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ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

APPLICATION OF DIFFERENT FORMS OF NICKEL ADSORBENT FOR
ADSORPTION OF MERCURY COMPOUNDS FROM A LIQUID HYDROCARBON



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In this study, removal of mercury compounds from liquid hydrocarbon by adsorption was investigated. Adsorbents were nickel, nickel oxide and nickel sulfide on silica support. Nickel content that was loaded on silica was 2.0 and 4.0 % by weight. A set of experiments was conducted at atmospheric pressure and temperature of 30°C, 50°C and 70°C. Mercuric (II) chloride and diphenylmercury were selected as model of ionic and organic forms of mercury compounds. Mercury compounds were dissolved in toluene which represented liquid hydrocarbon to obtain feedstock solution that contained 1 ppm of mercury.

The results show that nickel adsorbents can remove both mercuric (II) chloride and diphenylmercury from liquid hydrocarbon. Removal of mercury compounds depends on type of mercury compounds, operating temperatures and nickel contents. Percent removal of mercury compounds increases with increasing operating temperature and nickel content. Ability of adsorbents on removal of mercuric (II) chloride is in the following order: nickel sulfide > nickel > nickel oxide. In the adsorption of diphenylmercury, ability of each adsorbent is similar. In the adsorption of mercuric (II) chloride, nickelmercury (NiHg) and mercuric sulfide (HgS) are detected on spent nickel and nickel sulfide adsorbents respectively.

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การวิจัยนี้เป็นการศึกษาการกำจัดสารประกอบปรอทจากไฮโดรคาร์บอนเหลวโดยการดูดซับ ตัวดูดซับที่ใช้ในการวิจัยครั้งนี้คือ นิกเกิล นิกเกิลออกไซด์ และนิกเกิลซัลไฟด์เคลือบฝังบนตัวรองรับซิลิกา ปริมาณนิกเกิลบนตัวดูดซับคือ ร้อยละ 2.0 และ 4.0 ของน้ำหนักตัวรองรับ ทำการทดลองที่ความดันบรรยากาศ และที่อุณหภูมิ 30 50 และ 70 องศาเซลเซียส ใช้เมอร์คิวริกคลอไรด์เป็นและไดฟิซิลเมอร์คิวริเป็นตัวแทนสารประกอบปรอทในรูปโลหะอินทรีย์และรูปของโลหะอินทรีย์ตามลำดับ สารประกอบปรอทแต่ละชนิดถูกละลายใน โทลูอิน ซึ่งเลือกเป็นตัวแทนของไฮโดรคาร์บอนเหลว เพื่อใช้เป็นสารตั้งต้นที่มีความเข้มข้นปรอทเริ่มต้น 1 ส่วนในล้านส่วน

จากผลการทดลองพบว่า ตัวดูดซับ นิกเกิล นิกเกิลออกไซด์ และนิกเกิลซัลไฟด์ สามารถกำจัดสารประกอบปรอททั้ง 2 ชนิดได้ โดยปริมาณการดูดซับขึ้นกับชนิดของปรอท อุณหภูมิ และ ปริมาณโลหะนิกเกิลที่เคลือบฝังบนตัวรองรับ ดังต่อไปนี้ ปริมาณการดูดซับจะเพิ่มตามอุณหภูมิ และ ปริมาณโลหะนิกเกิลที่เคลือบฝังบนตัวรองรับ ในการดูดซับของเมอร์คิวริกคลอไรด์ พบว่าประสิทธิภาพการกำจัดปรอทของตัวดูดซับแต่ละชนิดจะเพิ่มขึ้นตามลำดับดังนี้ นิกเกิลซัลไฟด์ > นิกเกิล > นิกเกิลออกไซด์ ส่วนกรณีการดูดซับของไดฟิซิลเมอร์คิวริ ประสิทธิภาพการกำจัดปรอทของตัวดูดซับแต่ละชนิดจะไม่แตกต่างกัน การดูดซับเมอร์คิวริกคลอไรด์บนตัวดูดซับนิกเกิลและตัวดูดซับนิกเกิลซัลไฟด์พบสารประกอบปรอทบนตัวดูดซับในรูปสารประกอบนิกเกิลเมอร์คิวริ และเมอร์คิวริกซัลไฟด์ ตามลำดับ

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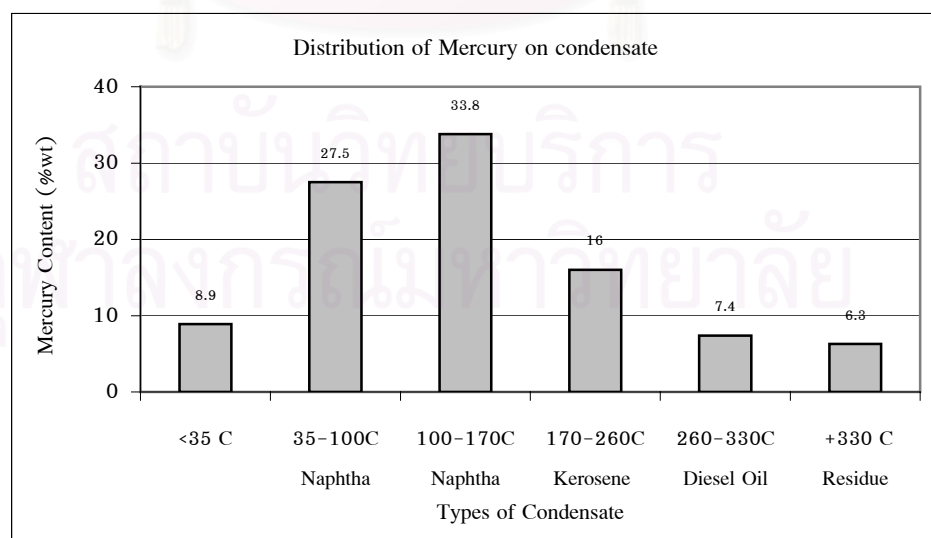
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CHAPTER I

INTRODUCTION

At present, most natural crude oil and petroleum products that produce in each day have two types of contaminant i.e. non-metallic compounds and metallic compounds. Non-metallic compounds have many types such as oxygen, sulfur compound and others. The majors of detrimental metallic compounds that are found in petroleum are mercury compounds.

It appears that a distribution of mercury compounds in petroleum samples varies widely. The relative distribution and amount of mercury compounds in liquid hydrocarbon depend on a sample source and history. Typical crude oil contains about 0.5-10 ppb of mercury. But some hydrocarbon condensate from natural gas contains higher level of mercury. For example, the amount of mercury compounds in the condensate from gas field in Indonesia and Algeria has been found to be as high as 100 to 300 ppb (Yan 1990). North Sea and San Joaquin crude oil has mercury contents of 55 to 110 ppb (Stockwell, 1993). Natural gas condensate from South East Asian is various range of mercury



compounds as shown in Figure1.1 (Sarrazin, 1993).

Figure 1.1 Distribution of mercury in natural gas condensate in South East Asian.

Mercury in natural gas is generally in elementary form. In natural condensate and hydrocarbon, there are various forms of mercury compounds i.e. elementary, ionic and organic form (Wilhelm, 2000). Ionic and organic forms are commonly found more than elementary form.

It has been determined that mercury can cause and increase human and animal health risk which are exposed to such mercury or to mercury-containing waste product. Mercury in liquid hydrocarbon can react with metal equipment and become metal amalgam. It is known to cause corrosion problem in industrial equipment (Chao, 1984). In addition, it can cause the deactivation of catalyst (Perepelitsa, 1979) (Morales, 1979). For this reason, mercury that may be presented in liquid and vapor streams must generally be removed so as to be at safe level.

Many methods have been proposed for mercury removal from both gas and liquid hydrocarbons. It can be divided into two methods i.e. chemical treatment (Yan, 1990) and adsorption (Audeh, 1989). The first method, mercury reacts with chemical compound and converts to mercury compound such as mercuric sulfide that easily to remove from feedstock. The other method, adsorption is more preferred to high efficiency of mercury removal. Mercury is adsorbed and remained in adsorbent. The adsorption method comprises contacting the hydrocarbon with an adsorbent at various conditions that depend on type of adsorbent used.

Adsorbents that are used for removal of mercury from liquid hydrocarbon usually have a metal as active species for adsorb of mercury. From the literature reviews, many types of adsorbents are proposed for removal of mercury from liquid hydrocarbon. There are several studies

used nickel as active metal (Torihata, 1991)(Ou, 1995). In addition, the forms of adsorbents are important factor in mercury removal (Yan, 1990). The role of reduced, oxidized and sulfided adsorbents in mercury removal was studied (Torihata, 1989). There are several factors that affect to mercury removal such as temperature (Yan, 1996) and nickel content in adsorbent.

The objectives of this experiment are the study of reduced nickel, nickel oxide and nickel sulfide adsorbent in removal of mercuric (II) chloride and diphenylmercury. In addition, this research also studies the effect of nickel content and operating temperature that affect the adsorbents in removal mercury compounds.

In this study, types of mercury compounds in feedstock are mercuric (II) chloride and diphenylmercury. Mercuric (II) chloride is selected as representative model of ionic mercury because it generally presents in crude oil. Diphenylmercury is used as representative model of organic mercury because it has the strongest metal-carbon bond of the organic mercury compound. It would therefore be reasonable to say that if it is able to remove diphenylmercury, it is able to remove other organic mercury compound. Toluene containing 1 ppm of mercury compound is used as the feedstock. Toluene is used as solvent because it can dissolve mercury compounds and its boiling point temperature is high. These experiments are conducted in batch system at atmospheric pressure and operating temperature 30°C, 50°C and 70°C.

After adsorption, liquid and spent adsorbent is separated by filter paper. Liquid samples are digested with concentrated acid and oxidizing reagents that conform to ASTM D-3223 to obtain mercury (II) ions in aqueous phase. Then, they are measured the remaining mercury by cold vapor atomic absorption spectrometer. The other product, some of spent adsorbents is digested to measure deposited mercury, which the procedure follows to ASTM D1997-91. In addition, it is stirred in fresh toluene to dissolve desorbed mercury and toluene is digested and

measured the content of desorbed mercury. Digestion and measurement procedures are described in Chapter III. The results and discussions of this study are in Chapter IV.



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CHAPTER II

LITERATURE REVIEWS

This chapter concern with the literature reviews of method to remove mercury compounds. The literatures are divided into three sections. The properties and problems of mercury are in the first section. The later section, the methods that use chemical reagent to react with mercury compound in liquid hydrocarbon. The last section which is divided into two parts are described the adsorption methods. The adsorption method uses adsorbents to remove mercury compounds. Part I concerns with nickel as an active metal which is impregnated on various supports. Part II concerns with the different forms of adsorbent that effect to the amount of adsorption of adsorbent.

2.1 Properties and Disadvantage of Mercury Compound

2.1.1 Chemistry

Mercury is one of two metallic elements that are liquid at room temperature. It is in the fifth period and the third member of the II B groups of periodic table. All of the elements in IIB group lose two electrons to form ions. The Oxidation State of mercury is 1 and 2. Atomic number of mercury is 80 while atomic weight is 200.59. The capable of mercury is reaction to hundreds of compounds which its own properties. Mercury metal has a high vapor pressure at ordinary temperature.

Mercury in Petroleum

Mercury is found in wide range of petroleum such as natural gas and crude oil. Mercury compounds are found in various forms. Quantities and types of mercury compounds depend on the source and type of crude oil. For example, amounts of mercury in natural gas condensate were generally 10-3000 ppb (Sarrazin, 1993) and 0.5-10 ppb in crude oil (Yan, 1990). Amounts

of mercury in natural gas condensate of each boiling range of condensate are different. The majority of mercury is found in the naphtha and kerosene fraction.

2.1.2 Mercury Species (Wilhelm, 2000)

Mercury is a naturally occurring component of geological hydrocarbons and is distributed through petroleum production. In liquid hydrocarbon, mercury compound occurs in three major forms.

Elemental Mercury

Elemental mercury can dissolve a few ppm in crude oil and hydrocarbon liquids in atomic form (Hg^0). The limiting solubility concentration of elemental mercury in liquid hydrocarbons depends strongly on temperature. Hg^0 is able to adsorb to surface of equipment in petrochemical processes.

Organic Mercury

Organic mercury compounds contain at least one covalent bond between mercury and carbon atom. These compounds are soluble in crude oil and gas condensate to a concentration higher than elemental mercury. The examples of these compounds are mono- or di- alkyl mercury and mono- or di- phenyl mercury. Like elementary mercury, these mercury compounds can adsorb to the surface of equipment in petrochemical processes.

Ionic Mercury

Ionic mercury compounds are slightly soluble in crude oil and gas condensate but preferentially partition to the water phase. Mercuric (II) chlorides have a high solubility in organic phase (approximately five times more than elemental mercury).

2.1.3 Disadvantage of Mercury in Petroleum.

The wide ranges of mercury in raw condensates or crude oil and can cause many major problems that have specific negative effects on people, corrosion in equipment and deactivation of catalysts.

Mercury Corrosion

Traceable quantity of elemental mercury in natural gas can be a potential cause of problems in liquefied natural gas (LNG) plant. The problems often occurred with aluminum constructed equipment which it can form an amalgam with mercury for of, in the production of ethylene (Audeh, 1991). A natural gas condensate is commonly passed through a heat exchanger constructed of aluminum. It has been found that mercury tends to amalgamate with the aluminum. In addition, elemental mercury can react with iron oxide corrosion products on pipe and equipment walls equipment corrosion has resulted in plant shutdown, which required costly replacements and loss the production. It is necessary to remove mercury before processing.

Catalyst Deactivation

Catalyst used in catalytic processes such as catalytic hydrocarbon is susceptible to mercury poisoning. Many investigators studied an effect of mercury on catalysts

Perepelitsa et al. (1979) studied the effect mercury on hydrogen adsorption on Pd. They found that mercury inhibited the adsorption of hydrogen without changing significantly the bond energy and the ionization kinetics of the adsorbed hydrogen. The loss of adsorption capacity depended on structure of Pd.

Morales et al. (1979) studied the poisoning effect on the hydrogenolysis of cyclone on platinum alumna catalyst. The result showed that Hg^{2+} changed the reaction rate and adsorption properties of Pt.

Grinchina et al. (1991) studied the effect of mercury poisoning on Rh, Ru catalysts. They found that the mercury poisoning decreased the amount

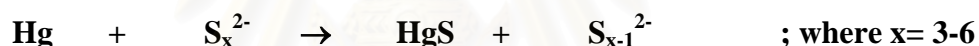
of adsorbed hydrogen on catalyst and the heat of adsorption was also decreased. They suggested that the mercury poisoning occurred by chemisorption and blockage of the surface of catalyst.

2.2 Study of Mercury Removal

Several methods for removal of mercury have been studied and proposed for many years. It can be classified into two methods i.e. chemical treatment and adsorption

2.2.1 Chemical Treatment

Chemical treatment is a method that converts mercury in petroleum to the form which is easily remove from petroleum. The method is used chemical compounds such as alkali polysulfide. The reaction between mercury and sulfur compounds is shown below



Mercuric sulfide (HgS) occurred is a solid material that cannot dissolve in hydrocarbon and is easy to remove from feed stream.

Yan (1990) proposed a method for removing mercury from natural gas condensate by contacting them with a dilute aqueous solution of alkali metal sulfide salt and recovering the treated liquid hydrocarbon. The alkali metal sulfide salt used was Na_2S_x . The mercury content in the condensate was 220 ppb. The study was carried out by mixing the condensate with Na_2S_x and aqueous NaOH solution of varied concentration at temperature of 75°C . The result shows that the important factors in removing mercury from the condensate are intensity of mixing, concentration of Na_2S_x , volume ratio of caustic solution of Na_2S_x , and efficiency of phase separation.

Yan (1991) studied the reaction of trace mercury in natural gas with polysulfide solution in a packed column. The residual Hg in the gas phase can be removed from about 0.1 to below 0.01 ppb. In this system, the gas was contacted with stainless steel packing wetted with a solution containing about

3 ppm of polysulfide salt. Polysulfide reacts with Hg in the gas phase to form insoluble mercuric sulfide, HgS, and thus remove Hg from gas.

Audeh (1989) studied the removal of residual mercury in liquid hydrocarbon by mixing with aqueous polysulfide solution. The process was carried out at temperature of 70°F and used 0.5 cc of sodium polysulfide which contained 22.2 wt% of sulfur. The mercury in product was decreased to less than 0.01 ppb from initial concentration of 13 ppb.

Furuta et al. (1988) studied the effect of mercury compounds on mercury removal by using aqueous solution of sulfur compound. The sulfur compound was represented by a general formula $MM'S_x$ where M is selected from a group consisting of alkali metal, ammonium radical, M' is selected from a group consisting of alkali metal, ammonium radical and hydrogen and x is a number of at least 1. The mercury compounds were elemental, inorganic as mercuric chloride and organometallic as diethylmercury. After shaking with 5-wt% of Na_2S_4 solution for 10 minutes. It was found that only elemental and mercuric chloride were removed from liquid feed. Furthermore, after mixed with Na_2S_4 solution, then, 0.5 wt% of $MoS/\gamma-Al_2O_3$ containing 7% of Mo was added at temperature below 200°C. After treating, the liquid hydrocarbon phase was found to have Hg content of 6 ppb from initial concentration of 200 ppb. It was found that $MoS/\gamma-Al_2O_3$ could also remove organometallic mercury from the liquid feed.

2.2.2 Adsorption

The disadvantage of chemical reaction in removing mercury is the contamination of chemicals that use for remove of mercury to the product. Adsorption is a high efficiency method for removing of mercury. The adsorption method comprises contacting the hydrocarbon with an adsorbent at various conditions, depending on type of adsorbent used. Mercury compounds are adsorbed and remained in adsorbent. Thus, the treated hydrocarbon is readily free from mercury contamination. There are many studies about removal of Hg by the adsorption.

Koyama (1976) used activated clay to remove Hg from waste oil. The oil contaminated with 350 ppm of mercury was stirred with activated clay at temperature of 80°C for 30 minutes. The mercury content in waste oil was decrease to about 2 ppm.

Leeper (1980) proposed corrosion of LNG plant caused by mercury and also method for removal of mercury. For example, natural gas contaminated with mercury is contacted with a fixed bed of metal sulfide on alumina-silica support.

Schnegula et al. (1985) proposed an adsorbent for Hg removal from gas and liquid. The adsorbent comprised a clay support that consists of activated carbon and sulfur as an active component. The results show that percent removal of mercury compounds by adsorbent is more than 80 %

Torihata (1988) studied the used of Cu^{2+} and Sn^{2+} for remove of Hg from heavy condensate. The result shown that Cu^{2+} and Sn^{2+} supported on porous material such as activated carbon can remove Hg to concentration about 2.7 ppb from initial concentration of 130 ppb, corresponding to 97.9% Hg removal.

Duisters et al. (1987) studied a process for removing mercury from natural gas condensate. The process comprises contacting the condensate with an ion exchange resin. The ion exchange resin used is a macroporous copolymer of styrene and divinylbenzene that contains active thiol groups. A natural gas condensate containing 35 ppb of mercury was found to have mercury content of less than 1 ppb.

Arakawa (1991) used a fixed bed of cation exchange resins. A fixed bed of cation exchange resin was pretreated with the 5 %wt CuCl_2 aqueous solution. Hydrocarbon oil containing 200 ppm of HgCl_2 was treated at temperature of 30 to 75°C. The remaining mercury was found to below 10 ppm.

Arakawa (1991) also used anion exchange resins in a packed column. The anion exchange resins was treated with 5 %wt of NH_2S solution. Hydrocarbon oil containing 400 ppm of Hg was passed through the column at temperature of 50°C . The result found that mercury was decreased to below 10 ppm.

Audeh (1989) used a hydrodesulfurization catalyst such as CoMo catalyst for removing mercury. Natural gas condensate contained 200 ppb of mercury was mixed with H_2S and the mixture was passed through the reactor. Stripping gas used was CH_4 and the operating conditions was at 125 psig, $200\text{-}270^\circ\text{C}$, flow rate 10 ml/hr. The treated condensate had mercury content below 10 ppb with 95% mercury removal.

Audeh (1991) proposed a process for removal of mercury from natural gas condensate by contacting natural gas condensate with elemental selenium in a reactor vessel. The operating condition, the pressure could be set from about 1 to 40 atm. The temperature could be ranged from about $15\text{-}217^\circ\text{C}$. The space velocity kept below about 20. It could reduce the amount of mercury in condensate from above 1,100 ppb to below 20 ppb.

Ou (1990) studied a method for removal of mercury by using an adsorbent. This method was directed to an effective way of removing elemental and ionic mercury from liquid hydrocarbon. The adsorbent was packed in a column and the mercury-contaminated hydrocarbon was passed through the column at temperatures ranging from about ambient to about 100°C . The adsorbents used were reduced copper on zinc oxide and alumina that performed virtually removed all mercury in condensate feed. Another adsorbent used was reduced nickel on clay, which reduced 90% mercury of Algerian condensate containing 32 ppb of mercury.

Yan (1989) provided a method for Hg removal by high temperature reactive adsorption. Adsorbent used was Ag or CuS supported on alumina. The temperature used was in the range of $75\text{-}400^\circ\text{F}$. For initial mercury concentration of 200 ppb the result showed that $\text{CuS}/\text{Al}_2\text{O}_3$ provided 98.6%

mercury removal while $\text{CuO}/\text{Al}_2\text{O}_3$ and $\text{Ag}/\text{Al}_2\text{O}_3$ decreased mercury content to below 20 ppb. It was found that high temperature not only improve the adsorption rate but also increase the adsorption capacity.

Sookkho (1995) studied the removal of mercury compounds by adsorption on Cu-Zn adsorbent. His experiments were conducted at 30°C to 75°C and pressure of 200 psig. Mercuric (II) chloride was used as mercury compounds in ionic form. Phenylmercuric acetate and diphenylmercury used as mercury compounds in organometallic forms. Experimental results showed that removal of mercury was significantly dependent of temperature but independent on pressure. In addition, it was also depended on the nature of mercury compounds types.

Tantichaipakorn (1998) studied the removal of mercury compounds by adsorption on Ni-Cu adsorbent. The experiments were conducted at 30°C to 70°C and atmospheric pressure. Mercuric (II) chloride and diphenylmercury was selected as representative mercury compounds of ionic form and organic form respectively. Mercuric (II) chloride and diphenylmercury was dissolved in toluene to obtain feedstock at concentration of 1 ppm. The results showed that removal of mercury was significantly dependent of temperature. In addition, it was also depended on the nature of mercury compounds types.

Chokelarb (2000) studied the adsorption of mercury compounds on copper oxide and copper sulfide adsorbents. The copper content was 2.5 % by weight. This experiment used alumina as support. The experiments were conducted in batch system at 30°C to 70°C and atmospheric pressure. Mercuric (II) chloride and diphenylmercury was selected as representative mercury compounds of ionic form and organic form respectively. Mercuric (II) chloride and diphenylmercury was dissolved in toluene to obtain feedstock at concentration of 1 ppm. The results showed that removal of mercury was significantly dependent of temperature. In the adsorption of mercuric (II) chloride, percent removal decreased with increasing operating temperature. Unlike mercuric (II) chloride, percent removal of

diphenylmercury increased with increasing operating temperature. In addition, it was also depended on the nature of mercury compounds types.

Literature summary

1. Mercury compound in petroleum is in elemental, ionic and organic forms.
2. Mercury in petroleum leads to several major problems in chemical processes such as catalyst poison, equipment corrosion and pollution of environment.
3. Methods for mercury removal are classified in to two methods: chemical treatment and adsorption. Adsorption is the most widely used method because it provides high efficiency on mercury removal and convenient.
4. Mercury removal in the gas phase higher efficiency than in liquid phase. One of factors concerns with different forms of mercury in gas and liquid phase.
5. There are many metals used for removed mercury such as Mo, Ni, Cu, Zn, Pb or Fe.
6. In general, the ability of adsorbent in removal of mercury compounds depends on the support. The inert supports such as silica hardly adsorb mercury compounds from liquid hydrocarbon. In contrast, the other support such as alumina (Al_2O_3) activated carbon and clay are high ability in adsorption of mercury compounds.

7. In general, the operating temperature is range of 30°C to 200°C and operating pressure is range of 10 psig. to 1000 psig.



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CHAPTER III

EXPERIMENTAL AND ANALYTIC METHODS

The preparations of experiment and analytic methods are described in this chapter. It is divided into three sections. The first section concerns with the adsorbent preparation. Impregnation and calcination procedures are described in this section. The second part describes the experimental apparatus and adsorption procedures. The third section refers to analytical methods and errors of the experiments.

3.1 Adsorbents Preparations

Adsorbent was composed of metallic components and supports. In this study, silica was used as the inert support and metallic component was nickel metal. The adsorbent preparations were divided into two steps. The first step was impregnation and the last was calcination.

3.1.1 Impregnation

Impregnation was the procedure that loads the metal to surfaces of the support. Wet impregnation is used to impregnate nickel compound on the silica support. Supported nickel samples were prepared by impregnation of silica with solution containing the requisite amount of nickel nitrate to yield precursors of desired composition. This procedure used nitrate solution because it could easily dissolve in water and easily calcine to the other forms. Figure 3.1 shows the apparatus of impregnation. It comprised of a round bottom flask, which was connected with a pipette, a vacuum pump and a heater. Procedures of impregnation are described below.

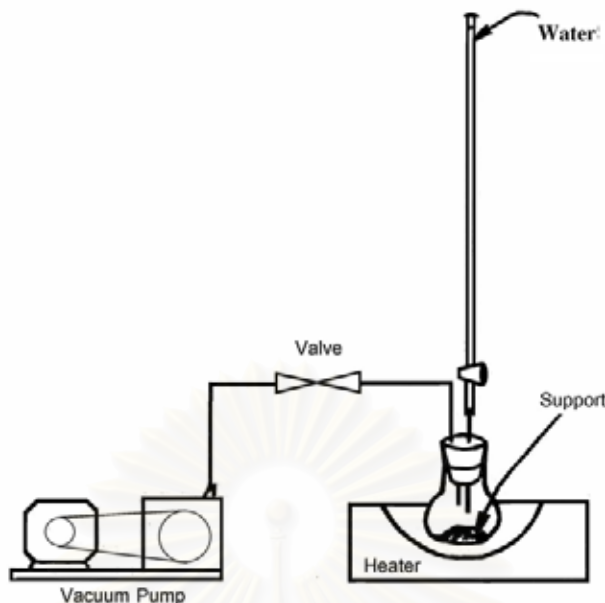


Figure 3.1 Schematic diagram of impregnated apparatus.

- 1. Approximately 10 grams of silica support in a round-bottom flask was dehydrated by a vacuum pump under pressure at 10 mm Hg.**
- 2. The round-bottom flask was heat to 120 °C for 3 hours. The flask was allowed to cool to room temperature.**
- 3. Distilled water was dropped in the flask under vacuum pressure. The flask was vigorously shaken for well mixed between silica and distilled water.**
- 4. Silica support was poured to nickel nitrate solution. The concentration of the solution was calculated from the requisite amount of nickel metal loaded on silica support, 2.5 % and 5.0 % by weight of silica.**
- 5. The mixed solution was heated and stirred for dehydration until near dryness. Nickel in the solution penetrated to the silica support by capillary force.**
- 6. The impregnated silica was dried at 120 °C in the muffle furnace for 12 hours.**

3.1.2 Calcination

Calcination procedures were divided into three ways because forms of adsorbents that used in this study are three forms, reduced, oxide and sulfide form. Figure 3.2 shows the schematic of the apparatus of calcination. It was comprised of a pyrex glass tube with placing in a muffle furnace. A temperature controller and variac controlled the temperature of the furnace. Zero air or hydrogen gas was used to oxidize or reduce adsorbents. Procedures of calcination are described below.

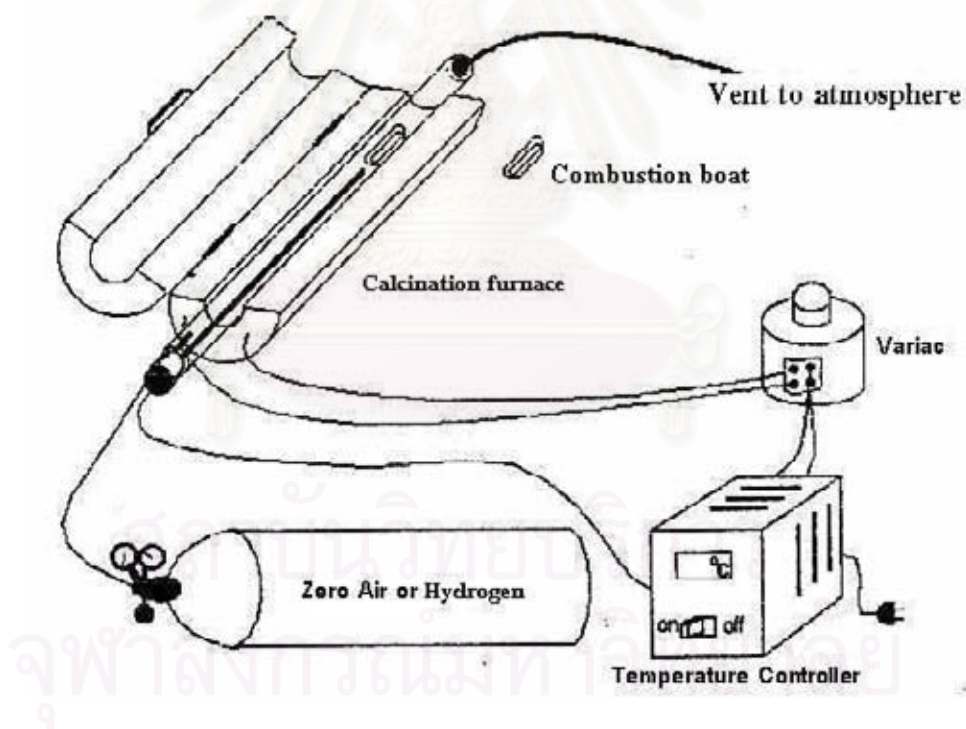


Figure 3.2 Schematic diagram of the apparatus of calcination.

Oxidation

- 1. The impregnated silica was put in a combustion boat and placed into the pyrex glass tube following placed in the muffle furnace.**
- 2. Atmospheric pressure of zero air was flown through the tube at rate of 12 l./hr.**
- 3. The temperature was increased from room temperature to 400 °C at the rate of 1 °C/min. and maintained at this temperature for 3 hours.**
- 4. The oxide adsorbent was cooled in air stream to room temperature. The adsorbent was kept in desiccator before using in an experiment.**

Reduction

- 1. The impregnated silica was put in a combustion boat and placed into the pyrex glass tube following placed in the muffle furnace.**
- 2. Atmospheric pressure of hydrogen gas was flown through the tube to reduce the adsorbents at rate of 12 l./hr.**
- 3. The temperature was increased from room temperature to 400 °C by the rate of 1 °C/min. and maintained at this temperature for 3 hours.**
- 4. The reduced nickel adsorbent was cooled in hydrogen stream to room temperature. The adsorbent was kept in toluene before using in each experiment.**

Sulfurization

- 1. The oxide adsorbent was impregnated with sulfur compound, 3,3'-thiodipropionic acid. The method of impregnation replaced nickel solution with sulfur compound. The quantity of sulfur was calculated from the stoichiometry of the reaction with nickel metal in the adsorbent.**
- 2. The impregnated adsorbent was put in a combustion boat and placed into the pyrex glass tube following placed in the muffle furnace.**
- 3. Atmospheric pressure of hydrogen gas was flown through the tube at rate of 12 l./hr.**
- 4. The temperature was increased from room temperature to 275 °C by the rate of 1 °C/min. and maintained at this temperature for 2 hours.**
- 5. The sulfide adsorbent in calcination tube was cooled in hydrogen stream from 275 °C to room temperature. The adsorbent was kept in desiccator before using in an experiment.**

Silica support

Silica was impregnated by distilled water instead of nickel solution. It was calcined at the same condition of each nickel adsorbent. Silica supports were used to adsorb mercury compounds compare with the adsorption of nickel adsorbents.

3.2. Experimental Apparatus and Adsorption Procedures

3.2.1 Experiment Apparatus

Figure 3.3 shows the apparatus of adsorption experiment. The apparatus was comprised of a 250-ml. flask, which was connected with a propeller and motor. The flask was immersed in an oil bath, which was heated by a heater. The temperature of the oil bath was controlled with the temperature controller for constant temperature at 30°C, 50°C and 70 °C. Table 3.1 showed variables of this experiment. The adsorption procedures are described below.

Table 3.1 Variable of the experiments.

Compound	Mercuric (II) chloride (HgCl_2) Diphenylmercury (DPM)
Nickel contents (%by weight)	2.5 5.0
Type of adsorbents	NiO Ni NiS
Temperature ($^{\circ}\text{C}$)	30 50 70

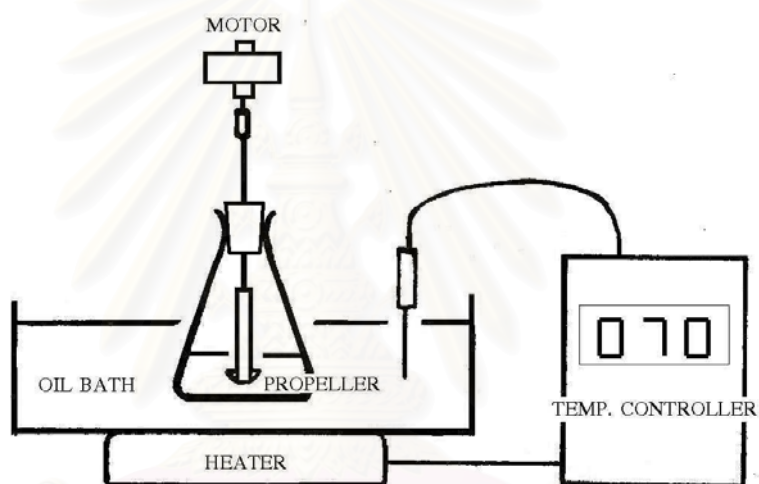


Figure 3.3 Schematic diagram of the experiment apparatus.

3.2.2 Feed Preparation

In this study, mercuric (II) chloride and diphenylmercury was selected as model of ionic and organic mercury compound respectively. The initial concentration of mercury compound in toluene was prepared at 5 ppm and 2 ppm. Mercury compound was weighted and put in 2.5-liter Erlenmeyer flask. 1500 g of toluene was poured to the flask. The solutions were stirred by a magnetic stirrer for at least 6 hours. Then, the solution was diluted the concentration to 1 ppm for used as feedstock and kept this feedstock in refrigerator.

3.2.3 Adsorption Procedures

- 1. Nickel adsorbents was weighed out approximately 1 gram and put to a 250-ml. Erlenmeyer flask.**
- 2. The flask was vacuumed by vacuum pump. Approximately 1 to 2 ml. of toluene was dropped in the sample flask to fill pore of the adsorbent. Slowly shake the flask for well mixed between toluene and the adsorbent.**
- 3. Approximately 100 grams of liquid feedstock was poured into the sample flask.**
- 4. The sample flask was placed in the oil bath that was controlled temperature. It was stirred at constant temperature for 60 minutes.**
- 5. The solution was filtered with filter paper to separate a spent adsorbent from liquid product.**
- 6. The spent adsorbent was kept in a plastic bag. It was analyzed the properties after adsorbed mercury compounds. The liquid product was digested to determine the mercury remaining.**

3.3. Analytical Methods and Errors of Experiments

This section is described analytical techniques and errors of experiments. In each experiment, fresh adsorbents and spent adsorbents were analyzed characteristics such as percent of nickel, form of nickel, mercury content, surface area and pore volume of adsorbents. Analytical procedures are described below. Analytical results are shown in the Chapter IV

3.3.1 Adsorbent Characterizations

Nickel Digestion

The determination of nickel content in the adsorbent followed the standard test method ASTM D1977-91. The procedure of digestion in standard test used concentrated acids to decompose nickel from the adsorbent. The procedures are described below.

1. Approximately 0.5 gram of the adsorbent was put in a crucible.
2. The sample was added with 10 ml. of concentrated sulfuric acid, 10 ml. of concentrated nitric acid, 5 ml. of concentrated hydrofluoric acid, and 10 ml. of distilled water.
3. The mixture was placed on a hot plate and slowly stirred. The adsorbent was first dissolved in acid solution and precipitated again after the acid was evaporated. The solution was evaporated to near dryness.
4. The crucible was removed from the hot plate and cooled to room temperature.
5. The sample was again added 20 ml. of 19 % hydrochloric acid and 30 ml. of 3 % hydrogen peroxide. The crucible was covered with a watch glass and returned to the hot plate.
6. The solution was heated and kept boiling until the adsorbent dissolved. The crucible was cooled to room temperature.
7. The solution was made volume to 100 ml. with deionized water. The finished solution was kept in refrigerator.

Forms of Nickel on Support Surface

In this study, the form of adsorbents was verified by using X-ray diffraction spectroscopy. The principle of X-ray diffraction technique was the scatter of X-ray through the crystalline sample to give the characteristic pattern of intensities. This pattern can be interpreted in terms of the location of atom in the molecules and give information about molecular structure.

Surface and Pore Volume

A micrometrics model ASAP 2000 is an instrument to measure surface area, pore volume and pore size distribution of the adsorbents. The instrument detects the volume of adsorbed nitrogen gas on surface at various relative pressures. There are two operating steps i.e. the degassing step and analysis step. Firstly, the adsorbent was heated and placed under vacuum to remove the moisture and other contaminants. The condition of degassing was operated at 150 °C and vacuum until pressure to 10 mm.Hg. After that, the sample cell was transferred the sample cell from a degas port to an analyze port.

At the analyze port, the sample was analyzed at various relative pressures and liquid nitrogen was used as coolant. Nitrogen gas was used as an analysis gas. The volume of adsorbed nitrogen on sample will relate with the relative pressure (P/P_0). The volumes of adsorbed nitrogen gas and relative pressures were plotted the graph. The Y-intercept and slope of the graph was calculated BET surface area of sample. The other results of the instrument were BJH cumulative pore volume and average pore diameter. In each experiment, adsorbents were analyzed by this instrument in order to study the variation of properties.

3.3.2 Mercury Digestion

Because mercury in toluene phase cannot be directly measured by an atomic absorption spectroscopy technique, the sample is always digested with acid reagent. Acid digestion is the method that uses strong acids and high temperature to change all mercury species in hydrocarbon phase to mercury II ion (Hg^{2+}). Figure 3.3 shows the apparatus of digestion. It was comprised of a round bottom flask that was connected with a condenser. The flask was immersed in the oil bath and heat at 95°C for 2 hours. Temperature controller controlled the constant temperature of the oil bath at 30°C, 50°C and 70°C. The procedure of digestion is described below.

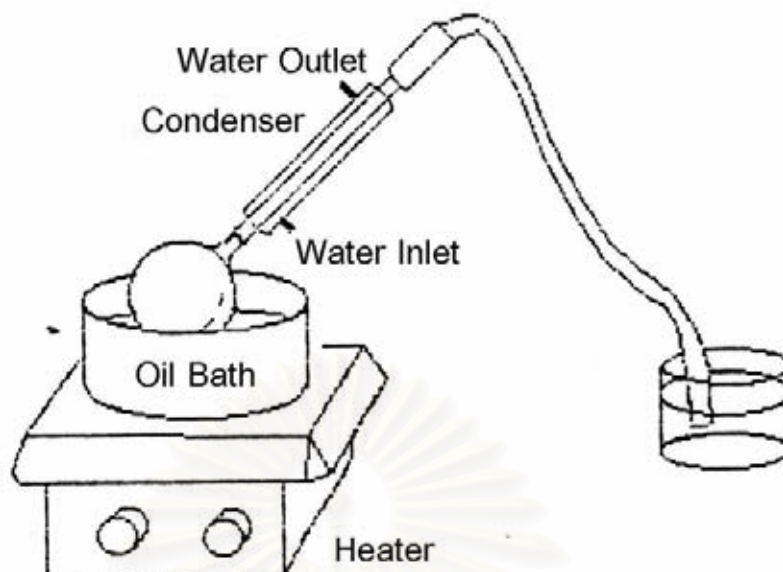


Figure 3.4 Schematic diagram of digestion apparatus

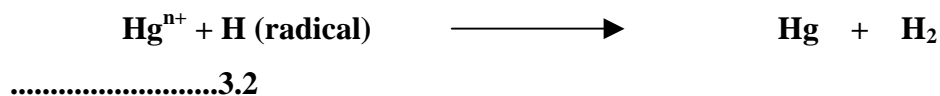
Digestion Procedure

- 1. Approximately 30 grams of the sample was transferred to a 250 ml. flat round flask.**
- 2. The sample was added with 5 ml. of concentrated sulfuric acid, 5 ml. of concentrated nitric acid and 15 ml. of 5% potassium permanganate solution.**
- 3. The sample was stirred at 600 rpm for 15 minutes. After that, 8 ml. of 5% potassium persulfate was added to the flask.**
- 4. The flask at the top was equipped with a reflux condenser and subsequently heated the oil bath at 95 °C for approximately 2 hours.**
- 5. After that, the flask was removed from the oil bath and cool to the ambient temperature.**

6. The sample was added 6 ml. of sodium chloride-hydroxylamine hydrochloride. The sample was transferred into a 250 ml.-separating funnel. Deionized water was added and shaken vigorously.
7. After both phases had separated, the water-phase was separated from toluene-phase. Then the remaining toluene-phase was extracted again by deionized water to extract the remaining mercury to water.
8. Finally, all water-phases were mixed and made the total volume to 100 ml.

Cold vapor technique

In this study, the high sensitivity measurement of mercury content is the cold vapor technique or the hydride technique. The cold vapor technique involves the reaction of acidified aqueous samples with a reducing agent such as sodium borohydride. Mercury is the only element apart from the inert gas with appreciable vapor pressure at room temperature. The reaction is shown in the following equations



Equation 3.1 shows the reaction between sodium borohydride and hydrochloric acid to generate radical hydrogen in quartz cell. In quartz cell,

radical hydrogen reacts with mercury (II) ion to gaseous mercury atoms as shown in Equation 3.2. Mercury atoms can absorb 253.7 nanometre of wavelength. The content of mercury is interpreted from the intensity of light that absorbed by mercury atoms. The sensitivity of this technique is approximately 10^{-9} g.

3.3.3 Experimental and Analysis Error

Experimental Error

In this section, experiments are conducted to verify repeatability, an average and a standard deviation value of the experiment. Equation 3.3 and Equation 3.4 define an average value and percent deviation.

$$\text{Average value } \bar{X} = \frac{\sum x}{n} \dots\dots\dots 3.3$$

$$\text{Percent deviation from average value} = \frac{\sqrt{(X - \bar{X})^2}}{\bar{X}} \times 100 \dots\dots\dots 3.4$$

After each experiment, the solution liquid, feed and spent adsorbents were analyzed for the mercury content by using atomic absorption spectroscopy techniques. The experiment was repeatedly adsorbed and digested at the same condition for 5 times. Average concentration of remaining mercury and the maximum percent deviation value were calculated and shown in Table 3.2 to Table 3.4.

Table 3.2 Average of mercury remaining and percent deviation in adsorption on Ni/SiO₂ repetitive study.

Temperature (°C)	Type of Mercury	%Metal on Adsorbent	Average (ppb)	Maximum % Deviation
30	HgCl ₂	2.5	638	2.10
	HgCl ₂	5.0	566	2.42
	DPM	2.5	879	1.72
	DPM	5.0	805	1.90
50	HgCl ₂	2.5	545	1.46
	HgCl ₂	5.0	507	3.92
	DPM	2.5	837	1.73
	DPM	5.0	723	1.20
70	HgCl ₂	2.5	502	3.48
	HgCl ₂	5.0	436	2.63
	DPM	2.5	793	1.36
	DPM	5.0	631	2.32

Table 3.3 Average of mercury remaining and percent deviation in adsorption on NiO/SiO₂ repetitive study.

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Temperature (°C)	Type of Mercury	%Metal on Adsorbent	Average (ppb)	Maximum % Deviation
30	HgCl ₂	2.5	797	2.68
	HgCl ₂	5.0	749	2.65
	DPM	2.5	896	1.11
	DPM	5.0	874	2.19
50	HgCl ₂	2.5	726	3.01
	HgCl ₂	5.0	679	2.68
	DPM	2.5	844	1.65
	DPM	5.0	725	1.75
70	HgCl ₂	2.5	672	2.75
	HgCl ₂	5.0	598	3.27
	DPM	2.5	787	3.17
	DPM	5.0	640	2.68

Table 3.4 Average of mercury remaining and percent deviation in adsorption on NiS/SiO₂ repetitive study.

Temperature (°C)	Type of Mercury	%Metal on Adsorbent	Average (ppb)	Maximum % Deviation
30	HgCl ₂	2.5	96	11.24
	HgCl ₂	5.0	95	11.31
	DPM	2.5	918	1.06
	DPM	5.0	878	1.13
50	HgCl ₂	2.5	60	18.01
	HgCl ₂	5.0	47	24.68
	DPM	2.5	847	0.92
	DPM	5.0	778	1.78
70	HgCl ₂	2.5	16	66.88
	HgCl ₂	5.0	17	57.34
	DPM	2.5	784	1.31
	DPM	5.0	630	2.35

Digestion Error

This experiment was conducted to study the error from digestion. In this experiment feedstock was digested at the concentration of 1-ppm. The experiment was repeated at the same condition for 3 times. Average concentration and maximum deviation of these experiments are shown in Table 3.5

Table 3.5 average concentration and maximum deviation of mercury compound in digestion error.

Compounds	1 (ppb)	2 (ppb)	3 (ppb)	Average Conc. (ppb)	Maximum Deviation (%)
Mercuric (II) chloride	985	973	934	964	3.11
Diphenyl mercury	945	952	966	954	1.22

Instrumental Error

This experiment was conducted to verify instrumental error, average and deviation of experiments. The same sample was analyzed for 3 times by the instrument at the same condition. From analysis, the maximum percent deviations were in range of 5 % for mercuric (II) chloride removal and diphenylmercury removal.

Mercury Content in Toluene

This experiment was to verify the mercury content that existed in toluene. Pure toluene was digested by the acid digest reagent and measured the digested solution by cold vapor atomic absorption technique as described in previous Section. This result shows that the mercury content is not over 1 ppb.

Blank Test

The experiment in this section verified the quantity of disappearance mercury compounds during operations. No adsorbent was used in this test. The concentrations of mercury product are shown in Table 3.6 and plotted with the operating temperatures in Figure 3.5. Noraphol (1995) and Pichan (1998) who conducted the experiment using nickel and copper adsorbents also obtained similar results. It was found that mercuric (II) chloride and diphenylmercury concentration in product and feed was almost identical. It indicates that mercuric (II) chloride and diphenylmercury disappear by adsorption of the glassware.

Table 3.6 Percent of mercury compounds losses from feed at various temperatures.

Component	Mercury losses from feed(%)		
	30 °C	50 °C	70 °C
Mercuric (II) chloride	2.63	3.11	3.00
Diphenylmercury	1.30	1.07	2.15

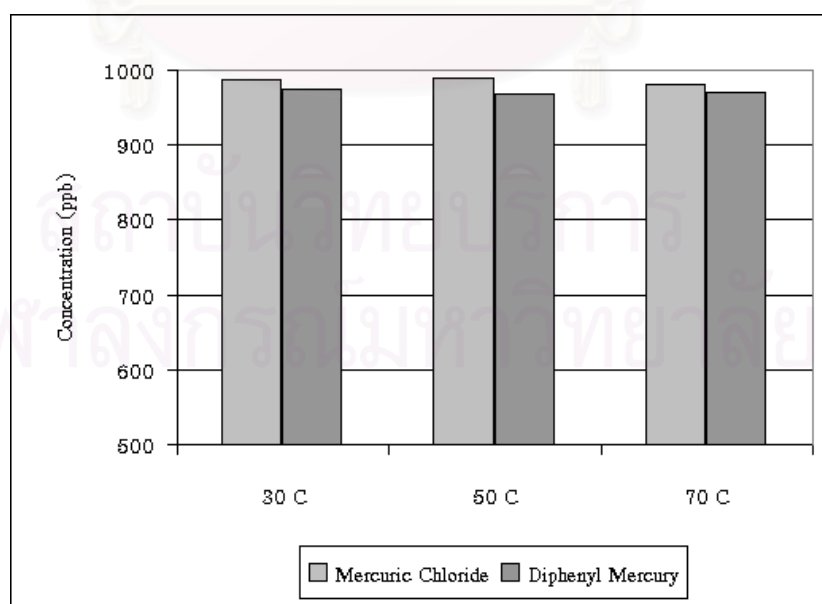


Figure 3.5 Remaining mercury of blank test at various temperatures.



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CHAPTER IV

RESULTS AND DISCUSSIONS

Study on removal of mercury compounds was conducted in a batch system. Mercuric (II) chloride (HgCl_2) and diphenylmercury (DPM) were selected as representative compounds of ionic and organic mercury compounds respectively. Different type of nickel adsorbents was used to study adsorption of mercury compound from solution containing 1 ppm. Silica support was impregnated with nickel nitrate solution and calcined in a muffle furnace. Impregnation and calcination procedures are described in Chapter III. After calcination, the adsorbents were digested to determine the nickel content and were also verified the form of nickel. Properties of adsorbents are reported in Section 4.1. The effect of adsorbent types, nickel contents and temperatures on mercury removal is described in Section 4.2 and Section 4.3.

4.1 Characteristics of Silica Support and Nickel Adsorbents

4.1.1 Silica Support

In generally, silica or silicon dioxide was an inert support. It can resist reaction with acid. It was classified as an insulator oxide like alumina and magnesium oxide (Bond, 1986). It did not interact with oxygen. In this experiment, silica support was a commercial product that was produced by Carlo Erba company.

Average particle size of silica support which was measured by particle analyzer was approximately 15,000 Å. Surface area of silica support was approximately 394 m²/g. It had an average pore diameter approximately 168 Å which was in the range of mesopores (20 Å < size < 500 Å) (Leofanti, 1998).

4.1.2 Nickel and Sulfur Content in Nickel Adsorbents.

After impregnation and calcination, adsorbents were analyzed for nickel and sulfur content. Nickel content was determined using flame atomic absorption spectroscopy. The digestion procedure followed the standard test method ASTM D1977-91 as described in Chapter III. The results of nickel and sulfur contents are shown in Table 4.1.

Table 4.1 Nickel and sulfur contents in the adsorbent

Type of adsorbents	Nickel content (%wt)		% Error		Sulfur content (%wt)	
	2.5 %wt	5.0 %wt	2.5 %wt	5.0 %wt	2.5 %wt	5.0 %wt
Ni	2.08*	4.05*	17	18	-	-
NiO	2.01*	4.14*	19	16	-	-
NiS	1.93**	3.94**	22	19	0.97**	1.93**

* Analyzed by AA method.

** Analyzed by XRF method.

They show that nickel contents in the adsorbents are less than the desired values. It was suspected that nickel nitrate crystal had moisture because it could absorb moisture from surroundings. It was later determined for its moisture content using standard test ASTM D 2216-98. The results of moisture contents are shown in Table 4.2.

Table 4.2 Percent of moisture in nickel nitrate

Sample No.	Weight of samples (g)		Percent of moisture(%)
	Before dryness	After dryness	
1	2.9987	2.1943	36.7
2	4.8490	3.5665	36.0
3	4.9006	3.5742	37.1

They can be observed that there was moisture approximately 36.5 % in nickel nitrate crystal. Because of moisture in nickel nitrate, concentration of nickel in solution that used to impregnate silica support was less than the desired values. Nickel content of adsorbents was also less than 2.5% and 5.0 %. It indicates that the moisture content in nickel nitrate crystal is the cause of error in adsorbent preparation.

Sulfur contents were determined by the X-ray fluorescence method. The results show that 2.5% and 5.0% NiS contains sulfur approximately 0.97 %wt and 1.93 %wt. The mole ratio of Ni:S is approximately 1:1. Figure 4.1 and Figure 4.2 show XRF pattern of sulfide on nickel sulfide adsorbent.

Because 2.0% and 4.0% of nickel content are almost the actual value of nickel content on adsorbents, this study uses 2.0% and 4.0% instead of the desired values 2.5% and 5.0% respectively.

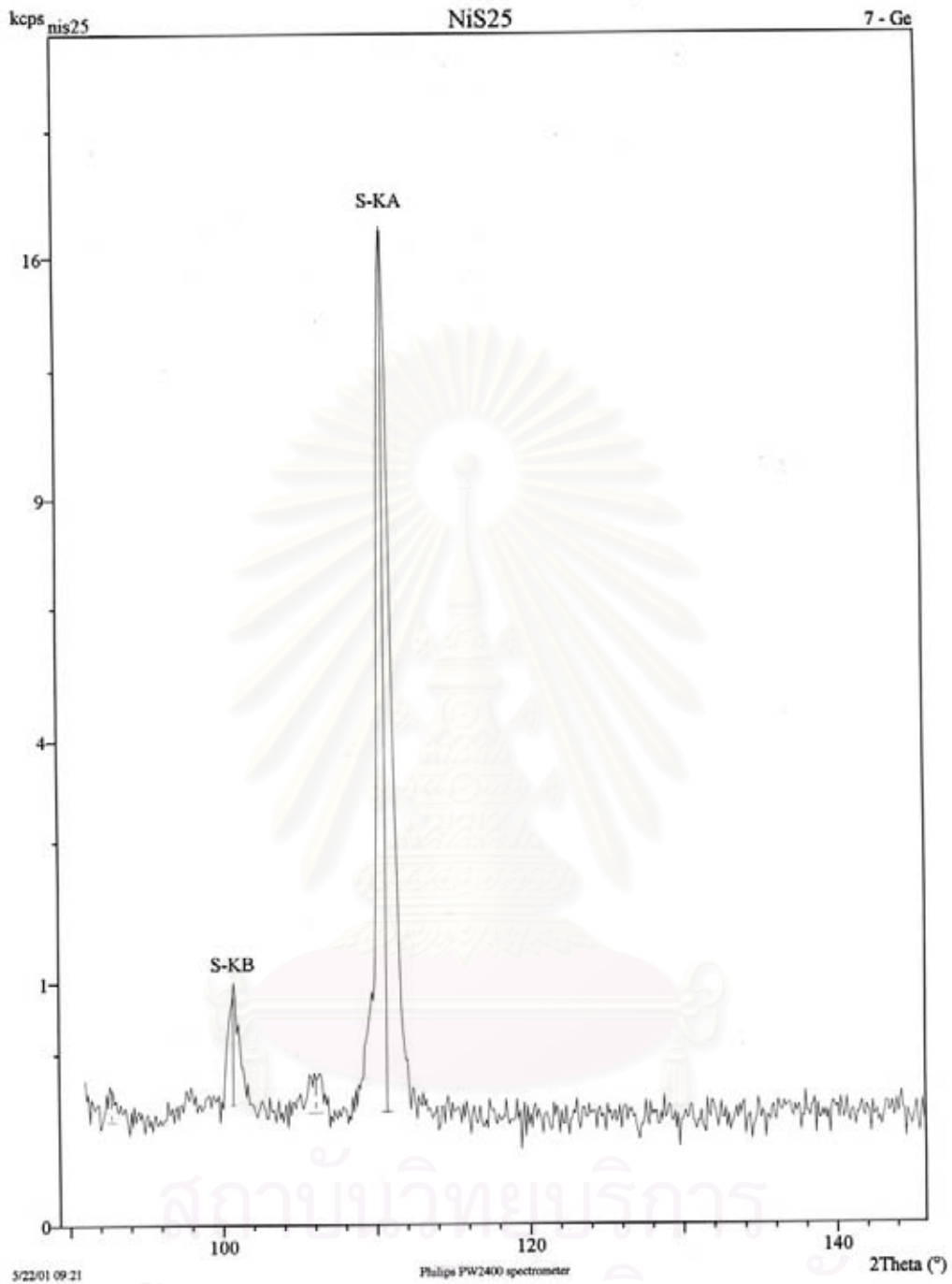


Figure 4.1 XRF pattern of a 2.0 NiS adsorbent.

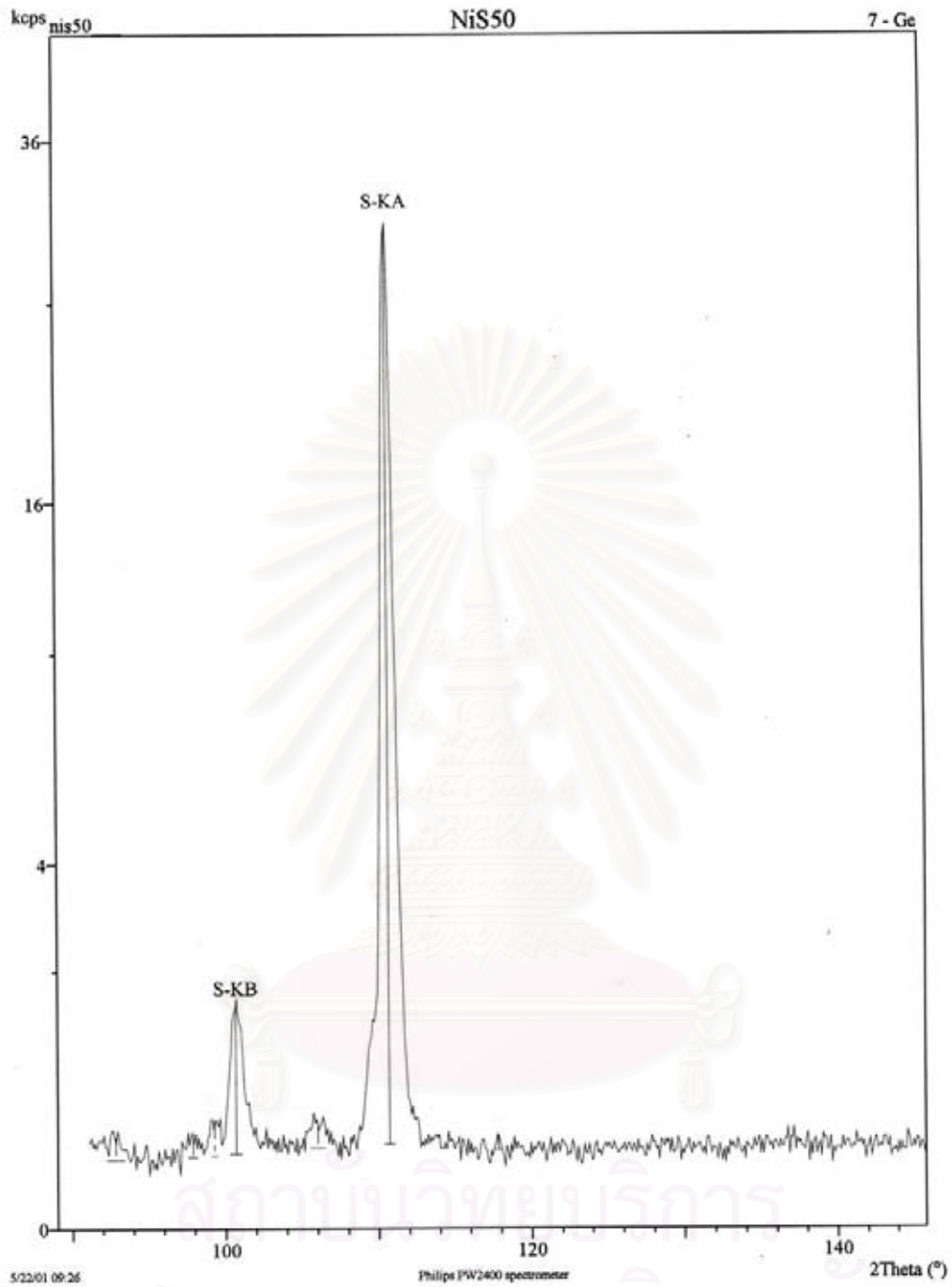


Figure 4.2 XRF pattern of a 4.0 NiS adsorbent.

4.1.3 Surface Area, Pore Volume, and Average Pore Diameter.

In this section, surface area, pore volume and average pore diameter of adsorbents were reported. The different characteristics between silica support and nickel adsorbents were determined after impregnation and calcination. All results are summarized in Table 4.3.

Table 4.3 Surface area, pore volume and average pore diameter of adsorbents.

Adsorbent Types	BET Surface Area (m ² /g)	Pore Vol. cc/g	Average Pore Dia. (°A)	Micropore Surface Area(m ² /g)
SiO ₂	394	1.659	167	28
2.0 Ni	334	1.228	147	8
4.0 Ni	333	1.213	146	11
2.0 NiO	326	1.239	152	19
4.0 NiO	324	1.204	149	21
2.0 NiS	328	1.214	148	13
4.0 NiS	323	1.143	142	18

They can be observed that surface area, pore volume and pore diameter of nickel adsorbent decrease when they are compared with silica support. The deposition of nickel compound on the surface of adsorbent may result in reduction of pore volume, surface area and average pore diameter.

In order to proof, pore-length was assumed from the model of pores was cylindrical, each pore had a uniform size along the length as shown in Figure 4.3. Pore-length was calculated from surface area and average pore diameter of adsorbents by Equation 4.1. After impregnation and calcination, if nickel compound evenly disperses on the surface of the adsorbents, pore-length of adsorbent will not decrease. Pore-length of each adsorbent is shown in Table 4.4.

$$\text{Pore-length (L)} = \left(\frac{S}{\pi D} \right) \dots\dots\dots 4.1$$

S = Surface area of each adsorbent (m²).

D = Average pore diameter (m).

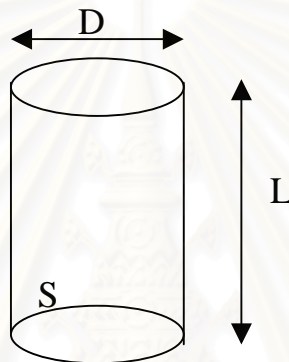


Figure 4.3 Cylindrical pore shape.

Table 4.4 Pore-length of each adsorbent

Adsorbent Types	Pore-Length(*10 ⁹ m)	% Change
SiO ₂	7.61	-
2.0 Ni	7.24	-4.97
4.0 Ni	7.29	-4.28
2.0 NiO	6.84	-10.13
4.0 NiO	6.94	-8.92
2.0 NiS	7.03	-7.64
4.0 NiS	7.25	-4.77

The results show that pore-length of each adsorbent slightly decreases. It indicates that nickel compound does not disperse throughout the adsorbent. Some of nickel compound may block some pores of adsorbents. It may affect on the decrement of pore volume, surface area and average pore diameter.

4.1.4 Forms of Adsorbents

The desired forms of adsorbents were nickel, nickel oxide and nickel sulfide adsorbent. Forms of adsorbents were verified using X-ray diffraction spectroscopy. Figure 4.4 to Figure 4.6 show X-ray diffraction pattern of nickel, nickel oxide and nickel sulfide respectively. The XRD results indicate that the form of nickel on each adsorbent is nickel oxide (NiO), nickel (Ni) and nickel sulfide (NiS) respectively.

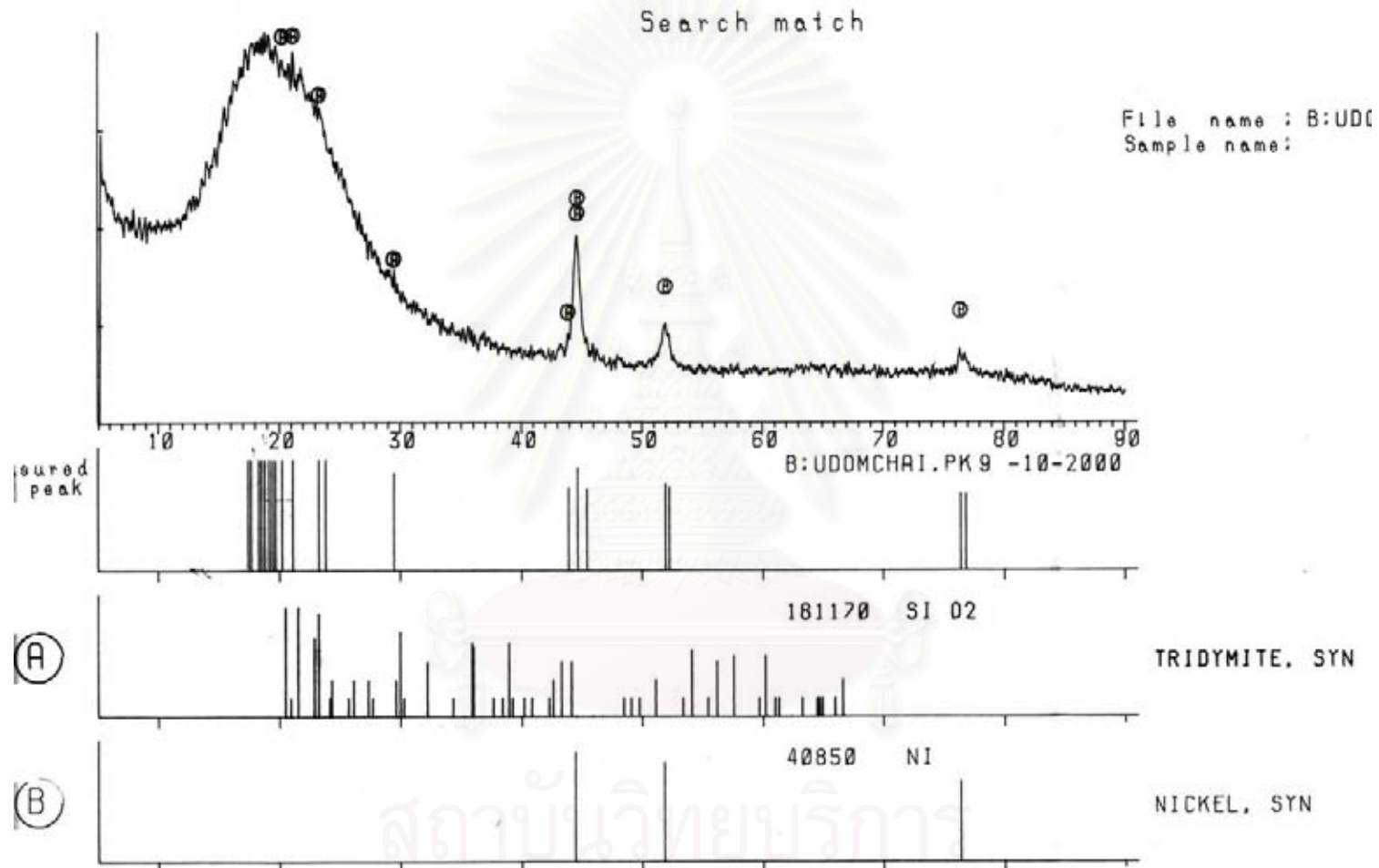


Figure 4.4 XRD pattern of a fresh nickel (Ni) adsorbent.

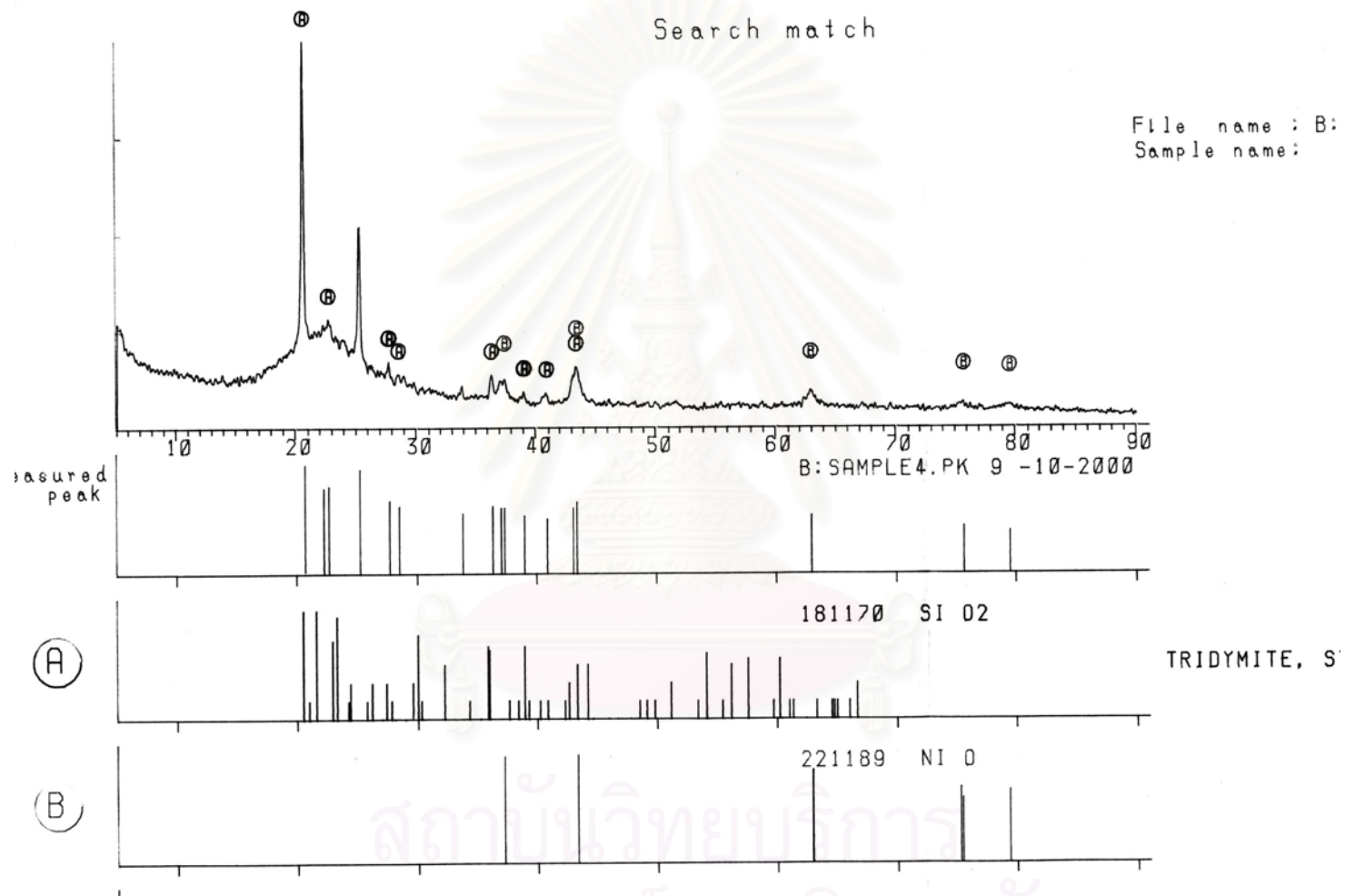


Figure 4.5 XRD pattern of a fresh nickel oxide (NiO) adsorbent.

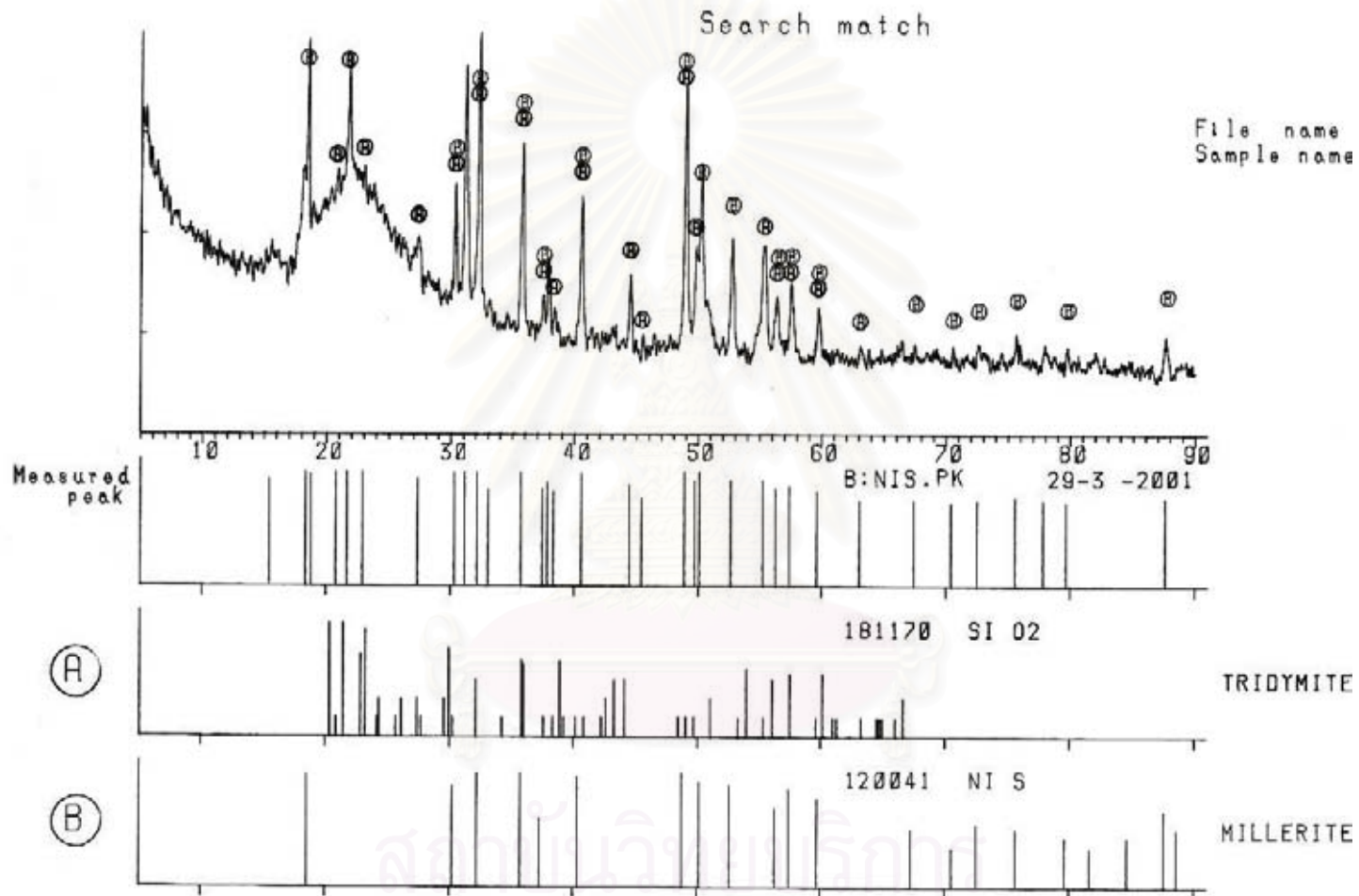


Figure 4.6 XRD pattern of a fresh nickel sulfide (NiS) adsorbent

4.2 Effect of Adsorbent Forms

4.2.1 Adsorption Procedure

In each experiment of adsorption, 100 g of solution containing approximately 1000 ppb of mercury compound was used as liquid feedstock. All operating conditions of this study are summarized in Table 4.5.

Table 4.5 Operating conditions of all experiments

Feed weight (g)	100
Adsorbent weight (g)	1.00
Feed concentration (ppb)	1000
Pressure (atm)	1
Time (min.)	60
Mercury compound	HgCl ₂ DPM
Form of adsorbents	Ni NiO NiS
Nickel content (%wt)	2.0 4.0
Temperature (°C)	30 50 70

The meaning of 2.0Ni, 2.0NiO and 2.0NiS were nickel, nickel oxide and nickel sulfide adsorbents that contained nickel metal 2.0% by weight. Like 2.0% adsorbent, the meaning of 4.0Ni, 4.0NiO and 4.0NiS were nickel, nickel oxide and

nickel sulfide adsorbents that contained nickel metal 4.0% by weight. This chapter used these abbreviations of adsorbent in Table and Figure.

After adsorption experiments, spent adsorbents were separated from liquid samples. Mercury content in toluene phase was not directly measured by an atomic absorption spectroscopy technique. Liquid samples were digested with acid reagent as described in Chapter III. Digestion was the method that changes the mercury compounds to mercury ion (Hg^{2+}). After digestion, the samples were extracted with deionized water to transfer mercury ion (Hg^{2+}) from toluene phase to aqueous phase. Mercury content in aqueous phase can be measured using cold vapor atomic absorption technique.

Selected spent adsorbents were digested to measure mercury that is adsorbed on the adsorbents. ASTM 1977-91 was used as a guideline for determination of mercury content. Desorption studies of selected spent adsorbents were conducted to determine the desorption capability of adsorbed mercury on adsorbents. The spent adsorbents were stirred in fresh toluene to allow mercury on the surface to desorb. The solution was digested by acid digest method and extracted Hg^{2+} by deionized water as previous description. All results of these experiments are shown in Appendix A. The results of these experiments were the remaining mercury after adsorption.

The results of adsorption experiments in Chapter IV were reported in percent removal instead of the remaining mercury because the concentration of feedstock was not constant at 1000 ppb, the concentration of mercury in feedstock was in the range between 950 ppb to 1050 ppb. In addition, it was easy to compare the efficiency of each adsorbent in percent removal. Percent removal was defined by Equation 4.2. The summation of errors that caused by digestion, instrumental analysis and the experiments was less than 10 %.

$$\text{Percent removal (\%)} = \frac{(C_f - C_r)}{C_f} \times 100 \dots\dots\dots 4.2$$

C_f = The concentration of feedstock (ppb).

C_r = The concentration of remaining mercury (ppb).

4.2.2 Adsorption of Mercury Compounds on Silica Supports.

A set of experiments was conducted to study the ability of silica supports on adsorption of mercury compound. Silica supports were prepared using the same procedure for preparation of nickel, nickel oxide and nickel sulfide adsorbents except that distilled water was used for impregnation instead of nickel nitrate solution. The results of mercury compounds removal by silica support at various temperatures are shown in Table 4.6 and plotted in Figure 4.7.

Table 4.6 Percent removal of mercury compounds by silica supports at various temperatures.

Calcination procedure	Removal of mercury compounds(%)					
	HgCl ₂			DPM		
	30 °C	50 °C	70 °C	30 °C	50 °C	70 °C
Oxidation	12.2	12.0	15.6	1.8	3.0	4.8
Reduction	11.0	13.3	15.8	1.9	3.2	4.7
Sulfurization	13.4	13.2	15.7	1.8	4.4	5.4

The results show that both HgCl₂ and DPM can be removed from liquid hydrocarbon by silica supports. In addition, HgCl₂ can be removed more effectively than DPM. This may be the result of polarity and complication of the molecule of mercury compounds. HgCl₂ is an ionic compound and it has more polar than DPM which is an organic compound. In contrast, DPM has two benzene rings that are stable because of its high resonance energy of π electron in molecular. The results indicate that type of mercury compounds strongly affects the removal of mercury compounds.

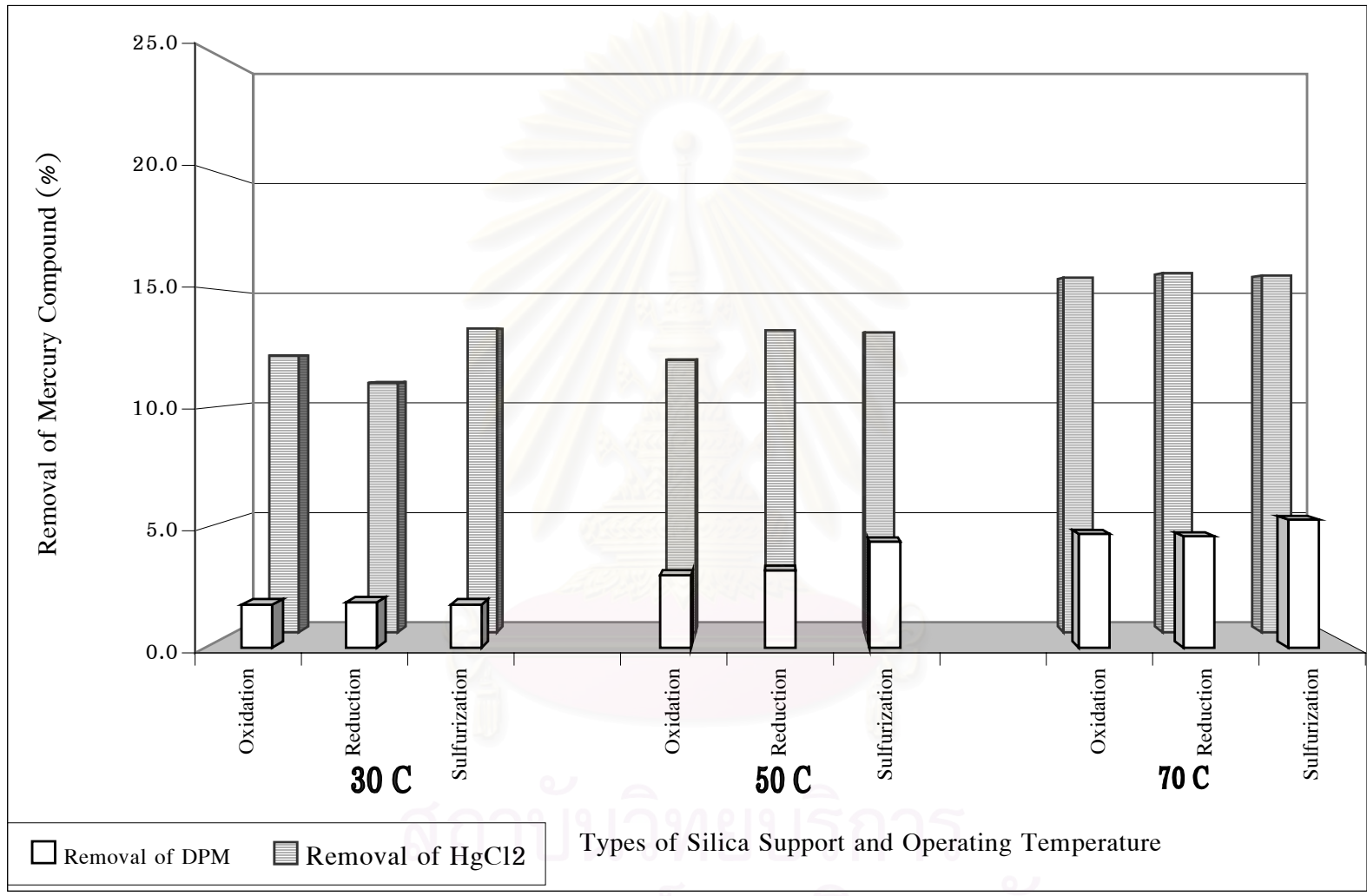


Figure 4.7 Percent removal of HgCl₂ and DPM by various silica supports at 30°C, 50°C and 70°C.

In the comparison between the adsorption of silica support and glassware (blank test), silica support is more effective than glassware in adsorption of HgCl_2 but DPM is hardly removed by both of glassware and silica support. This is the result from the difference of silica support and glassware.

It can be observed that the adsorption of mercury compounds does not depend on operating temperatures. Although mercury removal slightly increase with increasing operating temperatures but the increment of mercury removal is in range of error of experiments as described in Chapter III.

Figure 4.7 shows percent removal of HgCl_2 and DPM by each silica support prepared through different method, at operating temperature 30°C , 50°C and 70°C . It can be observed that percent removal of mercury compound by each silica support is approximately the same at each temperature. This is the result of silica inertness. Phase of silica support is not change at calcination conditions because the factor that must be considered with regard to silica support stability is temperature of 600°C (Alvin, 1983). Ability of each silica support in mercury removal is similar. The results indicate that the different methods of calcination do not affect the silica support in removal of mercury compounds.

Spent silica supports were analyzed by X-ray diffractometer to identify structure of mercury on the surface. The result of X-ray diffraction shows that it can not detect chemical structure of mercury compounds on silica support.

Some spent silica supports were stirred in fresh toluene to dissolve the amount of desorbed mercury. Table 4.7 shows the amount of removal mercury from liquid hydrocarbon and is plotted in Figure 4.8. Table 4.8 shows the results of the desorbed mercury by silica support at 70°C and is plotted in figure 4.9.

Table 4.7 Amount of mercury removal by silica support at various temperatures.

Calcination procedure	The amount of removal mercury ($\mu\text{g/g}$)					
	HgCl_2			DPM		
	30 °C	50 °C	70 °C	30 °C	50 °C	70 °C
Oxidation	12.2	12.0	15.6	1.8	3.0	4.8
Reduction	11.0	13.3	15.8	1.9	3.2	4.7
Sulfurization	13.4	13.2	15.7	1.8	4.4	5.4

Table 4.8 Amount of desorbed mercury at 70°C from spent silica support.

Type of Silica	Desorbed mercury at 70 °C ($\mu\text{g/g}$)	
	HgCl_2	DPM
Oxidation	10.6	3.1
Reduction	10.1	3.6
Sulfurization	11.8	3.3

Mercury on silica support can partially desorbed at approximately 75 % and 70 % of the adsorbed mercury, respectively. This result indicates that the adsorbed mercury can desorb from spent silica supports.

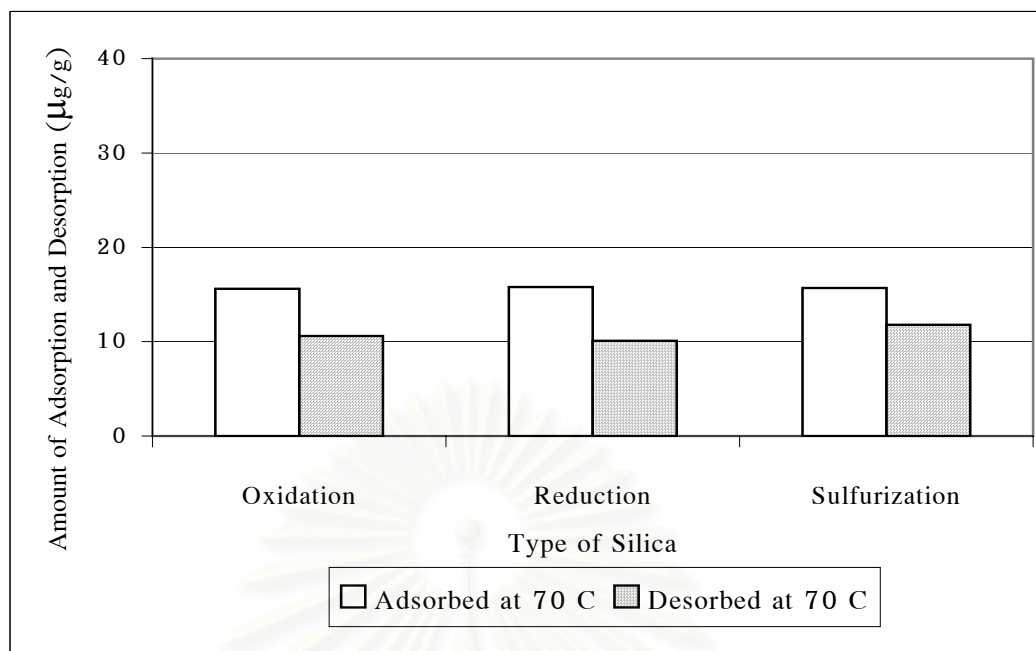


Figure 4.8 Amount of adsorption and desorption of HgCl_2 by silica supports at 70°C .

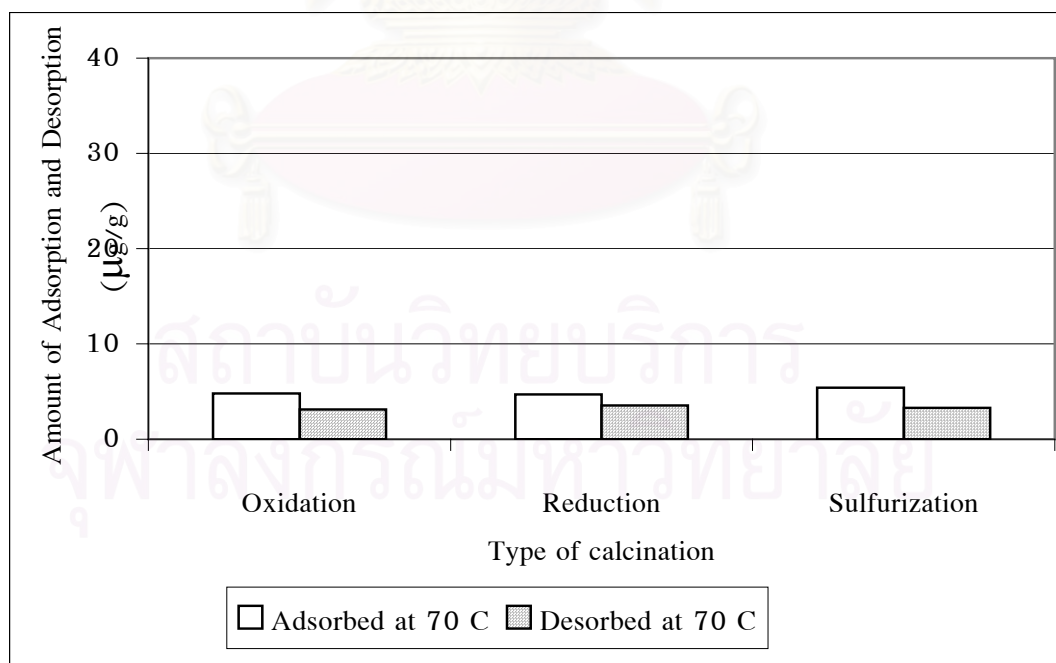


Figure 4.9 Amount of adsorption and desorption of DPM by silica supports at 70°C .

4.2.3 Adsorption of Mercury Compound by Nickel Adsorbents

In this section, removal of mercury compounds by nickel adsorbents was studied. Percent removal of HgCl_2 and DPM by nickel adsorbents at temperatures of 30°C , 50°C and 70°C were shown in Table 4.9 and plotted in Figure 4.10.

Table 4.9 Percent removal of mercury compounds by Ni adsorbents at various temperatures.

Mercury compound	Temperature ($^\circ\text{C}$)	Percent removal of mercury (%)		
		SiO_2	2.0Ni	4.0Ni
HgCl_2	30	11.0	33.6	40.8
	50	13.3	42.4	46.2
	70	15.8	46.8	53.4
DPM	30	1.9	10.8	18.2
	50	3.2	15.2	26.6
	70	4.7	18.6	34.8

In the comparison of mercury compounds removal between silica support and nickel adsorbents, two different results can be observed from the Table 4.9. Firstly, nickel adsorbents is more effective than silica support in removal of mercury compounds. Secondly, percent removal of mercury compounds increases with increasing of nickel content and operating temperatures. The results indicate that the amount of mercury compounds removal is increased by the influence of nickel on the adsorbents.

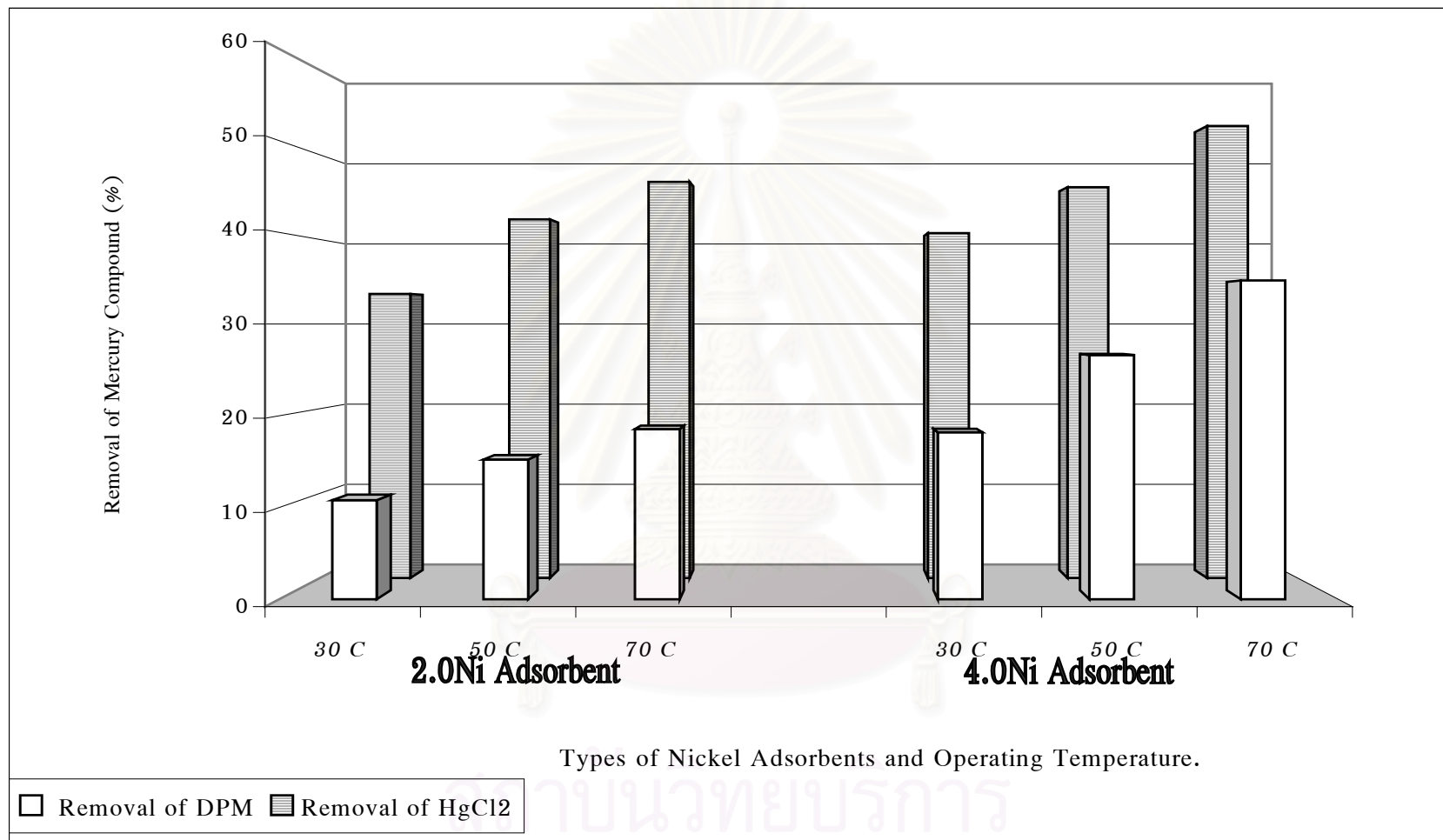


Figure 4.10 Percent removal of HgCl₂ and DPM by nickel adsorbents at 30°C, 50°C and 70°C.

Some spent nickel adsorbents were digested to determine the amount of mercury content that deposited on adsorbents. The results were shown in Table 4.10. The results do not agree with the results obtained from Table 4.9. It can be observed that the deposited mercury is less than the amount of mercury removal from liquid hydrocarbon. It is expected that some part of mercury compound vaporize while adsorbents were digested with acid.

Table 4.10 Mercury content deposited on nickel adsorbents

Compound	Temperature (°C)	Amount of mercury deposited on adsorbents (µg/g)	
		2.0Ni	4.0Ni
HgCl ₂	30	18.1	21.8
	50	24.7	25.4
	70	26.6	29.8
DPM	30	6.6	10.7
	50	8.7	14.8
	70	12.3	19.4

Desorption studies were conducted on selected spent nickel adsorbent to determine the amount of desorbed mercury. Table 4.11 shows the amounts of the desorbed mercury at 70°C of spent 4.0% of nickel adsorbents.

Table 4.11 Amount of desorbed mercury from spent 4.0% of nickel adsorbent at 70°C

Type of Asorbents	Temperature (°C)	Amount of desorbed mercury at 70 °C (µg/g)	
		HgCl ₂	DPM
4.0 Ni	30	7.0	2.5
	50	8.6	3.0
	70	9.6	4.5

Figure 4.11 and Figure 4.12 shows the comparison of adsorption and desorption mercury by 4.0% of nickel adsorbents. They show that small amount of the adsorbed mercury can partially dissolve from the spent adsorbents. It is expected that the amount of desorbed mercury probably dissolve from silica part of the adsorbent because the increase of desorbed amount is not proportional to the increase of adsorbed amount.

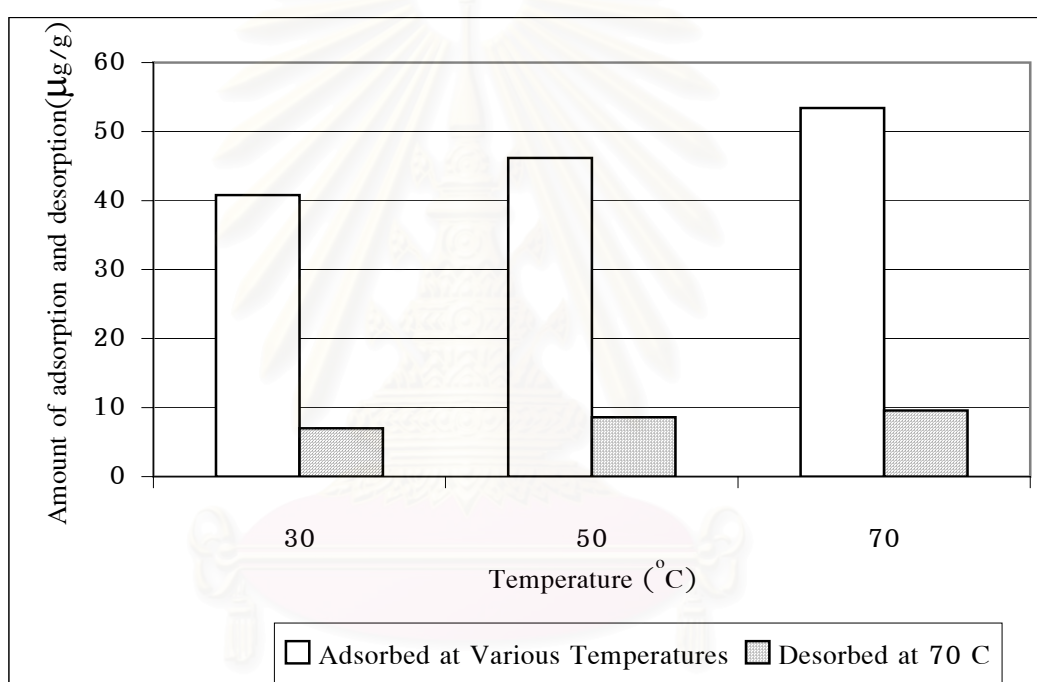


Figure 4.11 Amount of adsorption at various temperatures and desorption at 70°C of HgCl_2 by 4.0% of nickel adsorbent.

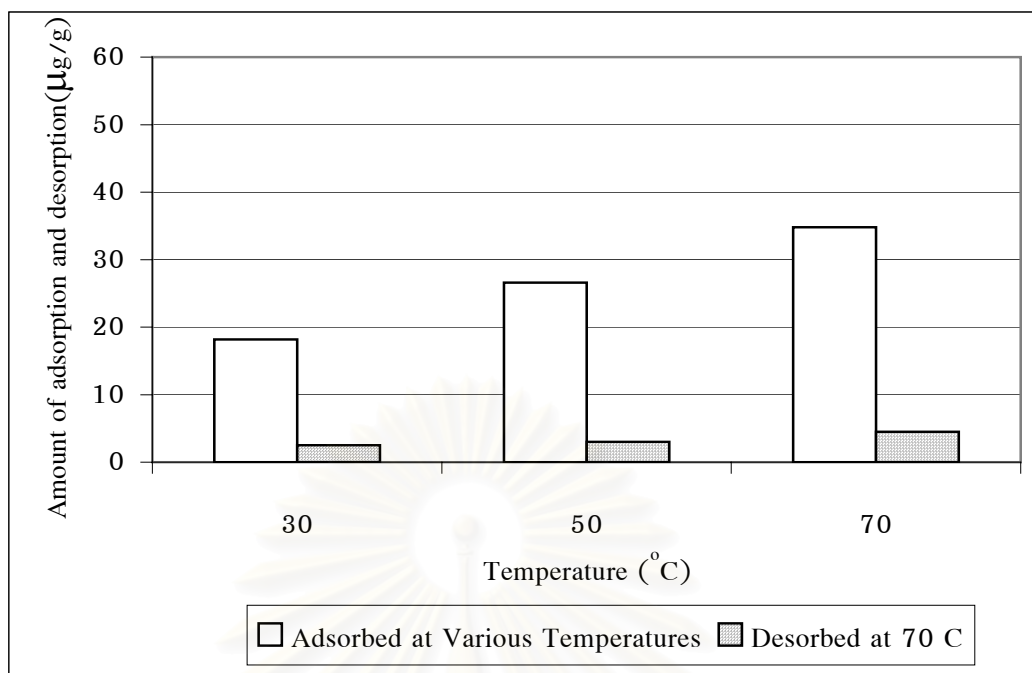


Figure 4.12 Amount of adsorption at various temperatures and desorption at 70°C of DPM by 4.0% of nickel adsorbent

Spent nickel adsorbents were analyzed to identify the structure of mercury on the adsorbent surface using the X-ray diffractometer. Figure 4.13 shows X-ray diffraction patterns of the spent nickel adsorbents that are adsorbed HgCl_2 . The XRD result shows chemical structure of mercury and nickel on spent adsorbent in the form of nickelmercury.

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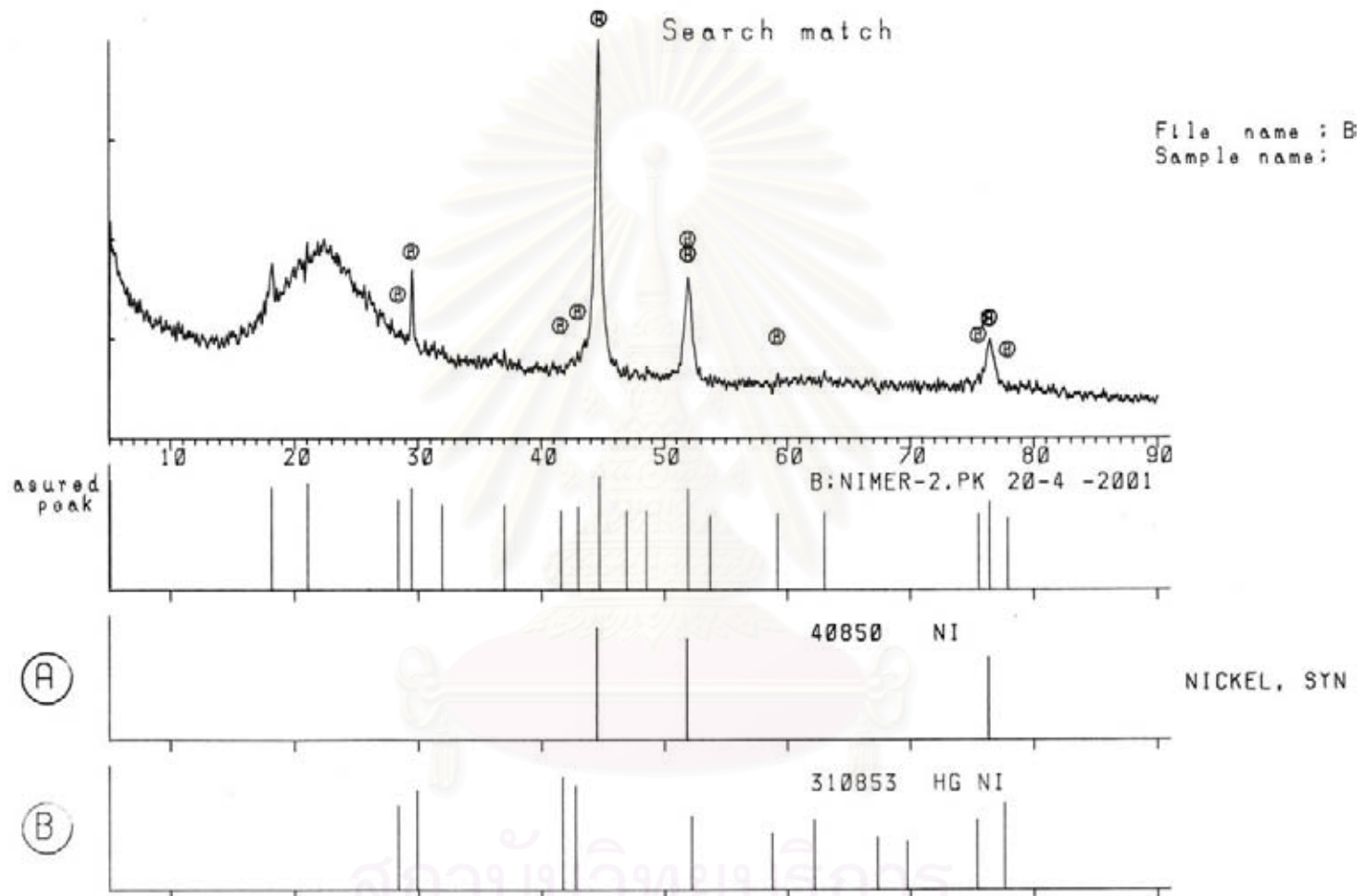


Figure 4.13 XRD pattern of nickelmercury on spent nickel adsorbent.

4.2.4 Adsorption of Mercury Compounds by Nickel Oxide Adsorbents

In this section, removal of mercury compounds by nickel oxide adsorbents was studied. Percent removal of HgCl_2 and DPM by nickel oxide adsorbents at temperature of 30°C , 50°C and 70°C were shown in Table 4.12 and plotted in Figure 4.14.

Table 4.12 Percent removal of mercury compounds by nickel oxide adsorbents at various temperatures.

Mercury compound	Temperature ($^\circ\text{C}$)	Percent removal of mercury (%)		
		SiO_2	2.0NiO	4.0NiO
HgCl_2	30	12.2	17.7	22.5
	50	12.0	24.3	29.0
	70	15.6	29.8	37.2
DPM	30	1.8	9.1	11.3
	50	3.0	14.5	26.4
	70	4.8	19.2	33.9

It can be observed that nickel adsorbents were more effective than silica supports in removal of mercury compounds. Percent removal of mercury compounds increases with increasing of nickel content and operating temperatures. It indicates that nickel oxide on the adsorbent affects the increase of mercury compounds removal. The increase of percent removal of HgCl_2 and DPM is almost equal so that the adsorption of DPM by nickel oxide compound is approximately equal HgCl_2 .

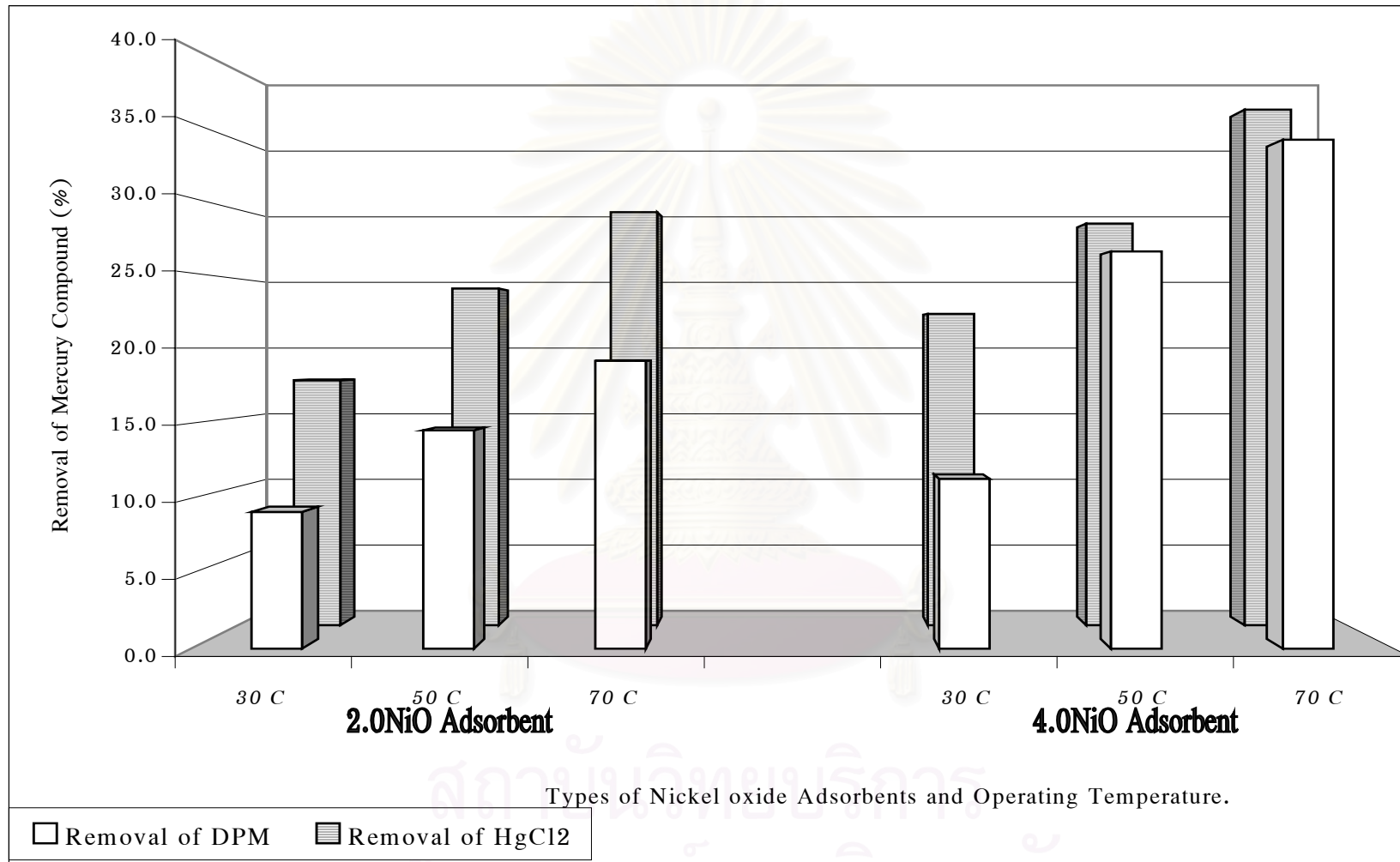


Figure 4.14 Percent removal of HgCl₂ and DPM by nickel oxide adsorbents at 30°C, 50°C and 70°C.

Selected spent nickel oxide adsorbents were digested to measure the amount of mercury that deposited on the adsorbents. The results were shown in Table 4.13. It can be observed that the deposited mercury is less than the adsorbed mercury from liquid hydrocarbon. As described in section of nickel adsorbents, it is expected that part of mercury compound vaporize while adsorbents were digested with acid.

Table 4.13 Mercury content deposited on nickel oxide adsorbents

Compound	Temperature (°C)	Mercury content deposited on adsorbents($\mu\text{g/g}$)	
		2.0NiO	4.0NiO
HgCl_2	30	11.0	13.4
	50	15.1	16.5
	70	18.9	20.7
DPM	30	5.4	7.6
	50	8.1	14.9
	70	13.5	19.3

Nickel oxide adsorbents were analyzed by X-ray diffractometer to identify structure of mercury compound on the surface. The results of X-ray diffraction show that it can not detect the chemical structure of mercury on nickel oxide adsorbents.

Some spent nickel oxide adsorbents were determined the amount of desorbed mercury. They were stirred in fresh toluene to dissolve the desorbed mercury. Table 4.14 shows the results of desorption of spent adsorbents at 70°C.

Table 4.14 Amount of desorbed mercury from 4.0% of nickel oxide adsorbents at 70°C.

Asorbent Types	Temperature (°C)	Amount of desorped mercury at 70 °C ($\mu\text{g/g}$)	
		HgCl_2	DPM
4.0 NiO	30	9.5	2.1
	50	8.0	2.7
	70	12.0	5.5

Figure 4.15 and Figure 4.16 show the comparison between adsorption and desorption of mercury on 4.0% of nickel oxide adsorbents. It is found that only small amount of mercury is desorbed from the spent adsorbents when it is compared with the adsorbed amount. As described in nickel adsorbents Section, the amount of desorbed mercury probably dissolve from silica part of the adsorbent because the increase of the desorbed amount is not proportional to the increase of the adsorbed amount.

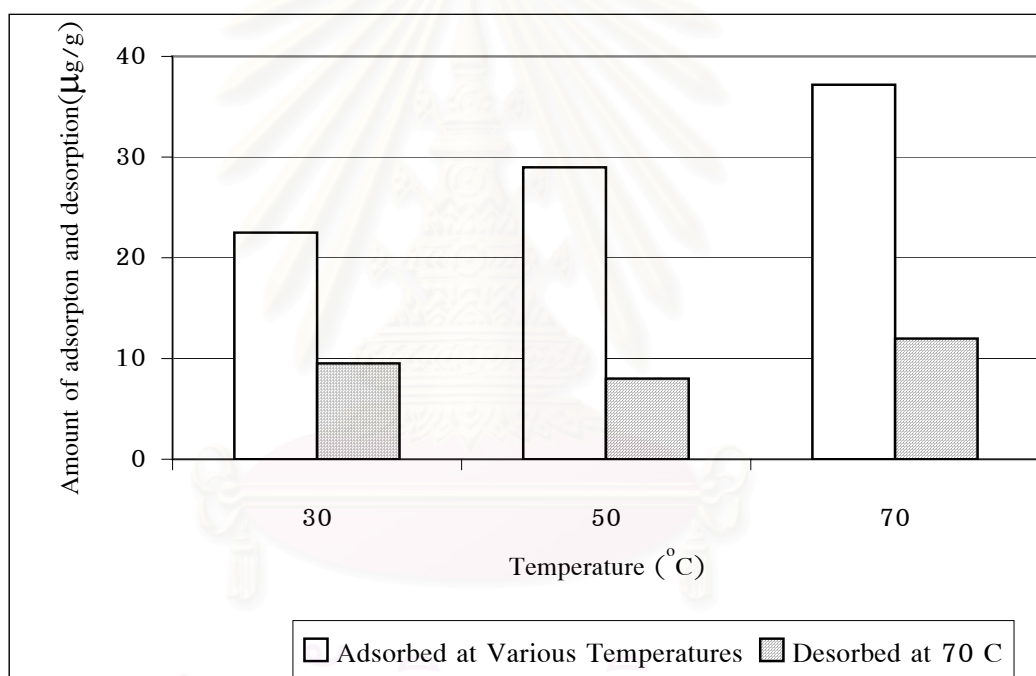


Figure 4.15 Amount of adsorption at various temperatures and desorption at 70°C of HgCl_2 by 4.0% of nickel oxide adsorbents.

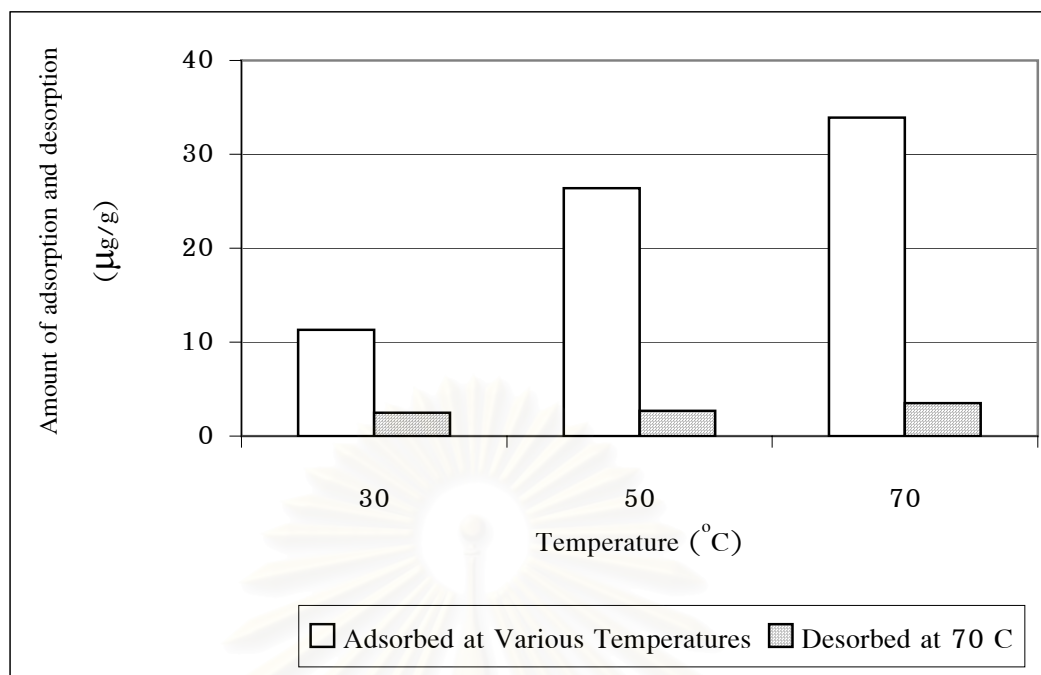


Figure 4.16 Amount of adsorption at various temperatures and desorption at 70°C of DPM by 4.0% of nickel oxide adsorbents

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4.2.5 Adsorption of Mercury Compound by Nickel Sulfide Adsorbents

In this section, removal of mercury compounds by nickel sulfide adsorbents was studied. Percent removal of HgCl_2 and DPM by nickel sulfide adsorbents at temperature of 30°C , 50°C and 70°C were shown in Table 4.15 and plotted in Figure 4.17.

Table 4.15 Percent removal of mercury compounds by nickel sulfide adsorbents at various temperatures.

Mercury Compound	Temperature ($^\circ\text{C}$)	Removal of Mercury Compounds (%)		
		SiO_2	2.0NiS	4.0NiS
HgCl_2	30	13.4	87.8	87.9
	50	13.2	90.9	92.2
	70	15.7	95.4	95.3
DPM	30	1.8	6.9	10.9
	50	4.4	14.2	21.1
	70	5.4	19.5	34.9

The results show that nickel sulfide adsorbents can remove HgCl_2 more effectively than DPM. This is the result of polarity and complication of the mercury compounds molecule as in Section 4.2.2. It can be observed that nickel sulfide adsorbents is more effective than silica support in mercury compounds removal. Percent removal of mercury compounds increases with increasing nickel content and operating temperature. The results indicate that the amount of mercury removal is increased by the influence of nickel sulfide on the adsorbents.

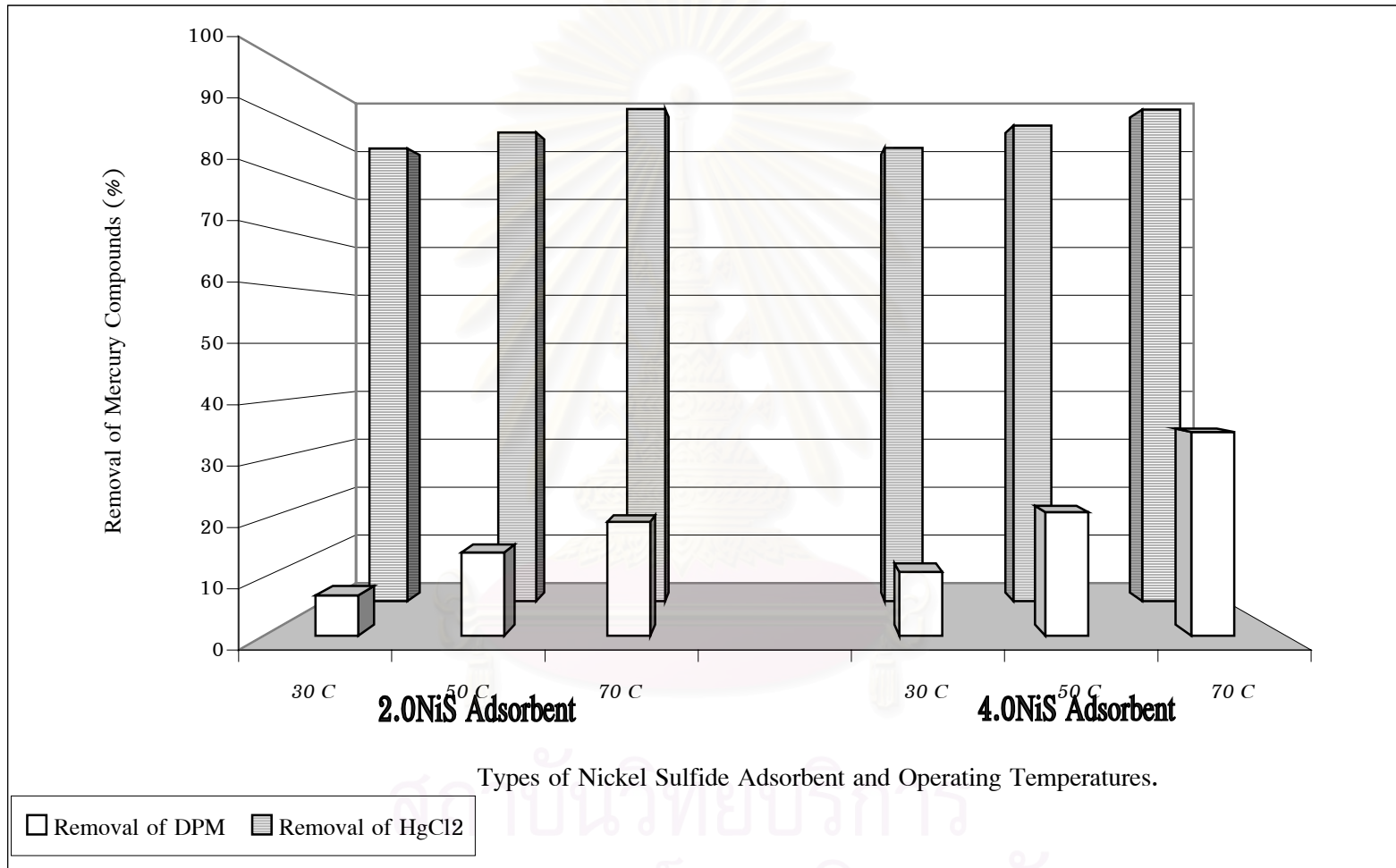


Figure 4.17 Percent removal of HgCl₂ and DPM by nickel sulfide adsorbents at 30°C, 50°C and 70°C.

Selected spent nickel sulfide adsorbents were also digested to analyze the amount of deposited mercury. The results are shown in Table 4.16.

Table 4.16 Mercury content deposited on nickel sulfide adsorbents.

Mercury compound	Temperature (°C)	Amount of mercury deposited on adsorbents (µg/g)	
		2.0NiS	4.0NiS
HgCl ₂	30	46.6	47.8
	50	47.4	50.4
	70	51.3	52.7
DPM	30	5.2	7.3
	50	7.9	12.7
	70	12.4	20.3

It can be observed that the results do not agree with the result obtained from Table 4.15. The deposited mercury content is less than the amount of mercury removal from liquid hydrocarbon. As described in adsorption of nickel adsorbent Section, it is expected that part of mercury compound vaporize while adsorbents were digested with acid.

Table 4.17 shows the results of desorbed mercury of 4.0% of nickel sulfide adsorbents at 70°C.

Table 4.17 Amount of desorbed mercury from 4.0% of nickel sulfide adsorbent at 70°C.

Type of Asorbents	Temperature (°C)	Amount of Desorbed Mercury at 70 °C (µg/g)	
		HgCl ₂	DPM
4.0 NiS	30	9.0	1.5
	50	8.2	3.5
	70	9.5	5.0

Figure 4.18 and Figure 4.19 shows the comparison of adsorption and desorption mercury on 4.0% of nickel sulfide adsorbents. They show that the adsorbed amount can partially dissolve from spent adsorbents. As described in Section 4.2.3, the desorbed amount probably dissolve from silica part of the adsorbent because the increase of the desorbed amount is not proportional to the increase of the adsorbed amount.

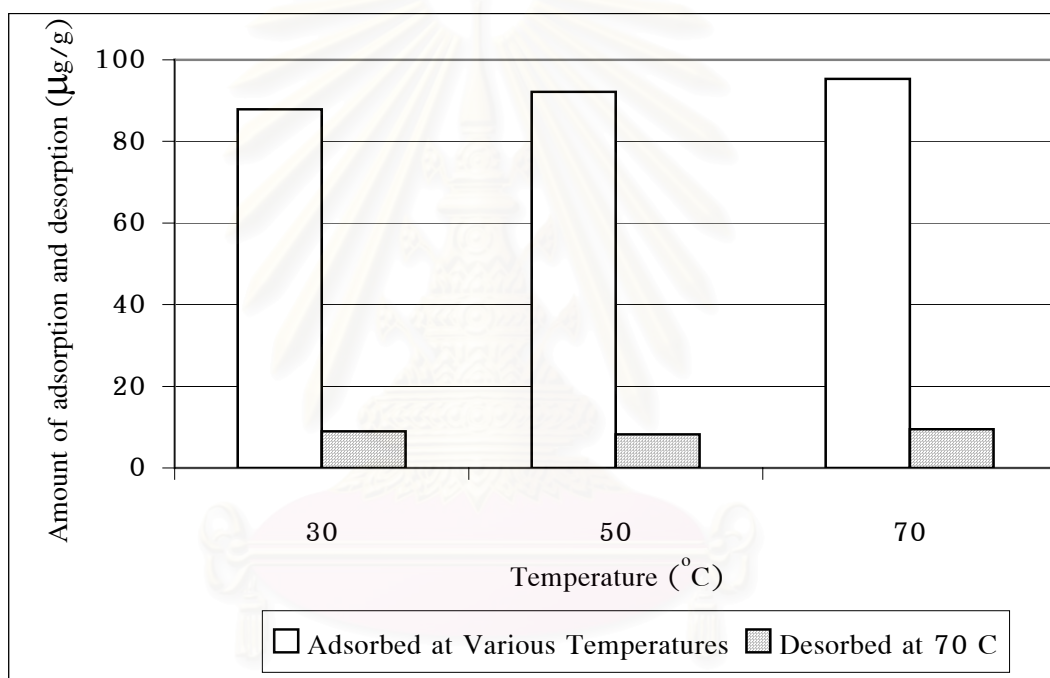


Figure 4.18 Amount of adsorption at various temperatures and desorption at 70°C of HgCl_2 by 4.0% of nickel sulfide adsorbent.

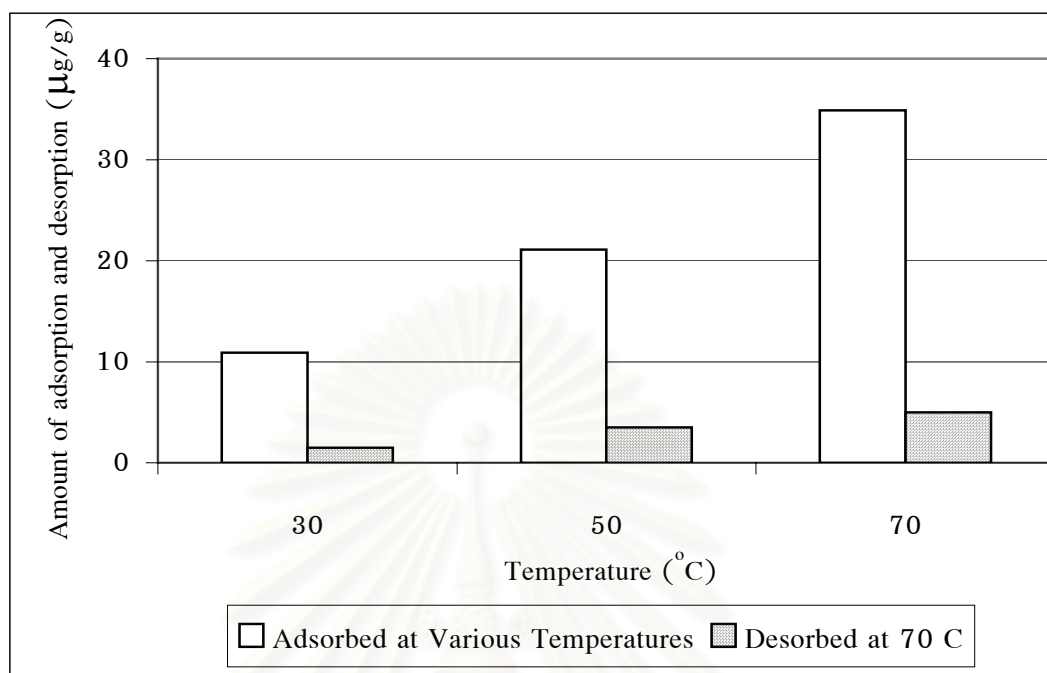


Figure 4.19 Amount of adsorption at various temperatures and desorption at 70°C of DPM by 4.0% of nickel sulfide adsorbent.

Spent nickel sulfide adsorbents were analyzed to identify the structure or the compound of mercury using the x-ray diffractometer. Figure 4.20 shows X-ray diffraction patterns of the spent nickel sulfide adsorbents that adsorb HgCl_2 . The XRD result shows chemical structure between mercury and sulfur on spent adsorbent in the form of mercuric sulfide (HgS).

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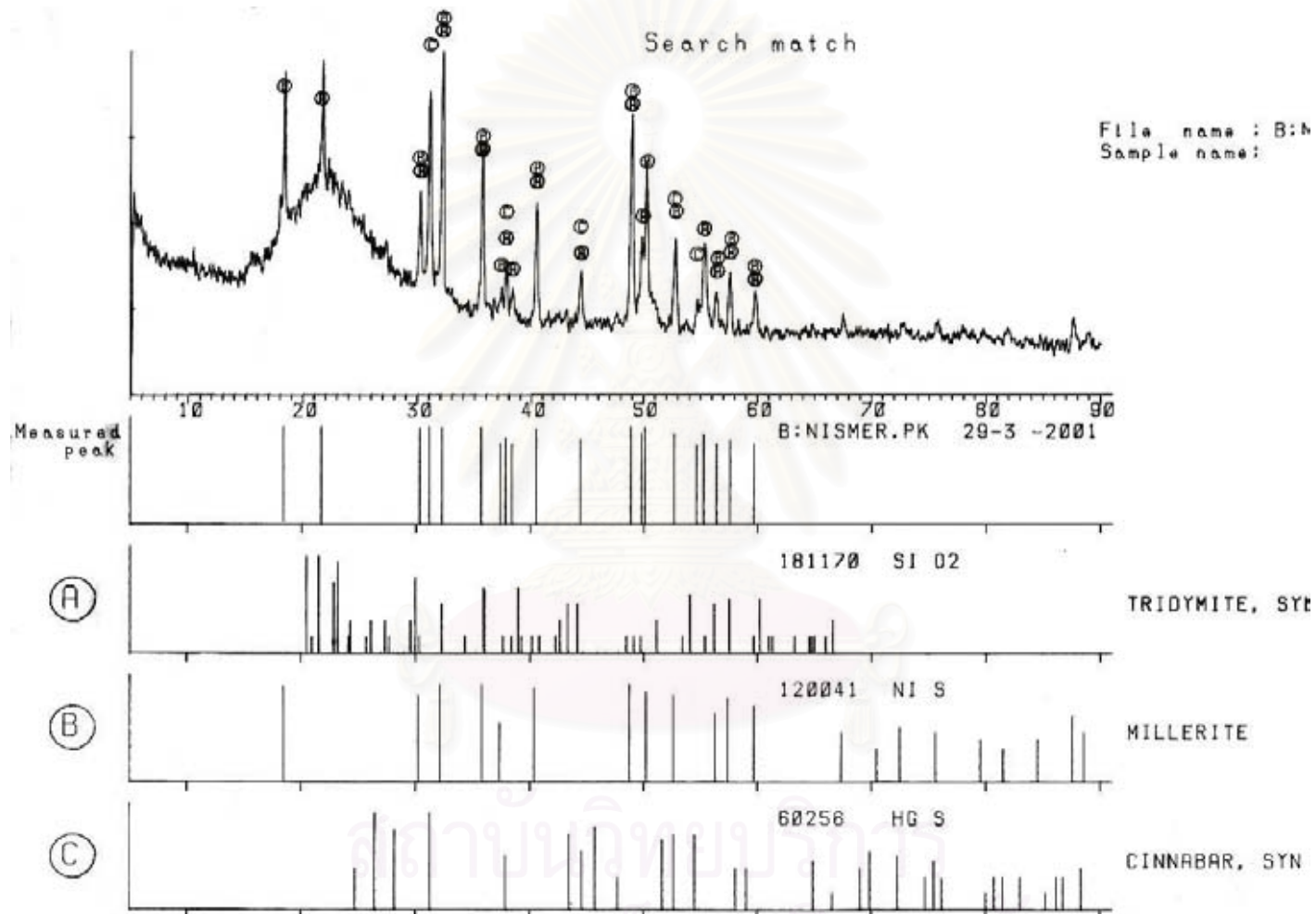


Figure 4.20 XRD pattern of mercuric sulfide on spent nickel sulfide adsorbent.

4.3 Comparison of Mercury Removal on Adsorbents

The objective of section 4.3 is comparison the efficiency of mercury removal on various nickel adsorbents, percent removal of mercury compounds on nickel, nickel oxide and nickel sulfide adsorbents were plotted in Figure 4.21 and Figure 4.22.

It is found that the amount of HgCl_2 removal depends on the types of adsorbent. Efficiency of adsorbent on HgCl_2 removal is in the following order: nickel sulfide > nickel > nickel oxide.

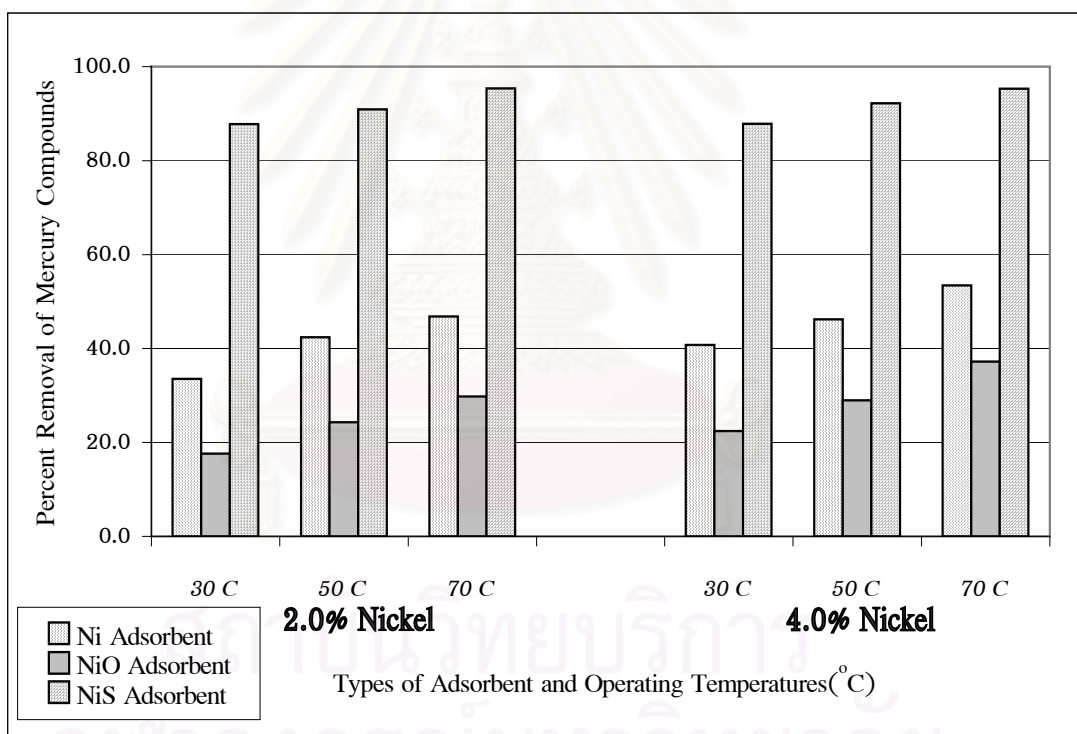


Figure 4.21 Percent removal of HgCl_2 by various nickel adsorbents.

It can be observed that the amount of DPM removal does not depend on the types of adsorbents. Ability in DPM removal of each adsorbent is similar. However, it depends on operating temperature and nickel content.

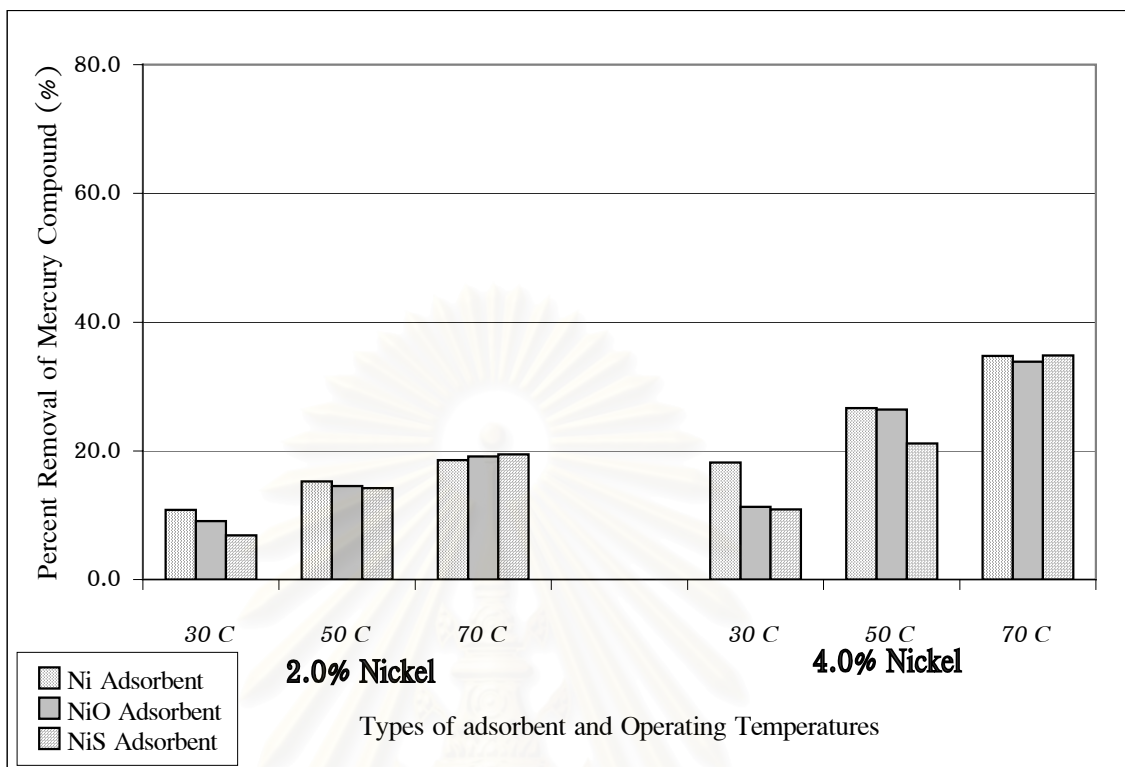


Figure 4.22 Percent removal of DPM by various nickel adsorbents.

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CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

The following conclusions are drawn from the study:

1. Nickel, nickel oxide and nickel sulfide adsorbents can remove mercuric (II) chloride more effectively than diphenylmercury.
2. Adsorption capability of nickel, nickel oxide and nickel sulfide adsorbents, percent removal increases with increasing of nickel contents and operating temperatures.
3. Efficiency of nickel adsorbents on the adsorption of HgCl_2 is in the following order: nickel sulfide > nickel > nickel oxide. Abilities of adsorbents to remove diphenylmercury are similar.
4. Mercuric sulfide is detected on nickel sulfide adsorbent and nickelmercury is detected on nickel adsorbent when they are used to adsorb HgCl_2 .

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Recommendations

1. The same experiment set should be conducted to removal mercury in natural crude oil in order to compare the efficiency of mercury removal.
2. Nickel adsorbents should be varied types of support in order to study the influence of support on mercury compounds adsorption.



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APPENDICES

สถาบันวิทยบริการ
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Appendix A

Table 1A Conditions and results of each experiment.

Exp. no.	Type of mercury	Type of adsorbents	Adsorbents weight(g)	Int. Conc. (ppb)	Temp. (°C)	Time (min)	Hg content (ppb)	% Removal
1	HgCl ₂	-	-	979.5	30	60	966.7	1.3
2	HgCl ₂	-	-	979.5	50	60	969.0	1.1
3	HgCl ₂	-	-	979.5	70	60	958.4	2.2
4	DPM	-	-	1023.0	30	60	996.1	2.6
5	DPM	-	-	1023.0	50	60	991.2	3.1
6	DPM	-	-	1023.0	70	60	992.3	3.0
7	HgCl ₂	Oxi/SiO ₂	0.9994	965.3	30	60	829.2	14.1
8	HgCl ₂	Oxi/SiO ₂	1.0022	985.7	30	60	843.8	14.4
9	HgCl ₂	Oxi/SiO ₂	0.9975	979.4	30	60	824.7	15.8
10	HgCl ₂	Oxi/SiO ₂	1.0022	965.3	50	60	823.4	14.7
11	HgCl ₂	Oxi/SiO ₂	1.0034	985.7	50	60	835.9	15.2
12	HgCl ₂	Oxi/SiO ₂	1.0014	979.4	50	60	828.6	15.4
13	HgCl ₂	Oxi/SiO ₂	1.0043	965.3	70	60	775.1	19.7
14	HgCl ₂	Oxi/SiO ₂	0.9987	985.7	70	60	807.3	18.1
15	HgCl ₂	Oxi/SiO ₂	1.0012	979.4	70	60	801.1	18.2
16	HgCl ₂	Oxi/SiO ₂	0.8143	0.0	70(desorbed)	60	86.3	-
17	DPM	Oxi/SiO ₂	1.0022	973.5	30	60	947.2	2.7
18	DPM	Oxi/SiO ₂	1.0014	959.4	30	60	930.6	3.0
19	DPM	Oxi/SiO ₂	1.0010	986.2	30	60	951.7	3.5
20	DPM	Oxi/SiO ₂	1.0004	973.5	50	60	934.3	4.0
21	DPM	Oxi/SiO ₂	0.9991	959.4	50	60	922.0	3.9
22	DPM	Oxi/SiO ₂	1.0011	986.2	50	60	943.8	4.3
23	DPM	Oxi/SiO ₂	1.0019	973.5	70	60	910.2	6.5
24	DPM	Oxi/SiO ₂	1.0007	959.4	70	60	891.3	7.1
25	DPM	Oxi/SiO ₂	0.9984	986.2	70	60	915.2	7.2

Table 1A Conditions and results of each experiment. (continued)

Exp. no.	Type of mercury	Type of adsorbents	Adsorbents weight(g)	Int. Conc. (ppb)	Temp. (°C)	Time (min)	Hg content (ppb)	% Removal
26	DPM	Oxi/SiO ₂	0.8916	0.0	70(desorbed)	60	27.8	-
27	HgCl ₂	2.0 NiO	1.0025	989.1	30	60	793.3	19.8
28	HgCl ₂	2.0 NiO	1.0008	968.7	30	60	751.7	22.4
29	HgCl ₂	2.0 NiO	1.0043	1015.4	30	60	796.1	21.6
30	HgCl ₂	2.0 NiO	0.9994	995.3	30	60	814.2	18.2
31	HgCl ₂	2.0 NiO	1.0012	979.2	30	60	788.3	19.5
32	HgCl ₂	4.0 NiO	0.9975	989.1	30	60	736.9	25.5
33	HgCl ₂	4.0 NiO	1.0022	968.7	30	60	713.9	26.3
34	HgCl ₂	4.0 NiO	1.0014	1015.4	30	60	768.7	24.3
35	HgCl ₂	4.0 NiO	1.0014	995.3	30	60	765.4	23.1
36	HgCl ₂	4.0 NiO	1.0004	979.2	30	60	723.6	26.1
37	HgCl ₂	4.0 NiO	0.9127	0.0	70(desorbed)	60	86.7	-
38	DPM	2.0 NiO	1.0002	1035.1	30	60	917.1	11.4
39	DPM	2.0 NiO	0.9991	984.7	30	60	894.1	9.2
40	DPM	2.0 NiO	1.0041	967.4	30	60	864.9	10.6
41	DPM	2.0 NiO	1.0024	1014.0	30	60	913.6	9.9
42	DPM	2.0 NiO	1.0009	989.2	30	60	882.4	10.8
43	DPM	4.0 NiO	0.9984	1035.1	30	60	902.6	12.8
44	DPM	4.0 NiO	1.0011	984.7	30	60	867.5	11.9
45	DPM	4.0 NiO	1.0019	967.4	30	60	827.1	14.5
46	DPM	4.0 NiO	1.0007	1014.0	30	60	894.3	11.8
47	DPM	4.0 NiO	0.9975	989.2	30	60	869.5	12.1
48	DPM	4.0 NiO	0.9284	0.0	70(desorbed)	60	0.0	-
49	HgCl ₂	2.0 NiO	1.0002	989.1	50	60	713.1	27.9
50	HgCl ₂	2.0 NiO	1.0004	968.7	50	60	686.8	29.1

Table 1A Conditions and results of each experiment. (continued)

Exp. no.	Type of mercury	Type of adsorbents	Adsorbents weight(g)	Int. Conc. (ppb)	Temp. (°C)	Time (min)	Hg content (ppb)	% Removal
51	HgCl ₂	2.0 NiO	1.0024	1015.4	50	60	736.2	27.5
52	HgCl ₂	2.0 NiO	0.9989	995.3	50	60	722.6	27.4
53	HgCl ₂	2.0 NiO	1.0017	979.2	50	60	731.5	25.3
54	HgCl ₂	4.0 NiO	1.0031	989.1	50	60	663.7	32.9
55	HgCl ₂	4.0 NiO	1.0000	968.7	50	60	643.2	33.6
56	HgCl ₂	4.0 NiO	0.9997	1015.4	50	60	707.7	30.3
57	HgCl ₂	4.0 NiO	1.0015	995.3	50	60	681.8	31.5
58	HgCl ₂	4.0 NiO	1.0007	979.2	50	60	664.9	32.1
59	HgCl ₂	4.0 NiO	0.9364	0.0	70(desorbed)	60	74.9	-
60	DPM	2.0 NiO	0.9978	1035.1	50	60	888.1	14.2
61	DPM	2.0 NiO	0.9995	984.7	50	60	831.1	15.6
62	DPM	2.0 NiO	1.0005	967.4	50	60	805.8	16.7
63	DPM	2.0 NiO	1.0024	1014.0	50	60	856.8	15.5
64	DPM	2.0 NiO	1.0014	989.2	50	60	831.9	15.9
65	DPM	4.0 NiO	1.0007	1035.1	50	60	747.3	27.8
66	DPM	4.0 NiO	1.0034	984.7	50	60	701.1	28.8
67	DPM	4.0 NiO	1.0029	967.4	50	60	713.0	26.3
68	DPM	4.0 NiO	1.0008	1014.0	50	60	728.1	28.2
69	DPM	4.0 NiO	0.9971	989.2	50	60	730.0	26.2
70	DPM	4.0 NiO	0.9427	0.0	70(desorbed)	60	25.5	-
71	HgCl ₂	2.0 NiO	0.9993	989.1	70	60	665.7	32.7
72	HgCl ₂	2.0 NiO	1.0049	968.7	70	60	668.4	31.0
73	HgCl ₂	2.0 NiO	0.9989	1015.4	70	60	671.2	33.9
74	HgCl ₂	2.0 NiO	1.0047	995.3	70	60	672.8	32.4
75	HgCl ₂	2.0 NiO	0.9986	979.2	70	60	644.3	34.2

Table 1A Conditions and results of each experiment. (continued)

Exp. no.	Type of mercury	Type of adsorbents	Adsorbents weight(g)	Int. Conc. (ppb)	Temp. (°C)	Time (min)	Hg content (ppb)	% Removal
76	HgCl ₂	4.0 NiO	0.9972	989.1	70	60	578.6	41.5
77	HgCl ₂	4.0 NiO	1.0013	968.7	70	60	598.7	38.2
78	HgCl ₂	4.0 NiO	1.0027	1015.4	70	60	608.2	40.1
79	HgCl ₂	4.0 NiO	0.9971	995.3	70	60	585.2	41.2
80	HgCl ₂	4.0 NiO	1.0007	979.2	70	60	589.5	39.8
81	HgCl ₂	4.0 NiO	0.9180	0.0	70(desorbed)	60	110.2	-
82	DPM	2.0 NiO	1.0025	1035.1	70	60	788.7	23.8
83	DPM	2.0 NiO	1.0008	984.7	70	60	768.1	22.0
84	DPM	2.0 NiO	1.0043	967.4	70	60	764.2	21.0
85	DPM	2.0 NiO	0.9994	1014.0	70	60	806.1	20.5
86	DPM	2.0 NiO	1.0012	989.2	70	60	800.3	19.1
87	DPM	4.0 NiO	0.0075	1035.1	70	60	644.9	37.7
88	DPM	4.0 NiO	1.0022	984.7	70	60	633.2	35.7
89	DPM	4.0 NiO	1.0014	967.4	70	60	629.8	34.9
90	DPM	4.0 NiO	1.0031	1014.0	70	60	641.9	36.7
91	DPM	4.0 NiO	1.0004	989.2	70	60	642.0	35.1
92	DPM	4.0 NiO	0.9255	0.0	70(desorbed)	60	50.9	-
93	HgCl ₂	Re/SiO ₂	1.0028	995.3	30	60	860.9	13.5
94	HgCl ₂	Re/SiO ₂	0.9989	1032.4	30	60	888.9	13.9
95	HgCl ₂	Re/SiO ₂	1.0031	974.9	30	60	845.2	13.3
96	HgCl ₂	Re/SiO ₂	0.9984	995.3	50	60	837.0	15.9
97	HgCl ₂	Re/SiO ₂	0.9993	1032.4	50	60	857.9	16.9
98	HgCl ₂	Re/SiO ₂	1.0011	974.9	50	60	815.9	16.3
99	HgCl ₂	Re/SiO ₂	1.0018	995.3	70	60	811.2	18.5
100	HgCl ₂	Re/SiO ₂	1.0027	1032.4	70	60	831.1	19.5

Table 1A Conditions and results of each experiment. (continued)

Exp. no.	Type of mercury	Type of adsorbents	Adsorbents weight(g)	Int. Conc. (ppb)	Temp. (°C)	Time (min)	Hg content (ppb)	% Removal
101	HgCl ₂	Re/SiO ₂	1.0031	974.9	70	60	796.5	18.3
102	HgCl ₂	Re/SiO ₂	0.9152	0.0	70(desorbed)	60	92.4	-
103	DPM	Re/SiO ₂	0.9993	983.1	30	60	953.6	3.0
104	DPM	Re/SiO ₂	1.0011	1009.8	30	60	980.5	2.9
105	DPM	Re/SiO ₂	1.0037	1027.4	30	60	991.4	3.5
106	DPM	Re/SiO ₂	0.9987	983.1	50	60	936.9	4.7
107	DPM	Re/SiO ₂	1.0021	1009.8	50	60	967.4	4.2
108	DPM	Re/SiO ₂	0.9994	1027.4	50	60	986.3	4.0
109	DPM	Re/SiO ₂	1.0021	983.1	70	60	919.2	6.5
110	DPM	Re/SiO ₂	1.0023	1009.8	70	60	942.1	6.7
111	DPM	Re/SiO ₂	1.0007	1027.4	70	60	954.5	7.1
112	DPM	Re/SiO ₂	0.9029	0.0	70(desorbed)	60	32.1	-
113	HgCl ₂	2.0 Ni	1.0029	995.7	30	60	633.3	36.4
114	HgCl ₂	2.0 Ni	1.0016	978.2	30	60	611.4	37.5
115	HgCl ₂	2.0 Ni	0.9979	1024.1	30	60	664.6	35.1
116	HgCl ₂	2.0 Ni	1.0003	1005.0	30	60	651.2	35.2
117	HgCl ₂	2.0 Ni	0.0092	987.9	30	60	625.3	36.7
118	HgCl ₂	4.0 Ni	0.9972	995.7	30	60	576.5	42.1
119	HgCl ₂	4.0 Ni	1.0037	978.2	30	60	544.9	44.3
120	HgCl ₂	4.0 Ni	0.9984	1024.1	30	60	582.7	43.1
121	HgCl ₂	4.0 Ni	0.9975	1005.0	30	60	557.8	44.5
122	HgCl ₂	4.0 Ni	1.0014	987.9	30	60	561.1	43.2
123	HgCl ₂	4.0 Ni	0.9277	0.0	70(desorbed)	60	64.9	-
124	DPM	2.0 Ni	1.0007	1031.8	30	60	893.5	13.4
125	DPM	2.0 Ni	1.0038	1015.4	30	60	891.5	12.2

Table 1A Conditions and results of each experiment. (continued)

Exp. no.	Type of mercury	Type of adsorbents	Adsorbents weight(g)	Int. Conc. (ppb)	Temp. (°C)	Time (min)	Hg content (ppb)	% Removal
126	DPM	2.0 Ni	1.0018	1019.9	30	60	911.8	10.6
127	DPM	2.0 Ni	0.9976	991.7	30	60	873.7	11.9
128	DPM	2.0 Ni	1.0042	1027.4	30	60	900.0	12.4
129	DPM	4.0 Ni	0.9988	1031.8	30	60	815.1	21.0
130	DPM	4.0 Ni	0.9974	1015.4	30	60	823.5	18.9
131	DPM	4.0 Ni	1.0023	1019.9	30	60	820.0	19.6
132	DPM	4.0 Ni	1.0034	991.7	30	60	809.2	18.4
133	DPM	4.0 Ni	1.0016	1027.4	30	60	826.0	19.6
134	DPM	4.0 Ni	0.9167	0.0	70(desorbed)	60	22.9	-
135	HgCl ₂	2.0 Ni	1.0098	995.7	50	60	536.7	46.1
136	HgCl ₂	2.0 Ni	1.0032	978.2	50	60	540.0	44.8
137	HgCl ₂	2.0 Ni	1.0003	1024.1	50	60	556.1	45.7
138	HgCl ₂	2.0 Ni	1.0031	1005.0	50	60	555.8	44.7
139	HgCl ₂	2.0 Ni	0.9971	987.9	50	60	530.5	46.3
140	HgCl ₂	4.0 Ni	1.0025	995.7	50	60	501.8	49.6
141	HgCl ₂	4.0 Ni	0.9976	978.2	50	60	508.7	48.0
142	HgCl ₂	4.0 Ni	1.0005	1024.1	50	60	498.7	51.3
143	HgCl ₂	4.0 Ni	1.0014	1005.0	50	60	518.6	48.4
144	HgCl ₂	4.0 Ni	0.9992	987.9	50	60	500.9	49.3
145	HgCl ₂	4.0 Ni	0.9278	0.0	70(desorbed)	60	79.8	-
146	DPM	2.0 Ni	1.0002	1031.8	50	60	861.6	16.5
147	DPM	2.0 Ni	0.9978	1015.4	50	60	849.9	16.3
148	DPM	2.0 Ni	0.9986	1019.9	50	60	844.5	17.2
149	DPM	2.0 Ni	0.9985	991.7	50	60	827.1	16.6
150	DPM	2.0 Ni	1.0011	1027.4	50	60	874.3	14.9

Table 1A Conditions and results of each experiment. (continued)

Exp. no.	Type of mercury	Type of adsorbents	Adsorbents weight(g)	Int. Conc. (ppb)	Temp. (°C)	Time (min)	Hg content (ppb)	% Removal
151	DPM	4.0 Ni	1.0018	1031.8	50	60	732.1	29.0
152	DPM	4.0 Ni	1.0021	1015.4	50	60	736.2	27.5
153	DPM	4.0 Ni	1.0034	1019.9	50	60	732.2	28.2
154	DPM	4.0 Ni	1.0008	991.7	50	60	725.9	26.8
155	DPM	4.0 Ni	0.9987	1027.4	50	60	749.0	27.1
156	DPM	4.0 Ni	0.9381	0.0	70(desorbed)	60	28.1	-
157	HgCl ₂	2.0 Ni	0.9992	995.7	70	60	486.9	51.1
158	HgCl ₂	2.0 Ni	0.9982	978.2	70	60	508.7	48.0
159	HgCl ₂	2.0 Ni	1.0034	1024.1	70	60	514.1	49.8
160	HgCl ₂	2.0 Ni	1.0018	1005.0	70	60	499.5	50.3
161	HgCl ₂	2.0 Ni	0.9986	987.9	70	60	496.9	49.7
162	HgCl ₂	4.0 Ni	0.9993	995.7	70	60	423.2	57.5
163	HgCl ₂	4.0 Ni	1.0016	978.2	70	60	429.4	56.1
164	HgCl ₂	4.0 Ni	1.0009	1024.1	70	60	457.8	55.3
165	HgCl ₂	4.0 Ni	1.0037	1005.0	70	60	449.2	55.3
166	HgCl ₂	4.0 Ni	1.0024	987.9	70	60	416.9	57.8
167	HgCl ₂	4.0 Ni	0.9266	0.0	70(desorbed)	60	89.0	-
168	DPM	2.0 Ni	1.0017	1031.8	70	60	807.9	21.7
169	DPM	2.0 Ni	1.0004	1015.4	70	60	807.2	20.5
170	DPM	2.0 Ni	1.0019	1019.9	70	60	805.7	21.0
171	DPM	2.0 Ni	1.0003	991.7	70	60	794.4	19.9
172	DPM	2.0 Ni	0.9974	1027.4	70	60	820.9	20.1
173	DPM	4.0 Ni	0.9986	1031.8	70	60	636.6	38.3
174	DPM	4.0 Ni	1.0011	1015.4	70	60	646.8	36.3
175	DPM	4.0 Ni	0.9998	1019.9	70	60	658.9	35.4

Table 1A Conditions and results of each experiment. (continued)

Exp. no.	Type of mercury	Type of adsorbents	Adsorbents weight(g)	Int. Conc. (ppb)	Temp. (°C)	Time (min)	Hg content (ppb)	% Removal
176	DPM	4.0 Ni	1.0037	991.7	70	60	625.8	36.9
177	DPM	4.0 Ni	0.9976	1027.4	70	60	643.2	37.4
178	DPM	4.0 Ni	0.9245	0.0	70(desorbed)	60	41.6	-
179	HgCl ₂	Sul/SiO ₂	1.0014	1017.3	30	60	852.5	16.2
180	HgCl ₂	Sul/SiO ₂	1.0020	957.9	30	60	809.4	15.5
181	HgCl ₂	Sul/SiO ₂	1.0021	984.6	30	60	824.1	16.3
182	HgCl ₂	Sul/SiO ₂	0.9972	1017.3	50	60	856.6	15.8
183	HgCl ₂	Sul/SiO ₂	0.9983	957.9	50	60	798.9	16.6
184	HgCl ₂	Sul/SiO ₂	1.0016	984.6	50	60	823.1	16.4
185	HgCl ₂	Sul/SiO ₂	0.9993	1017.3	70	60	832.2	18.2
186	HgCl ₂	Sul/SiO ₂	1.0011	957.9	70	60	774.9	19.1
187	HgCl ₂	Sul/SiO ₂	1.0037	984.6	70	60	798.5	18.9
188	HgCl ₂	Sul/SiO ₂	0.9102	0.0	70(desorbed)	60	107.4	-
189	DPM	Sul/SiO ₂	0.9974	971.4	30	60	939.3	3.3
190	DPM	Sul/SiO ₂	1.0023	968.2	30	60	939.1	3.0
191	DPM	Sul/SiO ₂	0.9976	1034.4	30	60	1004.4	2.9
192	DPM	Sul/SiO ₂	1.0008	971.4	50	60	913.1	6.0
193	DPM	Sul/SiO ₂	1.0014	968.2	50	60	918.8	5.1
194	DPM	Sul/SiO ₂	1.0007	1034.4	50	60	978.5	5.4
195	DPM	Sul/SiO ₂	1.0013	971.4	70	60	895.6	7.8
196	DPM	Sul/SiO ₂	1.0035	968.2	70	60	894.6	7.6
197	DPM	Sul/SiO ₂	0.9981	1034.4	70	60	962.0	7.0
198	DPM	Sul/SiO ₂	0.9318	0.0	70(desorbed)	60	30.6	-
199	HgCl ₂	2.0 NiS	1.0015	979.4	30	60	104.8	89.3
200	HgCl ₂	2.0 NiS	1.0007	1042.8	30	60	95.9	90.8

Table 1A Conditions and results of each experiment. (continued)

Exp. no.	Type of mercury	Type of adsorbents	Adsorbents weight(g)	Int. Conc. (ppb)	Temp. (°C)	Time (min)	Hg content (ppb)	% Removal
201	HgCl ₂	2.0 NiS	1.0013	1009.4	30	60	89.8	91.1
202	HgCl ₂	2.0 NiS	1.0028	989.3	30	60	98.9	90.0
203	HgCl ₂	2.0 NiS	0.9989	991.2	30	60	92.2	90.7
204	HgCl ₂	4.0 NiS	1.0031	979.4	30	60	97.9	90.0
205	HgCl ₂	4.0 NiS	0.9984	1042.8	30	60	87.6	91.6
206	HgCl ₂	4.0 NiS	0.9993	1009.4	30	60	93.9	90.7
207	HgCl ₂	4.0 NiS	1.0011	989.3	30	60	99.9	89.9
208	HgCl ₂	4.0 NiS	1.0037	991.2	30	60	95.2	90.4
209	HgCl ₂	4.0 NiS	0.9118	0.0	70(desorbed)	60	82.1	-
210	DPM	2.0 NiS	1.0021	1034.7	30	60	947.8	8.4
211	DPM	2.0 NiS	1.0023	984.7	30	60	906.9	7.9
212	DPM	2.0 NiS	0.9976	1034.8	30	60	945.8	8.6
213	DPM	2.0 NiS	0.9983	971.4	30	60	901.5	7.2
214	DPM	2.0 NiS	1.0014	994.1	30	60	906.6	8.8
215	DPM	4.0 NiS	1.0007	1034.7	30	60	918.8	11.2
216	DPM	4.0 NiS	1.0014	984.7	30	60	861.6	12.5
217	DPM	4.0 NiS	1.0035	1034.8	30	60	898.2	13.2
218	DPM	4.0 NiS	0.9981	971.4	30	60	850.9	12.4
219	DPM	4.0 NiS	0.9978	994.1	30	60	877.8	11.7
220	DPM	4.0 NiS	0.9472	0.0	70(desorbed)	60	14.2	-
221	HgCl ₂	2.0 NiS	1.0014	979.4	50	60	48.0	95.1
222	HgCl ₂	2.0 NiS	1.0009	1042.8	50	60	68.8	93.4
223	HgCl ₂	2.0 NiS	0.9997	1009.4	50	60	67.6	93.3
224	HgCl ₂	2.0 NiS	1.0017	989.3	50	60	51.4	94.8
225	HgCl ₂	2.0 NiS	0.9984	991.2	50	60	63.4	93.6

Table 1A Conditions and results of each experiment. (continued)

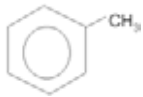
Exp. no.	Type of mercury	Type of adsorbents	Adsorbents weight(g)	Int. Conc. (ppb)	Temp. (°C)	Time (min)	Hg content (ppb)	% Removal
226	HgCl ₂	4.0 NiS	1.0025	979.4	50	60	51.9	94.7
227	HgCl ₂	4.0 NiS	1.0016	1042.8	50	60	44.8	95.7
228	HgCl ₂	4.0 NiS	1.0008	1009.4	50	60	59.6	94.1
229	HgCl ₂	4.0 NiS	0.9981	989.3	50	60	38.6	96.1
230	HgCl ₂	4.0 NiS	1.0029	991.2	50	60	43.6	95.6
231	HgCl ₂	4.0 NiS	0.9222	0.0	70(desorbed)	60	75.6	-
232	DPM	2.0 NiS	1.0014	1034.7	50	60	880.5	14.9
233	DPM	2.0 NiS	0.9984	984.7	50	60	831.1	15.6
234	DPM	2.0 NiS	0.9997	1034.8	50	60	875.4	15.4
235	DPM	2.0 NiS	1.0005	971.4	50	60	830.5	14.5
236	DPM	2.0 NiS	1.0026	994.1	50	60	836.0	15.9
237	DPM	4.0 NiS	1.0015	1034.7	50	60	801.9	22.5
238	DPM	4.0 NiS	0.9984	984.7	50	60	752.3	23.6
239	DPM	4.0 NiS	0.9993	1034.8	50	60	809.2	21.8
240	DPM	4.0 NiS	1.0021	971.4	50	60	757.7	22.0
241	DPM	4.0 NiS	1.0027	994.1	50	60	783.4	21.2
242	DPM	4.0 NiS	0.9391	0.0	70(desorbed)	60	32.9	-
243	HgCl ₂	2.0 NiS	0.9992	979.4	70	60	18.6	98.1
244	HgCl ₂	2.0 NiS	1.0018	1042.8	70	60	11.5	98.9
245	HgCl ₂	2.0 NiS	1.0029	1009.4	70	60	11.1	98.9
246	HgCl ₂	2.0 NiS	0.9971	989.3	70	60	12.9	98.7
247	HgCl ₂	2.0 NiS	1.0034	991.2	70	60	26.8	97.3
248	HgCl ₂	4.0 NiS	1.0027	979.4	70	60	26.4	97.3
249	HgCl ₂	4.0 NiS	0.9973	1042.8	70	60	20.9	98.0
250	HgCl ₂	4.0 NiS	1.0033	1009.4	70	60	3.0	99.7

Table 1A Conditions and results of each experiment. (continued)

Exp. no.	Type of mercury	Type of adsorbents	Adsorbents weight(g)	Int. Conc. (ppb)	Temp. (°C)	Time (min)	Hg content (ppb)	% Removal
251	HgCl ₂	4.0 NiS	0.9995	989.3	70	60	14.8	98.5
252	HgCl ₂	4.0 NiS	0.9986	991.2	70	60	20.8	97.9
253	HgCl ₂	4.0 NiS	0.8997	0.0	70(desorbed)	60	85.5	-
254	DPM	2.0 NiS	0.9992	1034.7	70	60	807.1	22.0
255	DPM	2.0 NiS	1.0016	984.7	70	60	773.0	21.5
256	DPM	2.0 NiS	1.0013	1034.8	70	60	800.9	22.6
257	DPM	2.0 NiS	1.0028	971.4	70	60	765.5	21.2
258	DPM	2.0 NiS	0.9973	994.1	70	60	788.3	20.7
259	DPM	4.0 NiS	0.9984	1034.7	70	60	657.0	36.5
260	DPM	4.0 NiS	0.9992	984.7	70	60	635.1	35.5
261	DPM	4.0 NiS	1.0022	1034.8	70	60	642.6	37.9
262	DPM	4.0 NiS	1.0017	971.4	70	60	598.4	38.4
263	DPM	4.0 NiS	1.0032	994.1	70	60	631.3	36.5
264	DPM	4.0 NiS	0.9257	0.0	70(desorbed)	60	46.3	-

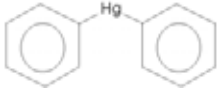
Appendix B

Table B – 1 Properties of Toluene*

Formula	C ₇ H ₈
Structure	
Chemical Name	Toluene
Physical Properties	
Molecular Weight	92.13
Status at 25 °C	Liquid
Color	Colorless
Boiling Point (°C)	110.8
Melting Point (°C)	-95
Specific Gravity	0.866
Solubility	Soluble in Ether and Alcohol
Purity	>99%
Supplier	HRC

* From Encyclopedia of Chemical Engineering.

Table B – 2 Properties of Diphenylmercury*

Formula	$C_{12}H_{10}Hg$
Structure	
Chemical Name	Diphenylmercury
Physical Properties	
Molecular Weight	354.8
Status at 25 °C	Solid
Color	White
Boiling Point (°C)	-
Melting Point (°C)	121-124
Specific Gravity	2.32
Solubility	Moderately Soluble in Toluene
Purity	> 97%
Supplier	Carlo Erba

* From Encyclopedia of Chemical Engineering.

Table B – 3 Properties of Mercuric (II) Chloride*

Formula	HgCl ₂
Chemical Name	Mercuric (II) Chloride
Physical Properties	
Molecular Weight	271.52
Status at 25 °C	Solid
Color	White
Boiling Point (°C)	302
Melting Point (°C)	277
Specific Gravity	5.44
Solubility	Soluble in Water
Purity	> 99%
Supplier	Fluka

* From Encyclopedia of Chemical Engineering.

Table B – 4 Properties of Nitric Acid*

Formula	HNO ₃
Chemical Name	Nitric Acid
Physical Properties	
Molecular Weight	63.02
Status at 25 °C	Liquid
Color	Colorless
Boiling Point (°C)	83
Melting Point (°C)	-41.59
Specific Gravity	1.502
Solubility	Soluble in Water
Purity	69.0-70.5%
Supplier	Merck

* From Merck Index.

Table B – 5 Properties of Sulfuric Acid*

Formula	H ₂ SO ₄
Chemical Name	Sulfuric Acid
Physical Properties	
Molecular Weight	98.09
Status at 25 °C	Liquid
Color	Colorless
Boiling Point (°C)	~ 290
Melting Point (°C)	10
Specific Gravity	1.84
Solubility	Soluble in Water
Purity	> 99%
Supplier	Merck

* From Merck Index.

Table B – 6 Properties of Hydrochloric Acid *

Formula	HCl
Chemical Name	Hydrochloric Acid
Physical Properties	
Molecular Weight	36.47
Status at 25 oC	Liquid
Color	Colorless
Boiling Point (°C)	-15.35
Melting Point (°C)	-83
Solubility	Soluble in Water and Alcohol
Purity	37%
Supplier	Merck

* From Encyclopedia of Chemical Engineering.

Table B – 7 Properties of Hydrofluoric Acid *

Formula	HF
Chemical Name	Hydrofluoric Acid
Physical Properties	
Molecular Weight	20.01
Status at 25 °C	Liquid
Color	Colorless
Boiling Point (°C)	112.2
Melting Point (°C)	-83
Specific Gravity	1.155
Solubility	Soluble in Water
Purity	48-51%
Supplier	Carlo Erba

* From Encyclopedia of Chemical Engineering.

Table B – 8 Properties of Hydrogen Peroxide *

Formula	H ₂ O ₂
Chemical Name	Hydrogen Peroxide
Physical Properties	
Molecular Weight	34.02
Status at 25 °C	Liquid
Color	Colorless
Boiling Point (°C)	151.4
Melting Point (°C)	0.89
Specific Gravity	1.13
Solubility	Soluble in Water, acid and Ether
Purity	35-35.6%
Supplier	Merck

* From Encyclopedia of Chemical Engineering.

Table B – 9 Properties of Nickel Nitrate Hexahydrate *

Formula	Ni (NO ₃)*6H ₂ O
Chemical Name	Nickel Nitrate Hexahydrate
Physical Properties	
Molecular Weight	290.8
Status at 25 °C	Solid
Color	Green
Boiling Point (°C)	136.7
Melting Point (°C)	56.7
Specific Gravity	2.05
Solubility	Soluble in Water and Ammoniumhydroxide
Purity	>99.0 %
Supplier	Fluka

* From Encyclopedia of Chemical Engineering.

Table B – 10 Properties of Potassium Permanganate *

Formula	KMnO ₄
Chemical Name	Potassium Permanganate
Physical Properties	
Molecular Weight	158.03
Status at 25 °C	Solid
Color	Dark Purple
Boiling Point (°C)	-
Melting Point (°C)	-
Specific Gravity	2.71
Solubility	Soluble in Water
Supplier	Carlo Erba

* From Merck Index.

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Table B – 11 Properties of Potassium Persulfate *

Formula	K_2SO_8
Chemical Name	Potassium Persulfate
Physical Properties	
Molecular Weight	270.32
Status at 25 °C	Solid
Color	White
Boiling Point (°C)	-
Melting Point (°C)	-
Specific Gravity	-
Solubility	Soluble in Water
Supplier	Carlo Erba

* From Merck Index.

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Table B – 12 Properties of Hydroxylamin-Hydrochloride *

Formula	$\text{NH}_2\text{OH}\cdot\text{HCl}$
Chemical Name	Hydroxylamine - Hydrochloride
Physical Properties	
Molecular Weight	69.49
Status at 25 °C	Solid
Color	White
Boiling Point (°C)	58
Melting Point (°C)	33
Specific Gravity	1.20
Solubility	Soluble in Water
Purity	> 99 %
Supplier	Carlo Erba

* From Merck Index.

Table B – 13 Properties of Sodium Chloride *

Formula	NaCl
Chemical Name	Sodium Chloride
Physical Properties	
Molecular Weight	58.54
Status at 25 °C	Solid
Color	White
Boiling Point (°C)	804
Melting Point (°C)	-
Specific Gravity	2.17
Solubility	Soluble in Water
Purity	> 99 %
Supplier	Carlo Erba

* From Merck Index.

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