



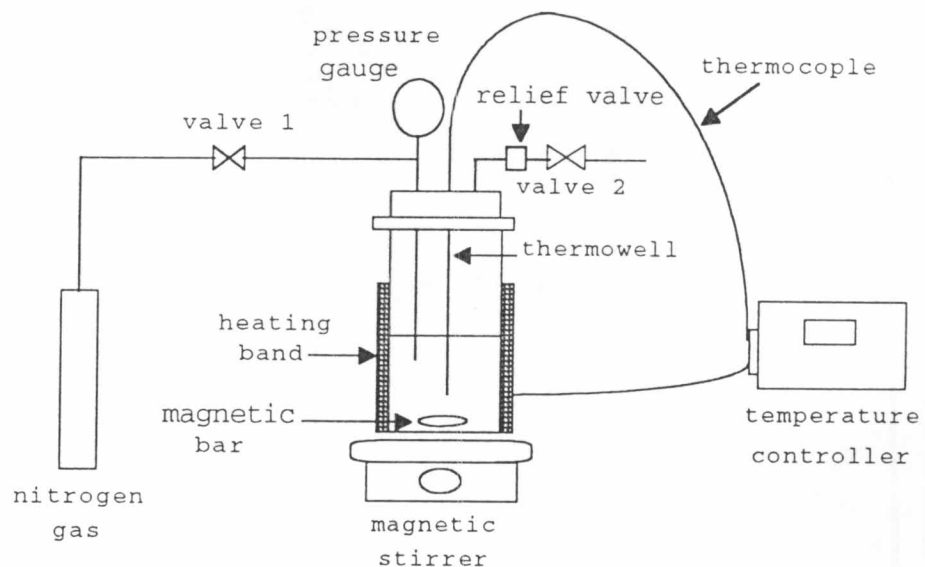
## CHAPTER III

### EXPERIMENTAL AND ANALYSIS TECHNIQUES

#### Experimental Apparatus

The study of arsenic removal was carried out in 300-ml batch reactor which was made of 316 stainless steel. A batch reactor was cylindrical shape having a 100-cm and a 10-cm in length and inner diameter, respectively. The maximum working pressure and temperature in reactor must have not exceed 1000 psig and 350°C, respectively.

A schematic diagram of the system is shown in Figure 3.1



Liquid feed and adsorbent were placed into the reactor. Nitrogen gas was passed through valve 1 (gas inlet valve) at the top of the reactor to control the pressure of the system. The gas inlet valve was connected to a dip tube which extended to a point near the bottom of the reactor. There was a relief valve attached to the gas inlet valve to protect the operator and the equipment from destructive high pressure (more than 750 psig). The heating band was directly sheltered on the reactor for rapid heating. The temperature of system was measured by a thermocouple that inserted into the thermowell. A reactor was connected with temperature controller that used for controlling the temperature of the system. A pressure gage, usually 0-1000 psi was mounted on the reactor head. Valve 2 (gas release valve) was connected to the top of the reactor head. Gas release valve was used to reduce or discharge the pressure in the reactor. A magnetic bar and magnetic stirrer were used for vigorous mixing and rapid adsorbent dispersion.

The products were taken after each experiments. Each products were filtrated with filter papers Whatman No.1 to separate the used adsorbent from liquid product.

#### **Adsorbent Preparation**

Adsorbents comprised one or two metallic components on suitable support that had been employed in the experiments. In the present study, neutral alumina (Addrich) was used as the support material. Adsorbents were prepared by dry impregnation of ammoniummolybdate

tetrahydrate and nickel nitrate onto alumina from their aqueous solution. Approximate 20 grams of neutral alumina were dehydrated in round-bottom flask that connected to vacuum pump under pressure at -750 mm Hg. Neutral alumina was heated at 120°C in oil bath about 3 hours or until pressure in flask was constant. After cooling to room temperature, this neutral alumina was impregnated by dropwise introduction of the aqueous solution under vacuum pressure. An amount of aqueous solution which used was equal to the pore volume of the particle. The concentration of the solutions were calculated so as to obtain the desired amount of metal on the alumina

The solution will penetrate the alumina to fill the pore by capillary forces. When the solution entered a pore, the metal salt was adsorbed onto the outer channels or pores of the support. The neutral alumina was maintained at these condition for 30 minutes and then adjusted to atmospheric pressure after the impregnation was completing. The neutral alumina was allowed to rest in wet atmosphere for 24 hour at room temperature. After that, the neutral alumina was followed by drying overnight at 120 °C in muffle furnace. At this time, the impregnated alumina was again placed in air at atmospheric pressure with a flow rate of 12 l/h. The temperature was progressively increased at the rate of 1°C/min to desiring temperature and maintained at this level for 3 hours. The activated adsorbent was cooled under an air stream to room temperature and kept in a desiccator before use. Four series of adsorbents were

prepared as described before: series (1) and (2) were obtained by separated impregnation of the alumina with a nickel nitrate and molybdenum solution containing the required loading of metal supported on alumina; series (3) and (4) were prepared by coimpregnation with metal salts described above. The adsorbents were referred as  $x$  Ni,  $y$  Mo,  $y-x$  MoNi and  $x-y$  NiMo, in which  $x$  and  $y$  stand for nickel and molybdenum loading, respectively. The total adsorbents were expressed as gram metal per 100 gram of alumina.

series 1

2.5 Ni :  $\gamma$  alumina was impregnated with nickel nitrate (2.5 wt% in one step), dried at 120°C and calcined at 500°C. NiMo-5.0-0: Neutral alumina was impregnated with nickel nitrate (5 wt% in one step), dried at 120°C and calcined at 500°C.

5 Ni :  $\gamma$  alumina was double impregnated with nickel nitrate (5.0 wt% in one step, respectively), dried at 120°C and calcined at 500°C. The impregnation of nickel on alumina took place stepwise.

7.5 Ni:  $\gamma$  alumina was double impregnated with nickel nitrate (5.0 wt% and 2.5 wt% in each steps), dried at 120°C and calcined at 500°C. The impregnation of nickel on alumina took place stepwise.

10 Ni:  $\gamma$  alumina was double impregnated with nickel nitrate (5.0 wt% in each steps), dried at 120°C and calcined at 500°C. The impregnation of nickel on alumina took place stepwise.

## series 2

2.5 Mo: ~~Gamma~~ alumina was impregnated with ammonium molybdatetetrahydrate (2.5 wt% in one step), dried at 120°C and calcined at 350°C.

5 Mo : ~~Gamma~~ alumina was impregnated with ammonium molybdatetetrahydrate (5 wt% in one step), dried at 120 °C and calcined at 350°C.

7.5 Mo: ~~Gamma~~ alumina was double impregnated with ammonium molybdatetetrahydrate (5.0wt% and 2.5wt% in each steps, respectively), dried at 120°C and calcined at 350°C.

10 Mo: ~~Gamma~~ alumina was double impregnated with ammonium molybdatetetrahydrate (5.0wt% in each steps), dried at 120°C and calcined at 350°C.

## series 3

7.5-2.5 MoNi : ~~Gamma~~ alumina was first impregnated with ammonium molybdatetetrahydrate (5 wt% and 2.5 wt% in each steps), dried at 120°C and calcined at 350°C. The impregnation of nickel (2.5 wt% in one step) on alumina was took place in the latter, dried at 120°C and calcined at 500°C.

5-5 MoNi : ~~Gamma~~ alumina was first impregnated with ammonium molybdatetetrahydrate (5 wt% in one step), dried at 120 °C and calcined at 350°C. The impregnation of nickel (5.0 wt% in one step) on alumina was took place in the latter, dried at 120 °C and calcined at 500°C.

2.5-7.5 MoNi : ~~Gamma~~ alumina was first impregnated with ammonium molybdatetetrahydrate (2.5 wt% in one step), dried at 120°C and calcined at 350°C. The

impregnation of nickel (5.0 wt% and 2.5 wt% in each steps) on alumina was took place in the latter, dried at 120°C and calcined at 500°C.

series 4

7.5-2.5 NiMo : Gamma alumina was first impregnated with nickel (5 wt% and 2.5 wt% in each steps), dried at 120°C and calcined at 500°C. The impregnation of ammonium molybdatetetrahydrate (2.5 wt% in one step) on alumina was took place in the latter, dried at 120°C and calcined at 350°C.

5-5 NiMo : Gamma alumina was first impregnated with with nickel (5 wt% in one step), dried at 120°C and calcined at 500°C. The impregnation of ammonium molybdatetetrahydrate (5 wt% in one step) on alumina was took place in the latter, dried at 120°C and calcined at 350°C.

2.5-7.5 NiMo : Gamma alumina was first impregnated with nickel (2.5 wt% in one step), dried at 120°C and calcined at 500 °C. The impregnation of ammonium molybdatetetrahydrate (5 wt% and 2.5 wt% in each steps) on alumina was took place in the latter, dried at 120°C and calcined at 350°C.

The nickel and molybdenum content of the different adsorbents are listed in Table 3.1.

Type of Adsorbent	Nickel content (%)	Molybdenum content (%)
2.5 Ni	2.5	-
5 Ni	5.0	-
7.5 Ni	7.5	-
10 Ni	10.0	-
2.5 Mo	-	2.5
5 Mo	-	5.0
7.5 Mo	-	7.5
10 Mo	-	10.0
2.5-7.5 MoNi	7.5	2.5
5-5 MoNi	5.0	5.0
7.5-2.5 MoNi	2.5	7.5
2.5-7.5 NiMo	2.5	7.5
5-5 NiMo	5.0	5.0
7.5-2.5 NiMo	7.5	2.5

### Experimental Procedures

The adsorbents used in this study were  $\text{Al}_2\text{O}_3$ ,  $\text{Ni}/\text{Al}_2\text{O}_3$ ,  $\text{Mo}/\text{Al}_2\text{O}_3$  and  $\text{Ni-Mo}/\text{Al}_2\text{O}_3$ . These adsorbents, except  $\text{Al}_2\text{O}_3$ , were prepared by dry impregnation technique. The reactions were carried out in a 300-ml reactor at temperature in the range of 30-75°C. Nitrogen gas was used to control the total pressure in the range of 200-600 psig. The liquid feed was pure toluene which containing arsenic compounds. Phenylarsine oxide and arsenic oxide were chosen for the models of arsenic compounds in petroleum. The degree of arsenic removal were measured using 0.02 to 1.0 g of adsorbent and 100 ml of liquid feed, with a 60-minute contacting time.

The spent adsorbents were separated from the products by filtration. They were also washed with

toluene and dried at 100°C for 3 hours to remove the volatile substance. Contacting between the adsorbent and the atmosphere would be avoided until the temperature of the adsorbent had reached to ambient temperature. The used adsorbent was then kept in desiccator before analysis. The liquid products were digested with acid for 3 hours then was extracted by water for transfer arsenic to water phase.

#### **Analysis technique**

After each experiment, feed and product were analyzed for arsenic content. Fresh and spent adsorbents were analyzed for their characteristics.

#### **Product characterization**

Graphite Furnace Atomic Absorption Spectroscopy was used to determine arsenic content in feed and product. A sample, a few of microliters, was introduced to electrothermal atomizer that constructed of graphite. A typical graphite tube would have a resistance of approximately 10 milliohms. When a low voltage was applied that made several hundred amp of current flow across the ends of such tube. Thus, very high temperature was created along the length of the tube. In the electrothermal atomizer, amount of sample was first evaporated at low temperature and then ashed at a somewhat higher temperature in a graphite tube. After ashing, the current was rapidly increased to several hundred amperes which caused the temperature more than 2500 oC. Atomization of a sample occurred in a few



milliseconds to seconds. When the temperature in graphite tube was raised to atomized step, it produced a cloud of neutral atom that could give atomic absorption in the optical steam of the spectrophotometer. The free atoms would absorb a portion of this light to make the intensity of the beam decreased. The absorbance of radiation from the external light source depended on the population of neutral ground state atoms. This absorbance is proportional to the concentration of metal in the solution originally pipetted into the furnace. The atomic absorption was measured by transient signal. The whole assembly was purged with argon to prevent rapid oxidation of the graphite tube.

Liquid feed and product were analyzed for arsenic content by Graphite Furnace Atomic Absorption Spectroscopy after each experiments. However, toluene, as liquid feed, was organic material that trended to interfered the absorption of arsenic during analysis. This problem could take out by using "digestion and extration method". Digestion was the method which used acid and heat for converting arsenic compounds to arsenic oxide. Then, arsenic oxide was transferred from toluene phase to water phase by extraction.

In this experiment, arsenic compounds were digested by nitric acid, chloric acid and hydeogen peroxide. A 50 ml aliquot of the sample solution was transferred to flat round flask and was added with 7 ml of nitric acid (concentration), 3 ml of chloric acid (concentration), 3 ml of hydrogen peroxide(35%) and 10 ml of distillated water. The flask was connected to a

reflux instrument to prevent of arsenic lossing and carefully heated at 100 oC for 3 hour. The mixture was cooled to ambient temperature and extracted with water. Lastly, the sample solution was made the total volume to 100 ml.

### **Adsorbent characterization**

In order to understand the behaviour of an adsorbent it is essential to be adequately characterized. In this study the properties studied included metal content, surface area, pore volume and pore distribution of the adsorbents are aimed to analyze. A brief description of these measurements is given below.

Nickel and molybdenum content : Nickel and molybdenum content of the adsorbents were determined by standard method of ASTM (base on Designation: D1977-91). This method was used for decomposing and dissolving samples for atomic absorption spectroscopy.

Approximately 500 mg of the adsorbent sample was weighed and transferred into a crucible. The sample was added with 10 ml of distillated water, 10 ml of concentrate sulfuric acid, 10 ml of concentrated nitric acid and 5 ml of concentrated hydrofluoric acid. The mixture in crucible was placed on a hot plate and stirred slowly. The adsorbent was first dissolved in acid solution and then precipitated again after the acid was evaporating. A sample was continually evaporated to near dryness. Then the crucible was removed from the hot plate and allowed to cool at room temperature. The sample was introduced again with 20 ml of 19%

hydrochloric acid and 30 ml of 3% hydrogen peroxide, covering with watch glass and returning crucible to hot plate. The sample was continually heated to boil until the precipitate was dissolved totally. After complete dissolution, the crucible was removed from the hot plate and cooled to room temperature. The sample was then diluted with distilled water to 100 ml and stored in polyethylene bottle.

Surface area and pore volume : Surface area and pore characteristics of the samples were measured by the BET method, with nitrogen as the adsorbent using a micromeritics model ASAP 2000. The ASAP 2000 system consisted of sample preparation or degassing and sample analysis. It contained one sample analysis port and two sample preparation ports.

Approximate 500 mg of the adsorbent was weighed and transferred into the sample preparation tube. Most solid adsorbents adsorbed moisture and other contaminants when used. The adsorbent must have been cleaned in sample preparation tube by thermal treating before analysis was performed. The sample preparation tube was attached to the vacuum system and the heater was placed around it. Sample preparation would then require more time to achieve the desiring preparation before proceeding with an analysis. Once sample preparation was completed, the sample tube might be allowed to cool to ambient temperature. The sample tube would then remove from the sample preparation port and placed onto the analysis port. Before the sample was automatically analyzed it must have the information files assigned to.

The files consisted of the information groups that collectively, identify the sample, run condition and the likes.

Properties of the chemicals used in these experiments are given in Tables 3.2 to 3.12 , respectively.

Table 3.2 Properties of Toluene\*

Formula	C <sub>7</sub> H <sub>8</sub>
Structure	
Chemical Name	Toluene
Physical Properties	
Molecular Weight	92.13
Form	liquid
Colour	colourless
Boiling Point (°C)	110.8
Melting Point (°C)	-95
Specific Gravity	0.866
Solubility	soluble in ether and alcohol
Purity	> 99%
Supplier	Merck

\* From Encyclopedia of Chemical Engineering

Table 3.3 Properties of Nitric Acid\*

---

Formula	HNO <sub>3</sub>
Structure	
Chemical Name	Nitric Acid
Physical Properties	
Molecular Weight	63.02
Form	liquid
Colour	colourless
Melting Point (°C)	-42
Boiling Point (°C)	86
Specific Gravity	1.502
Solubility	soluble in water
Purity	69.0-70.5%
Supplier	BDH

---

\* From Encyclopedia of Chemical Engineering

Table 3.4 Properties of Hydrogen Peroxide\*

---

Formula	H <sub>2</sub> O <sub>2</sub>
Structure	
Chemical Name	Hydrogen Peroxide
Physical Properties	
Molecular Weight	34.02
Form	liquid
Colour	colourless
Melting Point (°C)	-0.89
Boiling Point (°C)	151.4
Specific Gravity	1.13
Solubility	soluble in water, acid and ether
Purity	35-35.6%
Supplier	MERCK

---

\* From Encyclopedia of Chemical Engineering

Table 3.5 Properties of Hydrofluoric Acid\*

---

Formula	HF
Structure	.
Chemical Name	Hydrofluoric Acid
Physical Properties	
Molecular Weight	20.01
Form	liquid
Colour	colourless
Melting Point (°C)	-83
Boiling Point (°C)	19.4
Specific Gravity	1.155
Solubility	soluble in water
Purity	48-51%
Supplier	Carlo Erba

---

\* From Encyclopedia of Chemical Engineering

Table 3.6 Properties of Hydrochloric Acid\*

---

Formula	HCl
Structure	
Chemical Name	Hydrochloric Acid
Physical Properties	
Molecular Weight	36.47
Form	liquid
Colour	colourless
Melting Point (°C)	-15.35
Specific Gravity	19.2
Solubility	soluble in water and alcohol
Purity	37%
Supplier	Merck

---

\* From Encyclopedia of Chemical Engineering



Table 3.7 Properties of Sulfuric Acid\*

---

Formula	H <sub>2</sub> SO <sub>4</sub>
Structure	
Chemical Name	Sulfuric Acid
Physical Properties	
Molecular Weight	97.09
Form	liquid
Colour	colourless
Melting Point (°C)	205
Boiling Point (°C)	-
Specific Gravity	2.03
Solubility	soluble in water
Purity	95.7%
Supplier	Baker

---

\* From Encyclopedia of Chemical Engineering

Table 3.8 Properties of Phenylarsine oxide\*

---

Formula	C <sub>6</sub> H <sub>5</sub> AsO
Structure	
Chemical Name	Phenylarsine oxide
Physical Properties	
Molecular Weight	168.03
Form	solid
Melting Point (°C)	150
Solubility	soluble in toluene
Purity	97%
Supplier	Aldrich

---

\* From Encyclopedia of Chemical Engineering

Table 3.9 Properties of Phenylarsonic acid\*

---

Formula	$C_6H_5AsO_3H_2$
Structure	
Chemical Name	Phenylarsonic acid
Physical Properties	
Molecular Weight	202.04
Form	solid
Melting Point ( $^{\circ}C$ )	162-164
Solubility	soluble in toluene
Purity	97%
Supplier	Aldrich

---

\* From Encyclopedia of Chemical Engineering

Table 3.10 Properties of Nickel nitrate Hexahydrate\*

Formula	Ni(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O
Structure	
Chemical Name	Nickel nitrate Hexahydrate
Physical Properties	
Molecular Weight	290.80
Form	solid
Melting Point (°C)	56.7
Boiling Point (°C)	136.7
Specific Gravity	2.05
Solubility	soluble in water and ammoniumhydroxide
Purity	>99.0%
Supplier	Fluka

\* From Encyclopedia of Chemical Engineering

Table 3.11 Properties of Ammonium molybdate Tetrahydrate\*

Formula	$(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$
Structure	.
Chemical Name	Ammonium molybdate Tetrahydrate
Physical Properties	
Molecular Weight	1235.86
Form	solid
Melting Point (°C)	-
Boiling Point (°C)	-
Solubility	soluble in ammonium hydroxide, water
Purity	>99.0%
Supplier	Fluka

\* From Encyclopedia of Chemical Engineering

Table 3.12 Properties of Aluminum oxide, activated,  
neutral Brockmann\*

---

Formula	$\text{Al}_2\text{O}_3$
Structure	
Chemical Name	neutral alumina
Physical Properties	
Form	solid
standard grade	~150 mesh
surface area	155 $\text{m}^2/\text{g}$
pH of aqueous suspension	7.0+-0.5
Supplier	Aldrich

---

\* From Catalogue Handbook's Aldrich