization. Ordinary polyethylene synthesis is accomplished by using Ziegler-Natta catalyst.

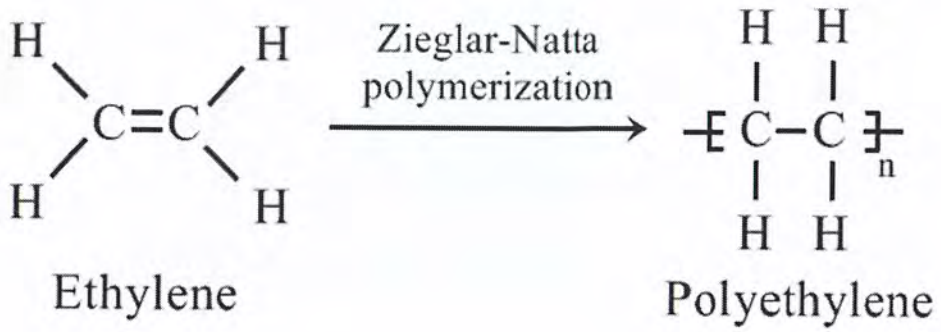


Figure 2.2 Structure of polyethylene

The properties of PE are nonpolar, saturated, and high molecular weight hydrocarbon. Therefore, their chemical behavior is similar to normal paraffin. Density of polyethylene is revers to amount of cross-linked in polymer back bone. The high density of PE is high crystallinity and physical/chemical stability. Typical polyethylene has excellent chemical resistance property which is not damaged with strong chemical substances (acid/base/oxidant/reducing agent). This property suitable applies for durable requirement of materials and adsorbents in our work as well. Main of PE types can be classified by density property which demonstrates in below.

- Low density polyethylene (LDPE) is flexible material which has both short and long branches of polymer structure. Because of these branches can prevent crystallinity, thus it is suitable apply to stiffness application whether packaging film, trash and grocery bags, agricultural mulch, wire and cable insulation, squeeze bottle, toys and housewares

- Linear low density polyethylene (LLDPE) is very similar to LDPE properties. The benefit of this type is lower energy requirement for manufacturing than LDPE.

- High density polyethylene (HDPE) regularly consists of lack branches in polymer chains, result in high strength and moderate stiffness. HDPE applications widely provide for toys, household appliances, bottle of milk, grocery bags, and bucket as well.

- Ultrahigh-molecular-weight polyethylene (UMWPE) is called in other name as "liner polyethylene" which extremely long hydrocarbon chain cause to high crystallinity, high stiffness and tensile strange. UMWPE suitable apply to various stiffness staffs such as armour, fishing line, climbing equipment, or medical equipment.

2.6 Introduction of polymer foam

Polymer foam is achieved by dispersion of a gas in a polymer matrix. It normally consists of two phases that are a solid polymer matrix and a gaseous phase. Other solid phases may be added in the foams in the form of fillers or additives for enhance some property. There are varies forms of polymeric foams, it may be either for rubbers, cellular elastomers or sponges. The properties and morphologies of the foam significantly depend on types of solid matrix material. For example, heat and sound insulation properties of polystyrene foam relate to styrene matrix type.

General polymeric foams have the ability to absorb a huge energy, which suitable apply in cushioning and packaging applications. In addition, small amount of solid polymer is needed in foaming process, therefore lower cost of manufacturing. Because of their light weight (densities ranging from as low as 1.6 to as high as 960 kg/m^3) and excellent strength to weight ratio and other properties, polymeric foam is rapidly replaced other similar properties material.

Large commercial polymeric foams are based on polyurethane, polystyrene and polyvinyl choline. Polymeric foam processing method mostly is continually slab-stock which is consequently done by pouring, foaming, extrusion, molding, spaying, rotation casting, frothing, precipitation, composites and lamination. Foaming process involves for three steps. First, blowing agent gaseous is injected to polymer, intermedia in this step still forms two-phase. After that, increase temperature or/and pressure cause to higher diffusivity and solubility of blowing agent gaseous result in it becomes single-phase solution. Finally, the conditions are disrupted by pressure quenching or/and temperature soaking which results of air trapping in polymer matrix.

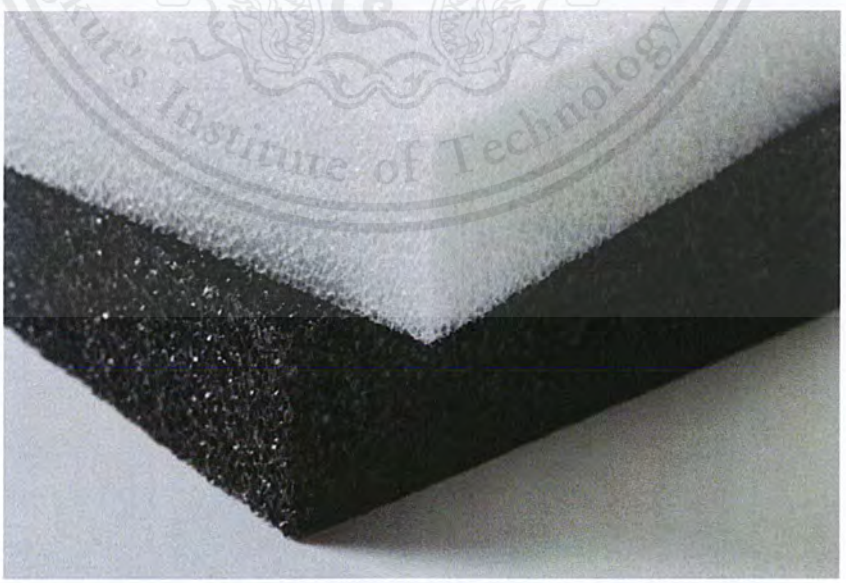


Figure 2.3 Example of polyethylene foam sheet

2.6.1 Polymer foam production techniques

Two main techniques for polymer foam production are physical foaming and chemical foaming. Both technique require gas or general be called "blowing gas" for expansion inside polymer matrix that separated into two types

First is chemical blowing agents, they are usually reactive species that can produce gases in foaming process. Blowing agents that produce gas via chemical reactions include baking powder and isocyanates when they react with water.

$$RNCO + H_2O \rightarrow RNH_2 + CO_2$$

Second is physical blowing agents, general physical foaming agents are volatile chemicals such as chlorofluorocarbons (CFC), volatile hydrocarbons and alcohols, or inert gases such as nitrogen, carbon dioxide, argon, and water.

2.6.1.1 Physical foaming

For physical foaming, gas phase is dissolved in polymer to form homogeneous phase which is done by pressurization. After that, the temperature increase or pressure quench results in supersaturation state, and gas starts to form nuclei and expand.

The CFC is widely used as physical blowing agents because of their good solubility in the polymer matrix and low diffusivity that results in largh pore size gain due to quick escape of gas from the foam after processing. Moreover, they have low thermal conductivity that result in good insulation of polymer foam. However, CFC can cause many problems to environment such as their high ozone depletion effect. Therefore, other foam blowing agents can use instead such as hydrocarbons gases (propane, butane, pentane, etc.); inert gases such as nitrogen, argon and CO_2.

2.6.1.2 Chemical foaming

The blowing gas for this technique can produce by chemical reaction such as polyurethane foaming process; CO_2 gas has to be incorporated in the final product by reaction between isocyanate group and water. The mechanisms are shown in figure 2.5.

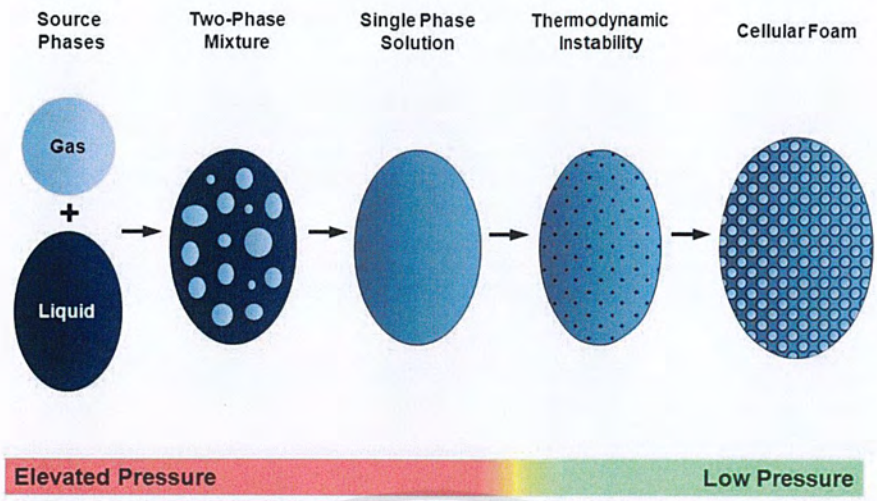


Figure 2.4 Physical foaming process mechanisms

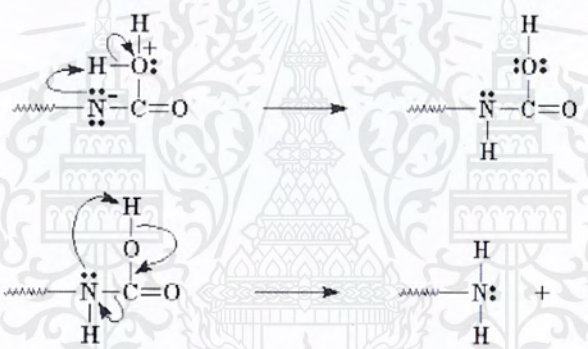


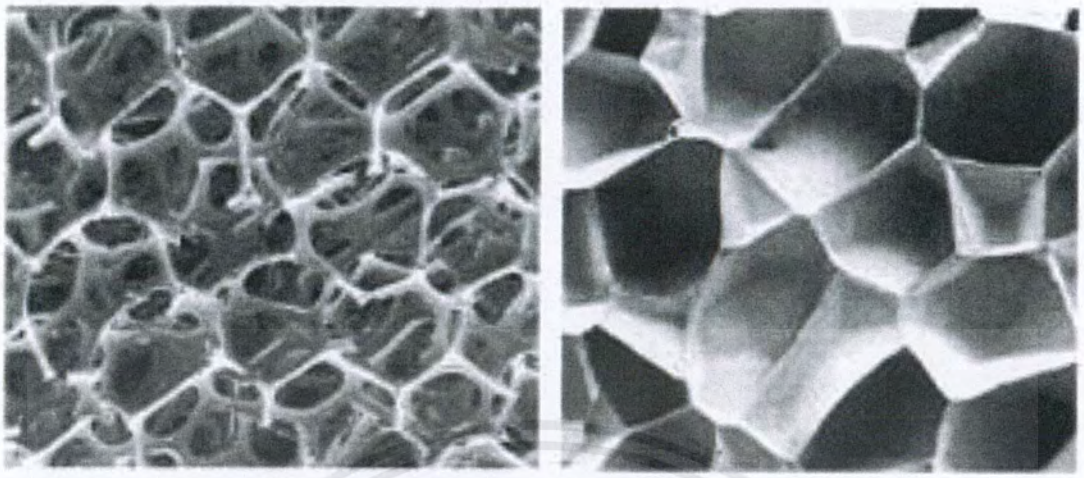
Figure 2.5 Blowing gas productions in a chemical foaming process

2.6.2 Classification of polymer foam

2.6.2.1 Close cell polymer foam

In closed cell foams, the foam cells are isolated from each other and cavities are surrounded by complete cell walls that make them leading to good insulation properties. Closed cell foams are usually characterized by their rigidity and strength, in addition to the high R-value (Resistance to heat flow). Closed cell polyurethane spray foam has among the highest R-values of any commercially available insulation.

2.6.2.2 Open cell polymer foam



(a) (b)

Figure 2.6 Examples of (a) open cell and (b) close cell foam of polyuretha foam

In open cell foams, each of cell are connected other and gas can easily pass inside. They have softer and spongier appearance comperaring to close cell type. Open cell foams are incredibly effective as a sound barrier in normal noise frequency ranges and provide better absorptive capability.

2.7 Diffusivity in polymer foam

Typical gases for diffusional mass transfer in polymer system are nitrogen, oxygen, helium, carbon dioxide, sulfur dioxide, methane, etc. at relatively low pressure or equivalently low activities. These gases can be called "permanent gases". The model law to find diffusivity of simple gases is Lennard-Jones equation

$$\Phi(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{2.13}$$

Where $\Phi(r)$ is the intermolecular energy of two molecules r distance apart, ε is the potential energy constant, and σ is the potential length constant. Note ε and σ are called Lennard-Jones scaling factors and σ can also called collision diameter of the molecule. Division of ε by Boltzmann constant (k) is Lennard-Jones temperature ε/k. The simple gases properties can be found in table 2.1 from Svehla et al. (1962)

Cause of weak interaction between simple gases and polymer, this diffusion coefficient does not depend on concentration but only on temperature. The relation between diffusion coefficient and temperature is expressed by Arrhenius-type equation.

$$D = D_0 exp\left(-E_D/R_g T\right) \tag{2.14}$$

Where D_0 and E_D are constants for particular gas-polymer system. D_0 is the pre-exponential factor for D, E_D is the activated energy of diffusion and R_g is universal gas constant.

In order to find diffusivity of gas in polymer in equation 2.14, the pre-exponential factor (D_0) and activated energy of diffusion (E_D) values can find from equations 2.15 and 2.16 in following.

$$10^{-3}\frac{E_D}{R_g} = \left(\frac{\sigma_{H_2S}}{\sigma_{N_2}}\right)^2\left[7.5 - 2.5\times 10^{-4}\left(T_g - 298\right)^{3/2}\right] \pm 1.0 \tag{2.15}$$

$$\log D_0 \cong \frac{E_D \times 10^{-3}}{R_g} - 5.0 \pm 0.8 \tag{2.16}$$

Where σ is collision diameter of the molecule in table 2.1, R_g is universal gas constant and T_g is glass transition temperature.

Table 2.1 Collision diameters and energy parameters for the Lennard-Jones equation

Molecule	*Compound*	$\sigma \times 10^{10}$ *(m)*	ϵ/k *(K)*
Cl_2	Chlorine	4.217	316.0
F_2	Fluorine	3.357	112.6
HBr	Hydrogen bromide	3.353	449
HCN	Hydrogen cyanide	3.630	569.1
HCl	Hydrogen chloride	3.339	344.7
HF	Hydrogen fluoride	3.148	330
HI	Hydrogen iodide	4.211	288.7
H_2	Hydrogen	2.827	59.7
H_2O	Water	2.641	809.1
H_2O_2	Hydrogen peroxide	4.196	289.3
H_2S	Hydrogen sulfide	3.623	301.1
Hg	Mercury	2.969	750
$HgBr_2$	Mercuric bromide	5.080	686.2
$HgCl_2$	Mercuric chloride	4.550	750
HgI_2	Mercuric iodide	5.625	695.6
I_2	Iodine	5.160	474.2
NH_3	Ammonia	2.900	558.3

2.8 Literature reviews

D. Wang studied about hydrogen sulfide from gases stream in pack-bed column. The typical hydrogen sulfide removal methods were demonstrated and explained. This paper demonstrated model of several non-catalytic gas-solid reactions. The pack-bed column design and its parameters were clearly shown.

J. Sun et al. studied about hydrogen sulfide removal by granular ferric (III) oxide in aqueous phase in batch experiment simulating water environment. Materials and methods were provided which simply understand. They showed several sulfide problems in aqueous environments and problems of typical methods. General information of hydrogen sulfide removal by granular ferric hydroxide was demonstrated in this paper such as using, regeneration, and reuse and also depicted simply of H_2S removal mechanism graphical. They also showed kinetic reaction and involved parameters. The results of experiment were concluded with effect of differential parameters and graphical.

S. Poulton et al. studied dissolved hydrogen sulfide from seawater has been examined under flow-through conditions by using zeolite. The basis environment condition and general separation techniques were demonstrated in this paper. They also determined sulphide removal parameters in laboratory fixed condition and also showed experimental results. Moreover, information of suitable ferric hydroxide coated in zeolite was also shown in this paper.

O. Iron et al. studied about hydrogen sulfide from gases stream. They showed background H_2S generation in industrial, removal methods, mechanical descriptions. In part of results, they showed various style which easy to understand.

C. Lee et al. studied adsorption of hydrogen sulfide gases by using Fe_2O_3-carbon foam. The analytical methods that are SEM, XRD, XRF and BET were performed to determine the characteristics of the material. Other metals oxide were compared efficiency and shown in this paper.

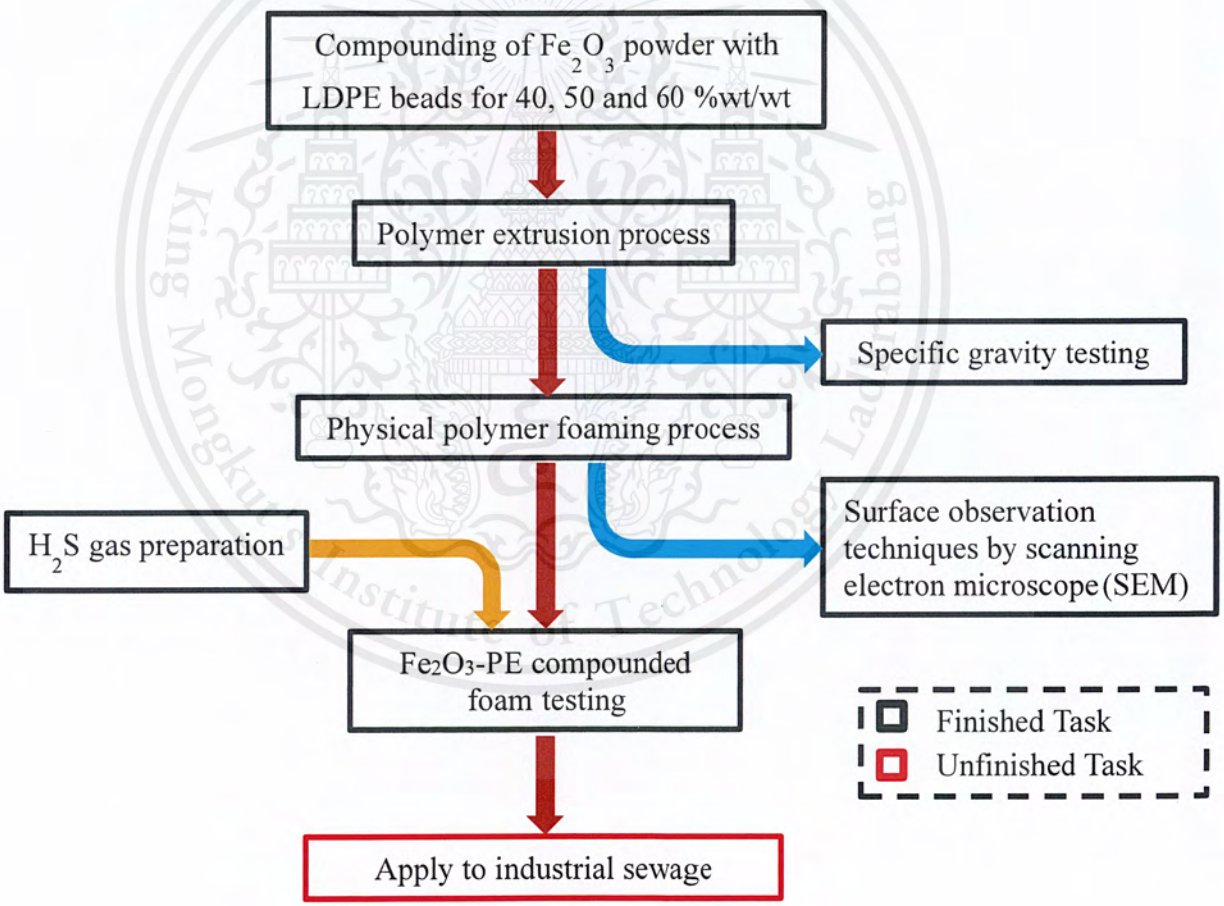
CHAPTER III
RESEARCH METHODOLOGY

3.1 Materials and equipment suppliers

Low-density polyethylene (LDPE) beads grade C150Y with melt flow index (MFI) of 5.24 g/10 minutes was supplied from Petronas Chemicals Limited Company. The ferric (III) oxide powder (Fe_2O_3) with 96% purity was provided from Henan Premtec Enterprise Company. Ferric (II) sulfide (FeS) for synthesis hydrogen sulfide gas production was supplied from Gammaco Company. The hydrogen sulfide gas detector (QREAII) was provided from Orange Innovation Limited Company.

3.2 Experimental procedures

3.2.1 Overall experimental flowsheet



3.2.2 Polymer foaming procedures

3.2.2.1 Mixing and extrusion process

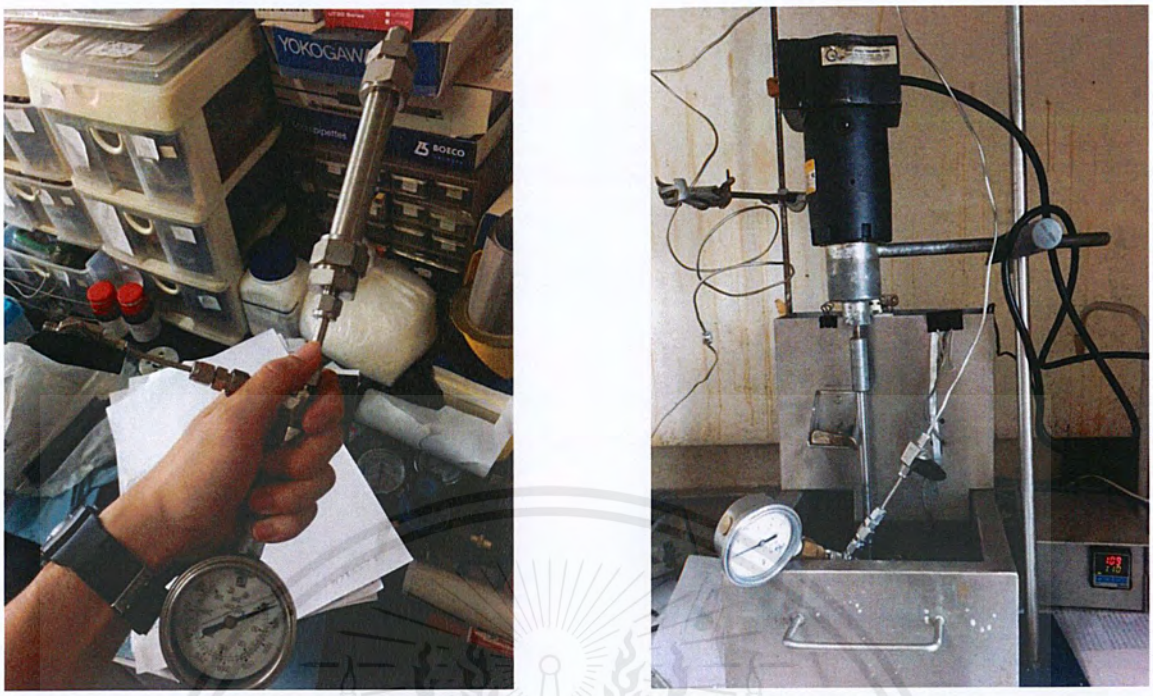
(a) (b)

Figure 3.1 (a) LDPE beads and Fe_2O_3 powder compounding in a bucket and (b) twin screw extruder

First, LDPE beads were compounded with Fe_2O_3 powder at 40 %wt/wt, 50 %wt/wt and 60 %wt/wt mixing ratio to form Fe_2O_3-PE compounded as physical mixing. After that, they were loaded to twin screw extruder machine which was set temperature at 200°C and rotational speed 200 ppm. In this case, we did not use molding after extrusion process thus extruded polymer must be manual controlled as thin as possible in order to be available in physical polymer foaming process.

3.2.2.2 Physical foaming process

The extruded polymer was cut as small pieces and placed into polymer foaming reactor that show in figure 3.1(a). This reactor was soaked by carbon dioxide gas at given pressure 1100 psi which used as blowing gas.



(a) (b)

Figure 3.2 (a) Physical polymer foam reactor
and (b) bucket of silicon oil with agitation and heater

After that, it was placed in bucket of silicon oil (figure 3.1(b)) which has agitation system and given uniform temperature at 120°C, then left it approximately two hours for homogeneous phase gain. Next, the system was disrupted by quenching pressure down result in nucleation and expansion of carbon dioxide gas was accomplished.

3.2.3 Hydrogen sulfide gas generation

The hydrogen sulfide gas for this study was produced from the reaction between ferric (II) sulfide (FeS) and hydrochloric acid solution. Amount of used FeS can calculated H_2S gain according stoichiometry number of reaction. In additional, high of solution for reaction should be low in order to avoid solubility effect of H_2S in aqueous phase.

(a) (b) (c)

Figure 3.3 Testing polyethylen foams at mixing ratio (a) 40, (b) 50 and (c) 60 %wt/wt of Fe_2O_3/PE

Figure 3.4 Testing bottles

3.2.4 Fe_2O_3-PE compounded foam testing

Testing of Fe_2O_3-PE compounded foam at each mixing ratio (40 %wt/wt, 50 %wt/wt and 60 %wt/wt) which show in figure 3.3 were put inside testing bottles in figure 3.4 and H_2S production was occurred inside at the same time. We left them in two days for reaction occurring and reached equilibrium state. The remaining H_2S after that was detected and measured by H_2S gas detector. Moreover, excess of Fe_2O_3-PE compounded foam loading at 3, 5, 15, 30 and 45 times compering to stoichiometry number of reaction were studied as well.

3.2.5 Testing of properties

3.2.5.1 Specific gravity

Figure 3.5 Specific gravity testing machine

specific gravity (SG) of extrude polymer values for each mixing ratio were measured for assuring perfect mixing from extrusion process. The Fe_2O_3-PE compounded foams were measured as well in order to assure polymeric foaming achievement (SG<1) and find expansion ratio after foaming processes.

3.2.5.2 Scanning electron microscope

Surface observation inside Fe_2O_3-PE compounded foam was accomplished by scanning electron microscope (SEM) technique. In the work, EVO® HD model in SEM from Carl Zeiss was applied. Delivering a groundbreaking increase in resolution over conventional SEM, the EVO® HD introduces high definition to electron microscopy.

3.2.6 Hydrogen sulfide detection and measurement

Figure 3.6 Hydrogen sulfide gas detectors (QRAEII)

The remaining H_2S inside testing bottles were measured by H_2S gas detector which named QREA II. They have high sensibility with real time measurement. Constituent of H_2S in a confided space is reported in QREA II display at range between 0-100 part per million (ppm). Carbon dioxide gas content can also be measured at range between 0-1000 ppm.

CHAPTER IV
RESULTS AND DISCUSSIOS

4.1 Fe_2O_3-PE compounded foam characterization

4.1.1 Specific gravity

Table 4.1 Specific gravity values of extruded polymer and Fe_2O_3-PE compounded foam at deferent spot of length

Extruded polymer		Fe_2O_3-PE compounded foam	
Fe_2O_3 powder/LDPE beads mixing ratio	Specific gravity values	Specific gravity values	Expansion ratio
40 %wt/wt	1.106	0.359	3.081
40 %wt/wt	1.118	0.367	3.047
50 %wt/wt	1.302	0.462	2.818
50 %wt/wt	1.276	0.452	2.823
60 %wt/wt	1.305	0.532	2.621
60 %wt/wt	1.424	0.538	2.648

To assure perfect mixing from extrusion process, the specific gravity (SG) of extruded polymers were measured at different spot of length. The similar SG values of each type can ensured us for non-gas trapping inside. Difficulty for transforming to Fe_2O_3-PE compounded foam can also implied by SG value which harder for high SG value. After foaming process, all SG values were decreased to range of 0.35 - 0.54 (-) that ensure of polymer foam achievement and have ability for floating. They obtained expansion ratio about 2.6- 3.1 times.

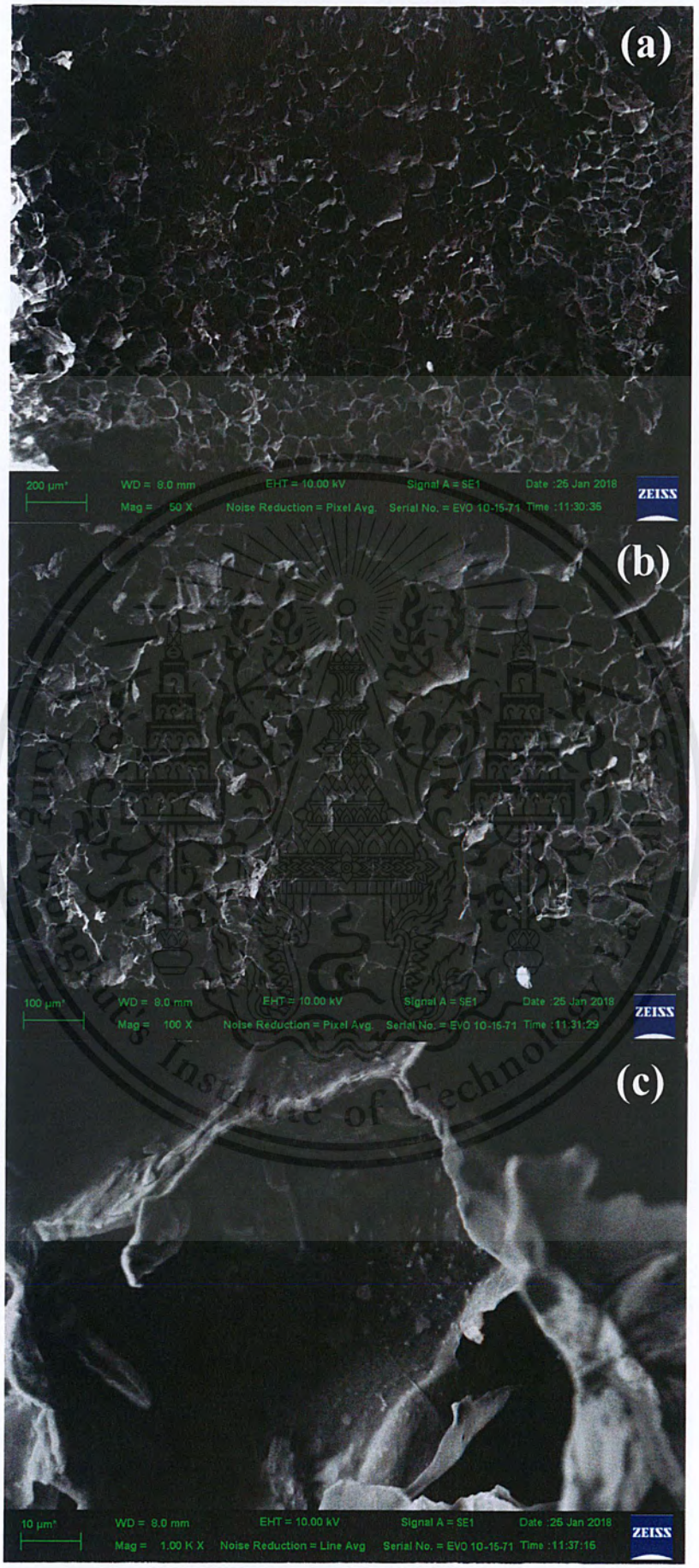


Figure 4.1 40 %wt/wt of Fe_2O_3-PE compounded foam at magnitude 50X (a), 100X (b) and 1000X (c) from SEM

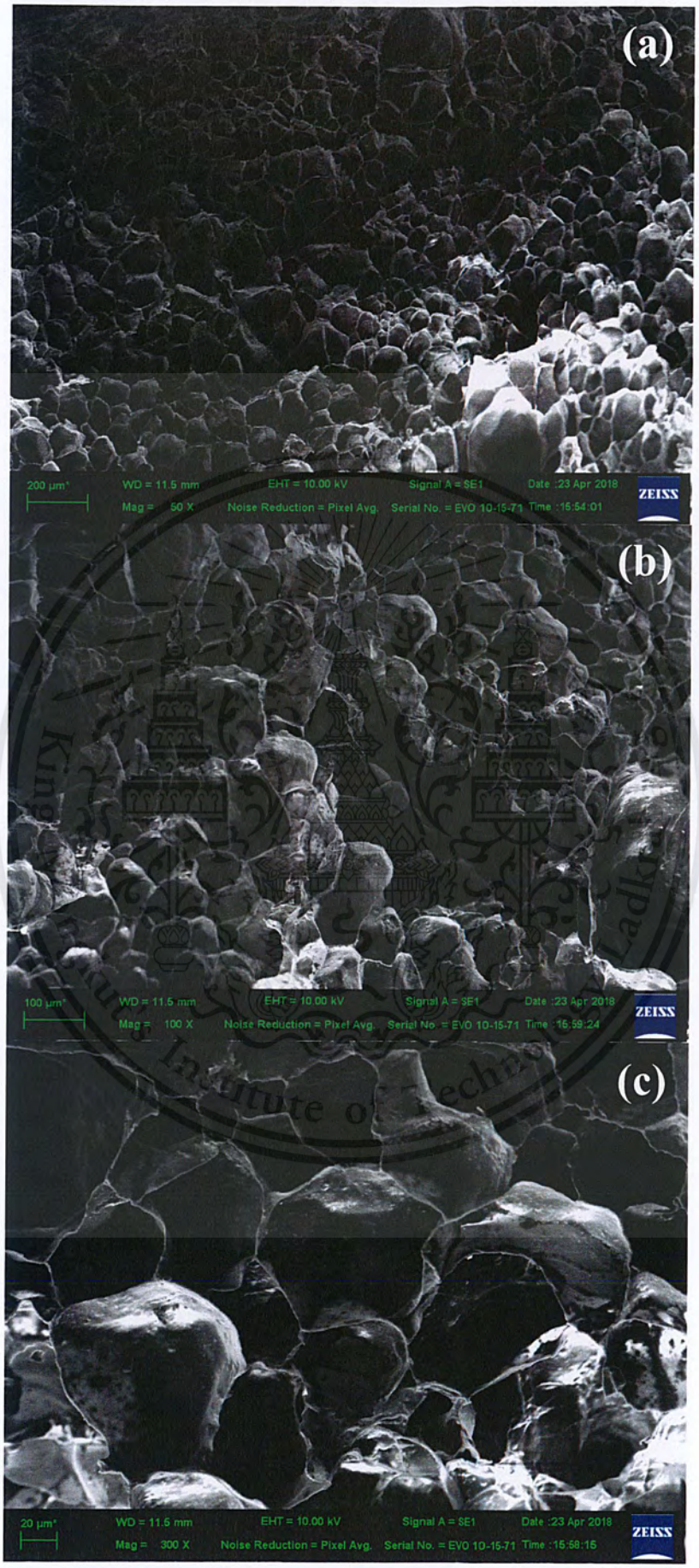


Figure 4.2 50 %wt/wt of Fe_2O_3-PE compounded foam at magnitude 50X (a), 100X (b) and 300X (c) from SEM

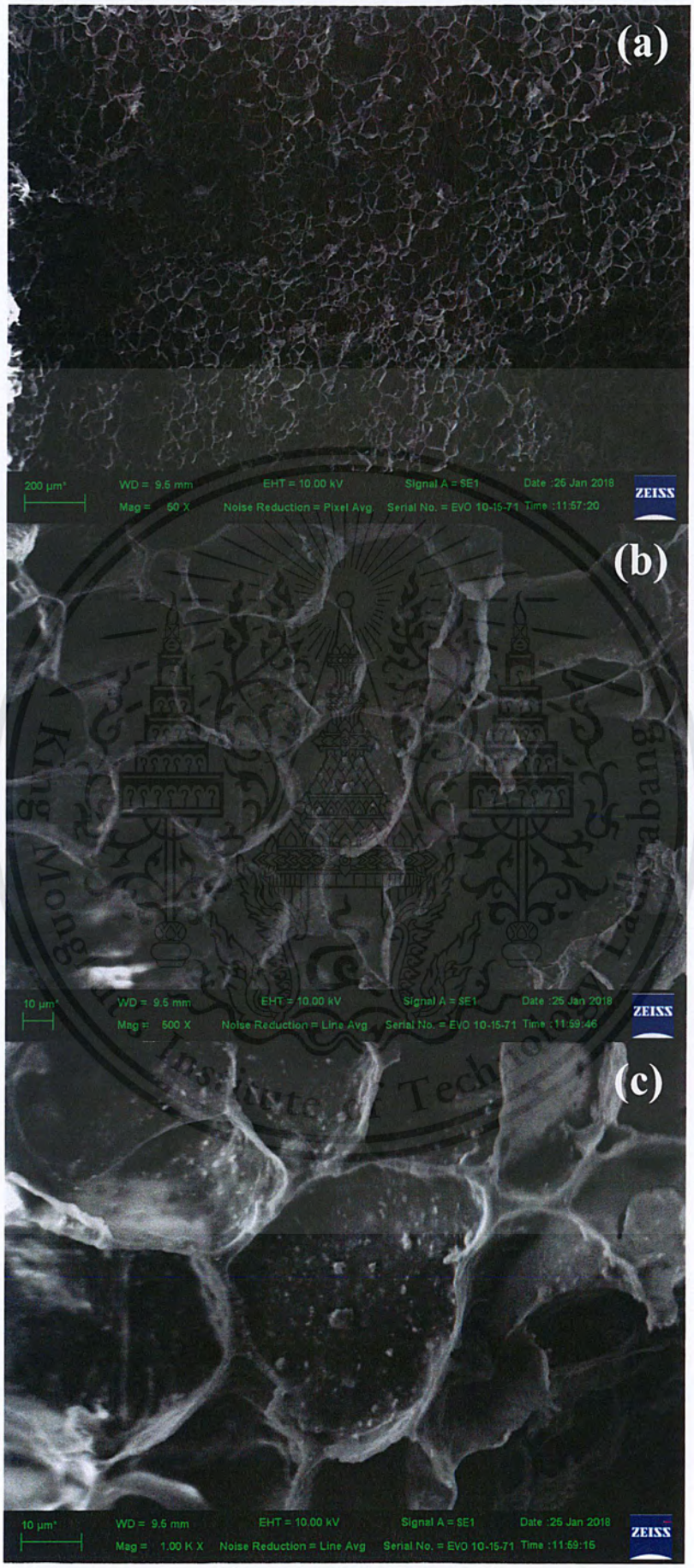


Figure 4.3 60 %wt/wt of Fe_2O_3-PE compounded foam at magnitude 50X (a), 500X (b) and 1000X (c) from SEM

4.1.2 Scanning electron microscope

4.1.2.1 40 %wt/wt of Fe_2O_3-PE compounded foam

This polymer form compounded has the highest expansion ratio according to table 4.1 which can imply for large pores gain. From figure 4.1, they have high dispersion of pore with non-perfect uniformity of pore size. The pore size of this form compounded approximately 90-300 micrometers which was classified as macrocellular polymer foam type. Therefore, gas can easily flow in and out inside polymer foam even low pressure of gas. But they are not fully open-cell polymer foam type, so gas may unable to react in some spot. According to figure 4.1(c), particles of Fe_2O_3 have well dispersion on polymer matrix that can ensure reaction occurring in inside polymer foam. However, this polymer foam compounded is the lowest Fe_2O_3 loading, thus the low reaction occurring was assumed.

4.1.2.2 50 %wt/wt of Fe_2O_3-PE compounded foam

This polymer form compounded has the close value of expansion ratio to 40 %wt/wt of Fe_2O_3-PE compounded foam according to table 4.1 which can imply for large pores gain as well. The pore size of this form compounded approximately 80-300 micrometers thus flowing of gas inside polymer foam phenomenon was similarly explained with previous polymer foam. In this polymer foam compounded, they have higher Fe_2O_3 loading, thus the reaction was easier occurred.

4.1.2.3 60 %wt/wt of Fe_2O_3-PE compounded foam

The lowest value of expansion ratio according to table 4.1 can imply small pores gain because of less of polymer matrix inside for gas expanding. They have high dispersion and perfect uniformity of pores size which range approximately 40-100 micrometers thus it is the most difficultly flowing of gas inside polymer foam. The highest Fe_2O_3 loading in this polymer foam compounded can assume that the highest reaction occurring.

4.2 Hydrogen sulfide removal by Fe_2O_3-PE compounded foam

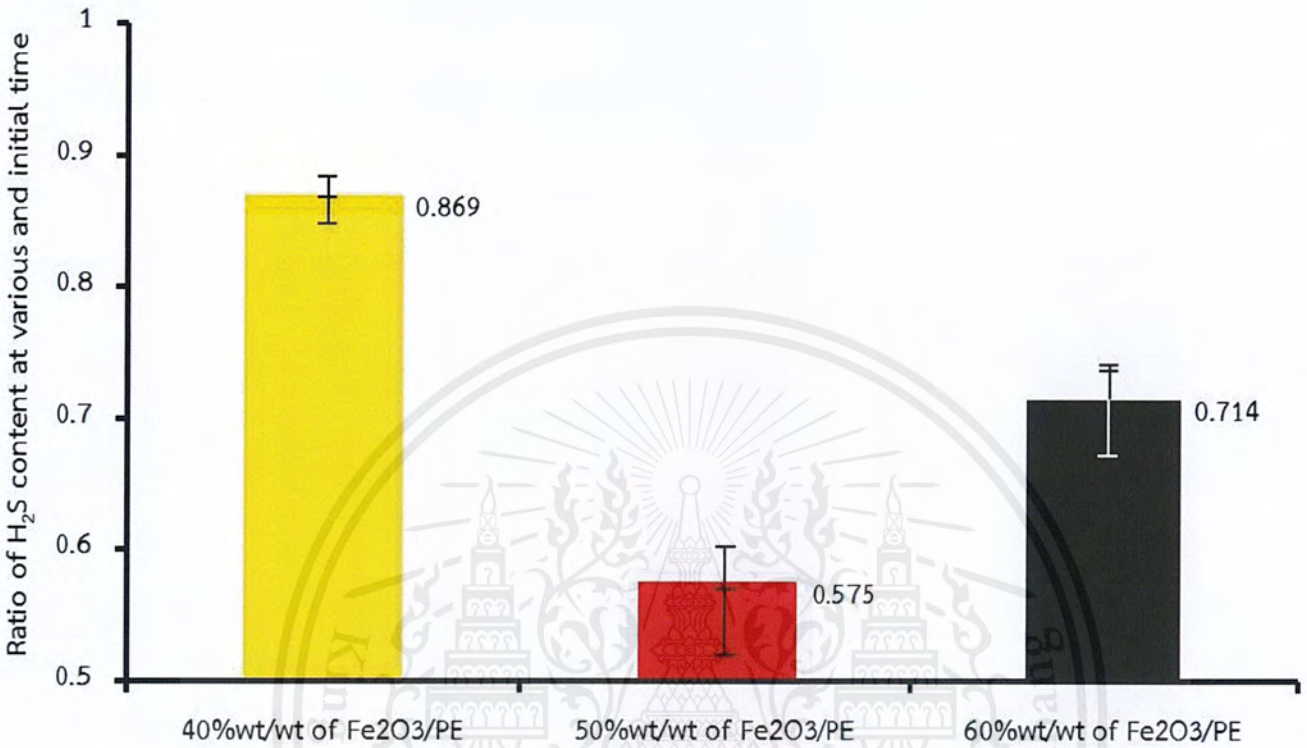


Figure 4.4 H_2S content ratio at using five times overload of Fe_2O_3-PE compounded foam compering to stoichiometry number of reaction

First experiment, Fe_2O_3-PE compounded foams were overloaded into testing bottles for five times due to Fe_2O_3 might be lost into polymer matrix or various reasons. Therefore, they should be compensated by overloading of polymer foam. From the experiment result, 40 %wt/wt polymer foam type has the lowest H_2S content removal because of low amount of Fe_2O_3 loading even though they have the highest pore size according from SEM. The 60 %wt/wt should be the best of H_2S sulfide removal for initial expectation, but experiment result show that 50 %wt/wt polymer foam type has better H_2S removal performance. It can be explained that gas cannot react with some spot of polymer foam because of it isn't fully-open cell polymer foam.

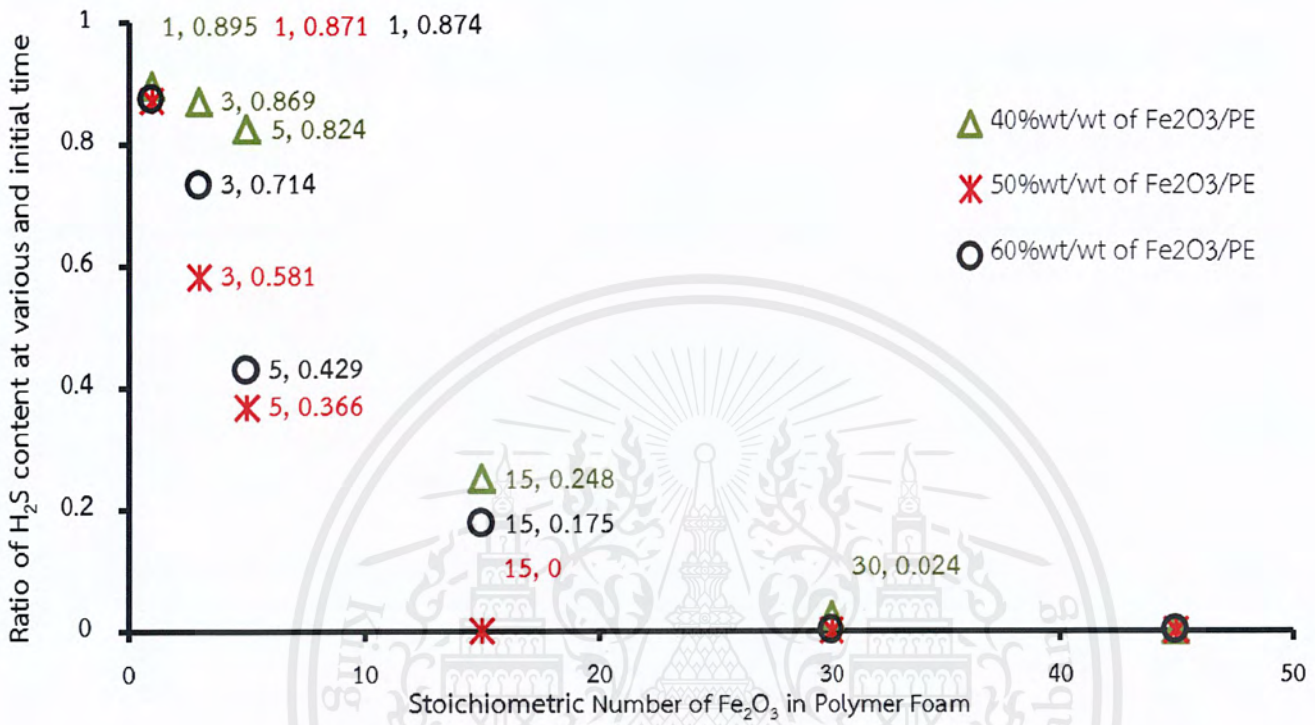


Figure 4.5 H_2S content ratio at different overload times of Fe_2O_3-PE compounded foam compering to stoichiometry number of reaction

The hydrogen sulfide gas in system can be completely eliminated by overloading Fe_2O_3-PE compounded foam than five times. According from experiment result, the best performance set front for 50 %wt/wt polymer foam type which can eliminate H_2S from system by overloading 5-15 times of polymer foam. Following by 60% and 40% %wt/wt polymer foam type which can also eliminate H_2S from system by overloading 15-30 times and 30-45 times of polymer foam. The experiment results show that it related to previous experiment which 50 %wt/wt polymer foam type is the best performance. But results from in this experiment can show H_2S reduction trend by overloading polymer foam which is not such a liner line.

4.3 Effect of Fe_2O_3 loading in polymer foam

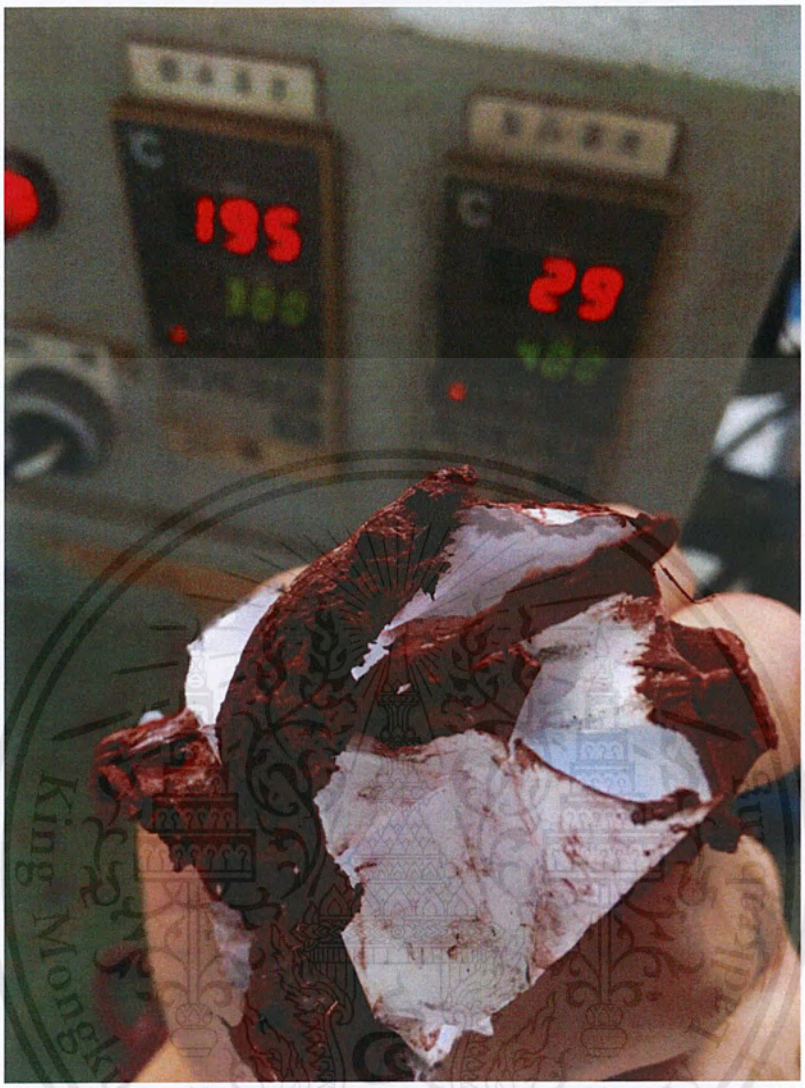


Figure 4.6 Extruded polymer at 70% wt/wt of Fe_2O_3 powder and PE beads

As everyone kwon, high loading of Fe_2O_3 must more react with H_2S in the system. So, we would like to add it as more as possible. But the problems is the extruded polymer that we obtained from extrusion machine was easily deform because of inadequate polymer matrix content. It also results to be very difficult for transforming into polymer foam. Even though it can be transformed into polymer foam, but the pores size must be smaller than our studied one. So, the mixing ratio at 50-60% wt/wt of Fe_2O_3 powder and LDPE beads was considerable for our work conditions whether blowing gas, type of foaming process, etc.

4.4 Effect of changing temperature in polymer foaming process

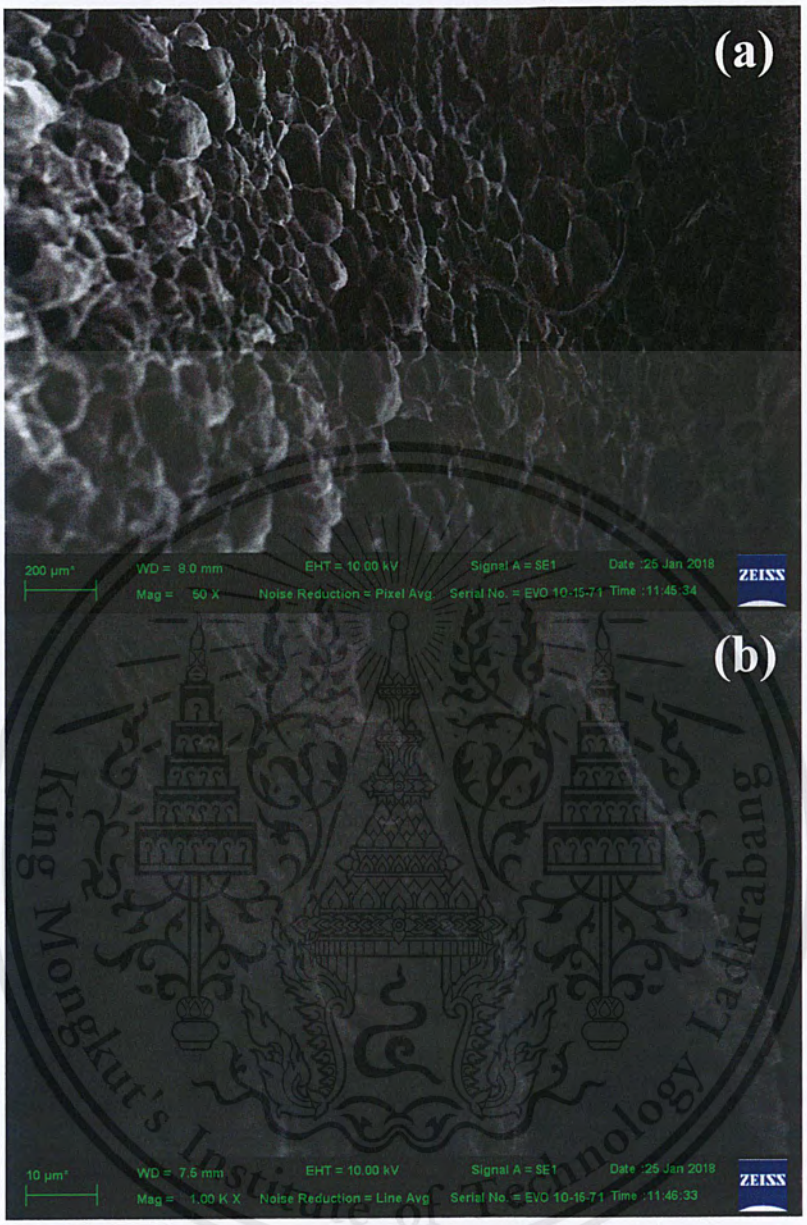


Figure 4.7 50 %wt/wt of Fe_2O_3-PE compounded foam at 130°C foaming temperature with magnitude 50X (a) and 1000X (c) from SEM

Foaming conditions such as gas blowing, temperature or pressure can effect to polymer foam structure. Figure 4.7 show cross-sectional picture of 5 0 % w t/w t polymer foam type which different from previous one by adjusting temperature for a little bit. We can explain that over adequate temperature in polymer foam process can cause slower solidization of polymer matrix and be collapsible as well.

CHAPTER V
CONCLUSION AND SUGGESTIONS

5.1 Conclusion

In this study, Fe_2O_3-PE compounded foams have specific gravity values for 0.35-0.53 and expansion ratio values around 2.6 – 3.1 times which could floated on waste water to remove H_2S gas. As expected, high loading of Fe_2O_3 as 50-60% revealed drastically removal of H_2S gas. The 50 %wt/wt Fe_2O_3-PE compounded foam is the best removal performance which can eliminate H_2S in the system by overloading polymer foam with 5-15 times. However, content of H_2S in system can also be eliminated by excess amount of polymer foam with 30 times for all of types.

5.2 Suggestions

The polymer foam with more than 60 %wt/wt can be achieved by adjusting polymer foaming conditions. Type of blowing gas and pressure of gas are first priority that we suggest to study. However, the safety for using those gases (such as propane and butane gas) must be concerned because of their high flammable and explosive properties. In addition, we also suggest for adding some nucleating agent in order to easier occur of foam nucleation.

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APPENDIX A
EXPERIMENT DATA

Appendix A-1: H_2S content ratio at fixed Fe_2O_3-PE compounded foam loading

Table A-1.1 H_2S content ratio in three days of experiment by excess of Fe_2O_3-PE compounded foam for three times

Reaction time (days)	H_2S content ratio		
	40%wt/wt of Fe_2O_3/PE	50%wt/wt of Fe_2O_3/PE	60%wt/wt of Fe_2O_3/PE
0.5	0.9821	0.9562	0.9812
1	0.9432	0.7563	0.8123
1.5	0.9034	0.6134	0.7778
2	0.8883	0.5852	0.7621
2.5	0.8693	0.5825	0.7334
3	0.8692	0.5812	0.7321

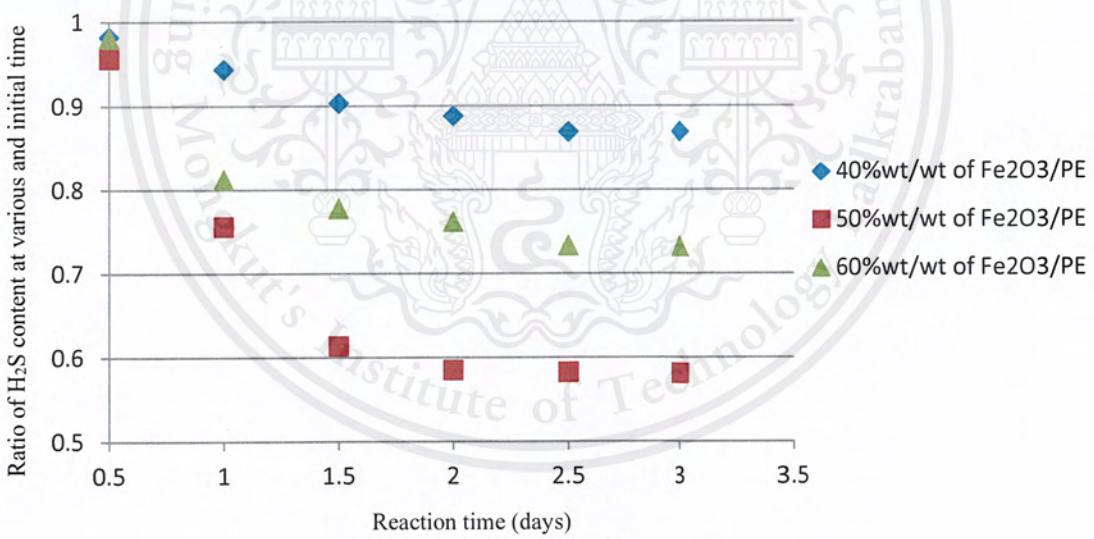

Figure A-1.1 H_2S content ratio in three days of experiment by excess of Fe_2O_3-PE compounded foam for three times

Appendix A-2: H_2S content ratio at various Fe_2O_3-PE compounded foam loading

Table A-2.1 H_2S content ratio at different overload times of Fe_2O_3-PE compounded foam compering to stoichiometry number of reaction

Excess of Fe_2O_3-PE compounded foam (times)	H_2S content ratio		
	40%wt/wt of Fe_2O_3/PE	50%wt/wt of Fe_2O_3/PE	60%wt/wt of Fe_2O_3/PE
1	0.8953	0.8717	0.8743
3	0.8692	0.5812	0.7321
5	0.8243	0.3666	0.4294
15	0.2487	0	0.1756
30	0.0243	0	0
45	0	0	0

APPENDIX B
CALCULATION

B.1 Diffusivity of H_2S in PE foam estimation

$$10^{-3}\frac{E_D}{R_g} = \left(\frac{\sigma_{H_2S}}{\sigma_{N_2}}\right)^2\left[7.5 - 2.5\times10^{-4}\left(T_g - 298\right)^{3/2}\right]$$

Where; $R_g = 8.314$ J/mol ^{o}K

$\sigma_{H_2S} = 36.23$ nm

$\sigma_{N_2} = 37.98$ nm

T_g of PE = 148 ^{o}K

Find activation energy of diffusion (E_D)

$$10^{-3}\frac{E_D}{8.314} = \left(\frac{36.23}{37.98}\right)^2\left[7.5 - 2.5\times10^{-4}(298-148)^2\right]$$

$$E_D = 14.229 \pm 8.3 \text{ kJ}$$

Find diffusivity of the corresponding completely amorphous material (D_0)

$$\log D_0 \cong \frac{E_D \times 10^{-3}}{R_g} - 5.0$$

$$\log D_0 \cong \frac{14.229 \times 10^{-3}}{8.314} - 5.0$$

$$D_0 \cong 1.001 \times 10^{-5}\ \text{cm}^2/\text{s}$$

Estimate the diffusivity (D) of hydrogen sulfide in polyethylene (PE) at 298°K

$$D \cong D_0\exp(-E_D/R_gT)$$

$$D \cong 1.001\times10^{-5}\exp(-1706/298)$$

$$D \cong 3.267 \times 10^{-8}\ \text{cm}^2/\text{s}$$

BIBLIOGRAHPY

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