การศึกษาเทคนิคการตกตะกอนร่วมโลหะมีค่าด้วยแมงกานีสไฮดรอกไซด์และการนำกลับคืนอนุภาคทองคำนาโนจากชิ้นส่วนไมโครโปรเซสเซอร์ในคอมพิวเตอร์

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STUDY OF PRECIOUS METALS COPRECIPITATION WITH MANGANESE HYDROXIDE AND RECOVERY OF GOLD NANOPARTICLES FROM COMPUTER MICROPROCESSOR SCRAP

Miss Chompunoot Wiraseranee

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering Program in Georesources Engineering
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การศึกษาเทคนิคการตกตะกอนร่วมโลหะมีค่าด้วยแมงกานีสไฮดรอกไซด์นี้ มีวัตถุประสงค์เพื่อพัฒนาวิธีการนำกลับคืนโลหะมีค่าจากขยะอิเล็กทรอนิกส์ เทคนิคการตกตะกอนร่วมโลหะมีค่าด้วยแมงกานีสไฮดรอกไซด์ จากการศึกษาพบว่า ณ อุณหภูมิห้อง ที่ pH 9 สามารถนำกลับคืนทองคำและพัลลาเดียม ได้ประมาณ 99% ขณะที่สามารถนำกลับคืนแพลทตินัมได้เพียงประมาณ 40% อย่างไรก็ตามการนำกลับคืนแพลทตินัมสามารถเพิ่มขึ้นถึงประมาณ 90% ภายใน 24 ชั่วโมง หากสารละลายที่ใช้ตกตะกอนร่วมประกอบด้วย ทองคำ แพลทตินัม และแมงกานีส ผสมกันในอัตราส่วนโดยโมลเท่ากับ 6:1:10 แสดงว่าทองคำช่วยเพิ่มประสิทธิภาพการตกตะกอนร่วมของแพลทตินัม นอกจากนี้ยังพบว่าทองคำที่ตกตะกอนร่วมกับแมงกานีสไฮดรอกไซด์ปรากฎในรูปของโลหะทองคำอนุภาคขนาดนาโน ซึ่งทดสอบยืนยันได้ด้วยการละลายในกรดไฮโดรคลอริกเจือจางและคุณสมบัติการเป็นสารเร่งปฏิกิริยาออกซิเดชันของก๊าซคาร์บอนมอนอกไซด์ โดยปรากฎอุณหภูมิครึ่งปฏิกิริยา ($T_{1/2}$) ที่ 80°C ทั้งนี้คาดว่าทองคำที่ตกตะกอนร่วมกับแมงกานีสไฮดรอกไซด์อาจถูกรีดิวซ์เป็นโลหะ Au(0) ด้วยการส่งผ่านอิเล็กตรอนระหว่างพันธะ Au-O-Mn ขณะที่แพลทตินัมและพัลลาเดียมไม่สามารถถูกรีดิวซ์ให้เป็นโลหะ ตะกอนร่วมที่ได้จึงปรากฎในรูป Pt(IV) และ Pd(II) ตามลำดับ โดยที่ตะกอนร่วมพัลลาเดียม-แมงกานีสสามารถละลายในกรดไฮโดรคลอริกเข้มข้น 0.1 mol dm^{-3} ขณะที่ตะกอนร่วมแพลทตินัม-แมงกานีสไม่ละลาย ดังนั้นหลังการตกตะกอนร่วม จึงสามารถแยกตะกอนร่วมแพลทตินัมออกจากตะกอนร่วมของพัลลาเดียมและทองคำได้ด้วยเทคนิคการละลาย เมื่อนำผลการศึกษาเทคนิคการตกตะกอนร่วมโลหะมีค่าดังกล่าวมาทดลองประยุกต์ใช้เพื่อการนำกลับคืนทองคำจากชิ้นส่วนไมโครโปรเซสเซอร์ในคอมพิวเตอร์ซึ่งประกอบด้วยโลหะอื่นๆ นอกเหนือจากโลหะมีค่า ปรากฎว่าทองคำตกตะกอนร่วมกับเหล็กไฮดรอกไซด์ในรูปไอออนเชิงซ้อนที่ pH 4 ซึ่งสามารถแยกทองคำออกจากมลทินและโลหะมีค่าอื่นๆได้ จากนั้นละลายตะกอนทองคำที่ได้ในกรดไฮโดรคลอริกเจือจาง (0.01 mol dm^{-3}) แล้วเติมสารละลายแมงกานีสคลอไรด์ (Mn(II)) โดยให้มีอัตราส่วนโดยโมลทองคำต่อแมงกานีส 6:10 แล้วทำการตกตะกอนร่วมอีกครั้งปรากฎว่าสามารถนำกลับคืนทองคำได้ถึง 81% ในรูปของตะกอนร่วมทองคำ-เหล็ก-แมงกานีส

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CHOMPUNOOT WIRASERANEE: STUDY OF PRECIOUS METALS COPRECIPITATION WITH MANGANESE HYDROXIDE AND RECOVERY OF GOLD NANOPARTICLES FROM COMPUTER MICROPROCESSOR SCRAP. ADVISOR: ASSOC.PROF. DAWAN WIWATTANADATE, Ph.D., CO-ADVISOR: ASSOC. PROF. QUANCHAI LEEPAWPANTH, Ph.D., 123 pp.

Recovery of gold (Au), platinum (Pt) and palladium (Pd) by coprecipitation with $Mn(OH)_2$ and their selective separation were investigated to develop an alternative method for recovery of precious metals from electronic wastes. It was found from the study that at pH 9, room temperature, nearly 99% of either Au or Pd was coprecipitated with $Mn(OH)_2$, while only 40% of Pt was coprecipitated after 24 hours. However, the coprecipitation of Pt was enhanced up to 90% within 24 hours when Pt(IV) coexisted with Au(III) and Mn(II) in the initial solution having Au:Pt:Mn mole ratio of 6:1:10. Au in coprecipitates was reduced to metallic Au (Au(0)) nanoparticles, which is considered to be caused by electron transfer through Au-O-Mn bonding, whereas Pt(IV) and Pd(II) were not reduced to metallic state. It is considered that Pt(IV) and Pd(II) were entrapped or incorporated into MnO_2 structure instead of adsorption on $Mn(OH)_2$ surface like Au. The existence of Au nanoparticles was confirmed by its solubility in dilute HCl solution and TEM analysis, and coprecipitated Au nanoparticles exhibited catalytic ability for CO oxidation at the half conversion temperature (T½) of 80°C. It was also found that the coprecipitated Au and Pd can be selectively separated from coprecipitated Pt by 0.1 mol dm^{-3} HCl dissolution. Results of the study were then applied to recover Au from CPU microprocessor scrap composed of various metals by coprecipitation with $Mn(OH)_2$. It was found that Au can selectively separated from the sample solution by coprecipitation with $Fe(OH)_3$ at pH 4 as Au(III) complexes. The Au-Fe coprecipitate was dissolved in 0.01 mol dm^{-3} HCl, and then $MnCl_2$ solution was added to the Au-Fe solution at Au:Mn mole ratio of 6:10 to achieve up to 81% Au recovered as metallic Au in $Fe(OH)_3$ and $Mn(OH)_2$ coprecipitates, or metallic Au supported on manganese and iron oxides surfaces.

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CHAPTER I

INTRODUCTION

1.1. Background

Precious metals including gold and platinum group metals (PGMs) have been extensively used in various industries due to their outstanding specific chemical and physical properties. According to their increasing price and demand, as well as their rarity in nature resulted from long continuous consumption, precious metals recovery and recycling from secondary sources become the significant global issues.

Electronic wastes, such as parts of used personal computer and spent automobile catalytic converters, are the potential secondary sources of precious metals including gold (Au), silver (Ag), platinum (Pt) and palladium (Pd) (Kang and Schoenung, 2005; Hall and Williams, 2007; and Shirahase and Kida, 2008), which are so called “urban mines”. The amount of electronic wastes is drastically increased in recent years due to the progressive technological developments leading to the rapid devices rejection. Therefore, precious metals recovery and recycling from electronic wastes can be considered as an advantageous option.

Nowadays, precious metals recovery from electronic wastes has been worldwide focused as the modern precious metals exploitation. The common expected features of a practical precious metals recovery technique are, for example, selective separation of precious metals from other coexisting metals; less energy consumption and environmental friendly recovery processing; and inexpensive operating costs. Since the content of precious metals in computer wastes is relatively low, the selective separation for recovery of the precious metals from the low-concentrated sources is necessary. In addition, the recovery process should be environmental friendly and consume minimal energy.

Coprecipitation is typically defined as the simultaneous removal of trace metals from an aqueous solution without regard to the specific mechanisms involved (Zhu et al., 2003). In precious metals recovery aspects, coprecipitation is one of the developing techniques for recovery of single target metal. General mechanism of the metal coprecipitation is that the target metal is precipitated from aqueous solution due to the precipitation of another metal, or “a carrier”, at an appropriate condition. Coprecipitation of precious metals can spontaneously or naturally proceed at ambient temperature in which energy provision is unnecessary.

Figure 1.1 Marine manganese nodules.

In nature, various significant metals such as iron, cobalt, copper, zinc, and nickel are concentrated in marine manganese nodules (Figure 1.1) in the oceans. Remarkably, gold and PGMs are also concentrated into marine manganese nodules from seawater or oceanic surroundings (Banerjee, 2004; Baturin et al., 2005; and Banakar et al., 2007).

Platinum is enriched in manganese crusts and nodules from Pacific Ocean, the content in which varies from 6 ppb to 940 ppb (Agiorgitis and Gundlach, 1978; Halbach et al., 1984; and Hodge et al., 1985). It is also reported that the platinum content in manganese crusts from Central Pacific seamount areas ranges from 0.14 to 1.02 ppm, the average content of which is 0.51±0.24 ppm (Halbach et al., 1989). The manganese crusts and nodules contain more than 100 times platinum compared to the platinum content about 5 ppb in the Earth’s upper continental crust (Wedepohl, 1975). Platinum concentration in ocean water increases from 0.1 ppt in shallow water (200 m in depth) to 0.3 ppt in deep water (>2000 m) (Halbach et al., 1989). The platinum concentrated in manganese crusts is 2 x 10^6 times more than platinum concentration in ocean water.

Gold content in manganese crusts and nodules ranges from <0.2 to 2.73 ppb (Terashima et al., 1975). The average gold content is lower than the crustal abundance of 5 ppb. Gold concentration in ocean water is 1 ppt in average (Mchugh, 1988). Therefore, gold concentration in ocean water, manganese crusts and nodules is 4.5 x 10^2 times more than that ocean water. According to these information, platinum is more likely to be concentrated than gold with respect to the crustal abundance.

Precious metals are probably concentrated by coprecipitation or adsorption with manganese oxides/hydroxide (Halbach et al, 1984; Halbach et al., 1989; and Jacinto and Van den berg, 1989). The concentration reaction of gold and PGMs onto manganese nodules can be a good example from the environmental-friendly separation and concentration of precious metals.

Moreover, the previous studies reported that Au(0) could be well supported on manganese(II) hydroxide ($Mn(OH)_2$) or manganese dioxide (MnO_2) (Ohashi et al., 2005 and Yamashita et al., 2008). Because $Mn(OH)_2$ can be oxidized to MnO_2, and because such precious metal as Au can be concentrated on the surface of both $Mn(OH)_2$ and MnO_2, separation of multiple target precious metals by coprecipitation with $Mn(OH)_2$ is possible. In addition, precious metals, especially gold, supported on metal oxides can have their unique catalytic properties (Haruta, 2003-2004), which increase the values to the recovered precious metals as the future catalysts.

Since coprecipitation method can be effectively applied to recover precious metals such as Au and Pt from electronic wastes samples (e.g., used mobile phones and automobile catalytic converters) by the chemical spontaneous reactions (e.g., Kitamoto et al., 2007 and Parinayok et al., 2007) and since concentration of precious metals by coprecipitation with $Mn(OH)_2$ can be possibly applied to recover trace-amounted precious metals, recovery of precious metals by coprecipitation with $Mn(OH)_2$ from computer scrap is substantially worth studying.

1.2. Objectives

The study aims to develop recovery of precious metals (e.g., Au, Pt and Pd) by coprecipitation with $Mn(OH)_2$ and their selective separation, and to study recovery of precious metals, mainly gold, by coprecipitation with $Mn(OH)_2$ from electronic wastes (e.g., computer CPU microprocessor).

1.3. Scope of study

To achieve the effective recovery of precious metals by coprecipitation with $Mn(OH)_2$, two stages of study are crucial. The first stage is study on methodology to develop the model experiments for the systematic recovery process, that is, the model experiments on coprecipitation of Au, Pt and Pd with $Mn(OH)_2$. The second stage is study on application of the coprecipitation method to recover Au and Pd from computer CPU microprocessors. The scope of study on each stage is explained as follow:

1.3.1. Model experiments

In model experiments, modelling reagents are prepared and used. Initial valence states of manganese, gold, platinum and palladium are Mn(II), Au(III), Pt(IV) and Pd(II), respectively. The coprecipitation experiments are carried out at the remarked pH at room temperature. Recovery effectiveness for Au, Pt and Pd is determined regarding yielded precious metals. Chemical states of gold, platinum and palladium before and after coprecipitation are mainly examined and used to imply the fundamental precious metals coprecipitation mechanisms. The selective separation of Au, Pt and Pd is studied and discussed. In addition, catalytic properties of the coprecipitates are determined. The expected experimental procedures for model experiments are as shown in Figure 1.2.

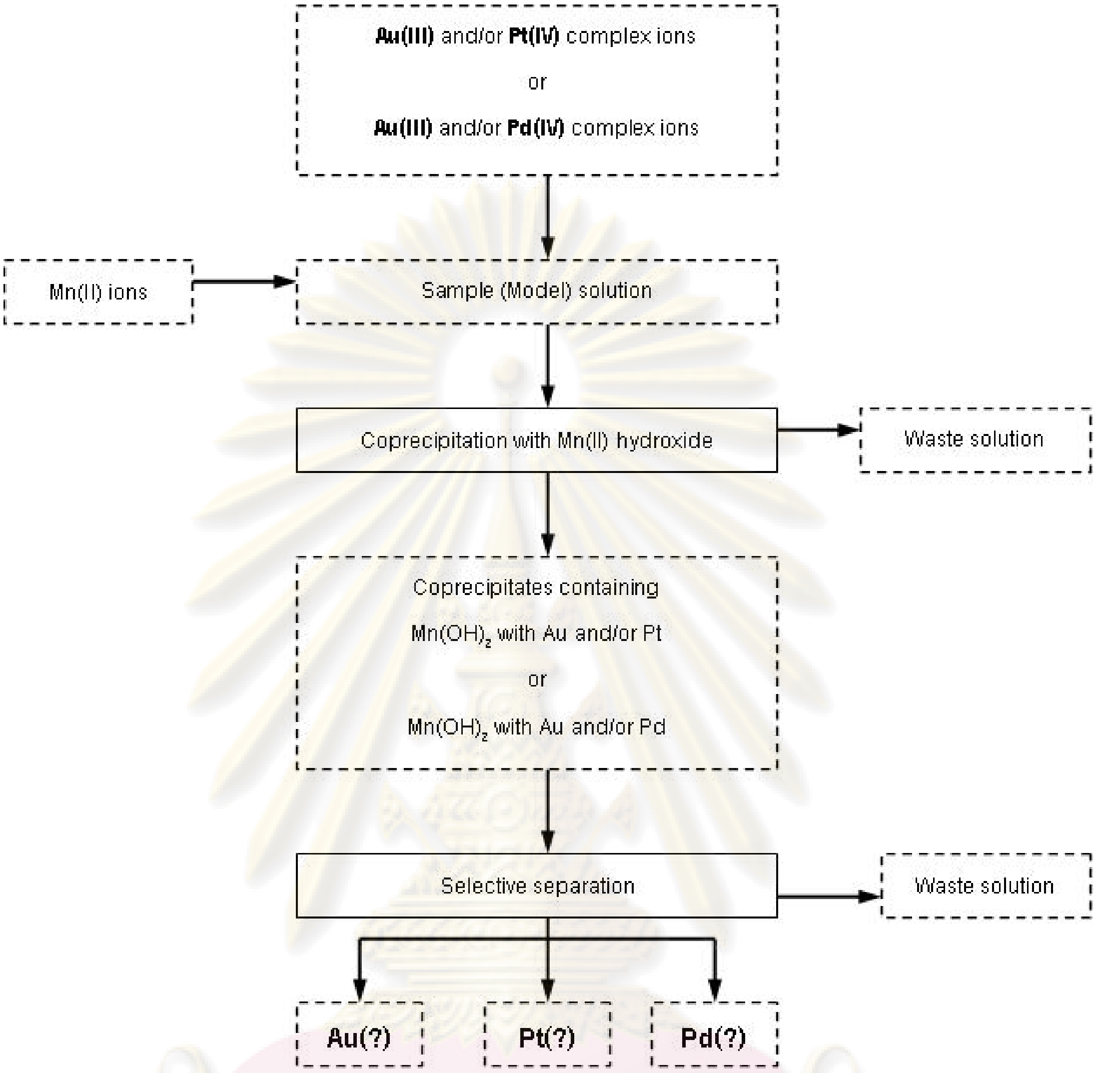


Figure 1.2 Expected experimental procedures of the model experiments.

1.3.2. Application of the model experiments to recovery of gold from microprocessor scrap

Recovery of precious metals from computer CPU microprocessor by coprecipitation technique is conducted. Gold is the main precious metal studied in the application. The microprocessor samples are primarily characterized to identify their metal composition. The samples are prepared by manually crushing to open the microprocessor package and leaching by aqua regia to dissolve all precious metals in the samples. The conditions from model experiments are implied and applied to recover precious metals from the computer CPU microprocessor. Effects of such factors as pH and the presence of Mn(II) are examined. The effectiveness of the applied coprecipitation technique to recover precious metals is discussed. The designed recovery process for recovery of precious metals from CPU microprocessor by coprecipitation method is introduced. The expected experimental procedure is shown in Figure 1.3.

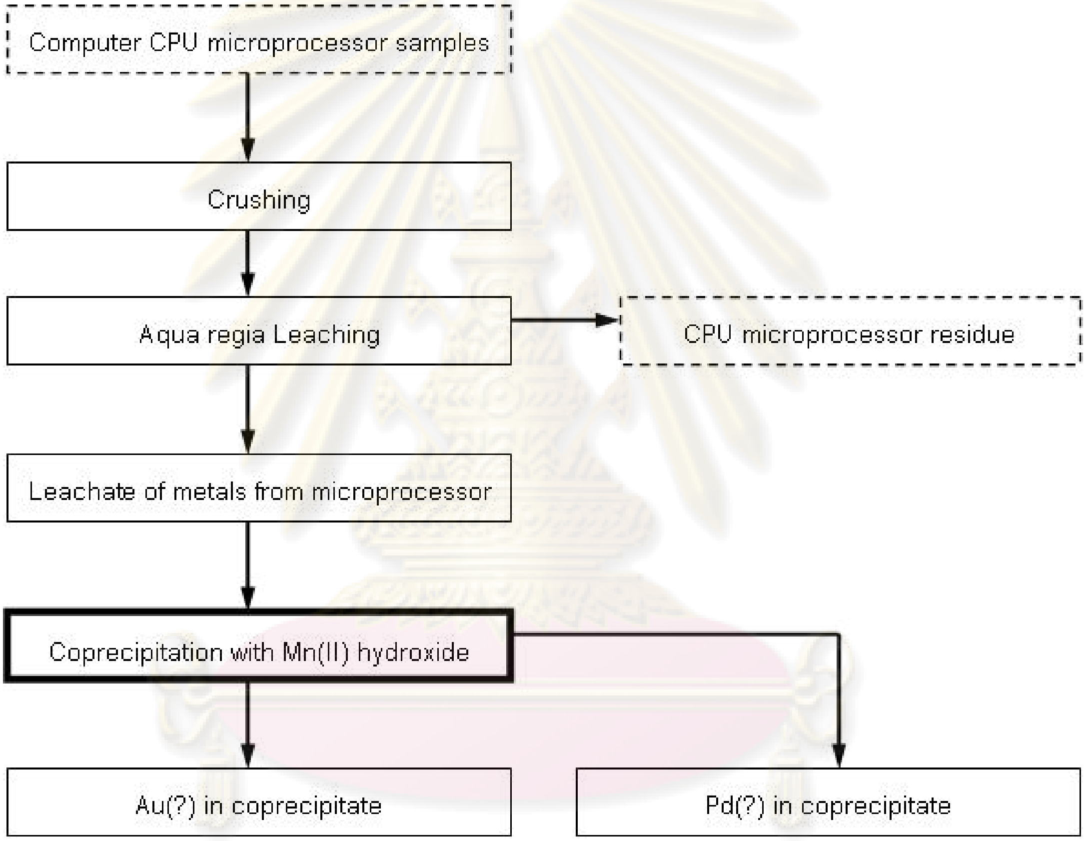


Figure 1.3 Expected experimental procedures for the application of coprecipitation method to recover precious metals from computer CPU microprocessors.

1.4. Expected benefits

Effectiveness of precious metals recovery by coprecipitation with $Mn(OH)_2$ is determined. The fundamental coprecipitation mechanisms of Au, Pt and Pd with $Mn(OH)_2$ is investigated. Selective separation of precious metals after coprecipitation with $Mn(OH)_2$ is studied and introduced. The advantages and effectiveness of coprecipitation of precious metals with $Mn(OH)_2$ are discussed.

Computer CPU microprocessor samples are characterized and their metals composition is clarified. Precious metals are recovered from the microprocessor samples by coprecipitation technique. Effectiveness of precious metals recovery from computer CPU microprocessor by coprecipitation method is discussed. The designed process for recovery of precious metals from CPU microprocessor is introduced.

1.5. Order of presentation

The thesis is composed of 6 chapters. The background, principles and implication are described in chapter I, II and VI. The experimental results are reported and discussed in chapter III, IV and V. Each experimental chapter also presents its principles, objectives of experiments, methodology, experimental and analytical procedures, results and discussions, respectively.

Chapter I and chapter II are introduction and literature reviews, respectively. The introduction includes background, objectives and scope of this research. The literature reviews suggests information related to the study, such as reviews of previous work about precious metals recovery method and coprecipitation of precious metals with metal hydroxides.

Chapter III reports and discusses coprecipitation of precious metals with $Mn(OH)_2$. Coprecipitation behaviors, changes in valence states of precious metals, and fundamental precious metals coprecipitation mechanisms are reported and discussed.

Chapter IV reports and discusses precious metals separation by dissolution of coprecipitates by HCl. In addition, coprecipitates are characterized for gold particles sizes and their catalytic properties.

Chapter V reports and discusses recovery of gold from computer CPU microprocessor scrap by coprecipitation methods. The characterization of computer CPU microprocessor scrap samples by SEM-EDX, XGT and ICP-AES is introduced. The results of recovery experiments are reported. Effectiveness of gold recovery as gold nanoparticles by coprecipitation technique is then discussed. Fundamental processes of gold recovery by coprecipitation with $Mn(OH)_2$ and Fe/Cu hydroxides are introduced.

Chapter VI summarizes the study. Implication of this research to recovery of precious metals from electronic wastes is introduced, and further study and investigation are recommended.

CHAPTER II

LITERATURE REVIEWS

2.1. Current uses of precious metals

2.1.1. Gold (Gold uses: Modern applications, Online)

Gold has been used by humans for thousands of years and the primary uses of this precious metal have not changed. Using gold as ornaments and jewelry and as the ultimate store of value are still the main uses of gold today. As technology advanced over the past decades, gold has found additional uses in areas such as electronics and medication but these new applications consume only a small proportion of gold mined every year.

Since prehistoric times, gold is primarily used to make ornaments. Until today, the biggest proportion of the annual production of gold is consumed by the jewelry industry. China and India are the two rising economic giants that will significantly alter the landscape of gold jewelry consumption. In both countries, gold has deep religious and cultural significance. For example, both Chinese and India marriage customs involve giving the bride gold jewelry such as gold bangles or necklaces.

Gold is accepted worldwide and is the real money that cannot be subjected to artificial devaluation. Money is functioned as a medium of exchange. Since the ideal money has to be easily identifiable, durable, stable and free from intrinsic price fluctuations, gold meets all of these criteria and is perhaps the only material in the world that does. Being the best form of money, gold is the traditional anti-inflation protection. In times of financial crisis, gold is the refuge of choice for those seeking a safe economic haven.

In electronic industries, gold plating is frequently used in electronic devices to give the anti-corrosive and conductive layer on copper in printed circuit boards and electrical connectors. Gold is not affected by air and most reagents, and is a very good conductor of heat and electricity. Heat, moisture, oxygen, and most corrosive agents have very little chemical effect on gold. This makes gold an excellent material for various electronic devices such as electrical switching mechanisms and plug contacts.

2.1.2. Platinum (Platinum precious metals uses, Online; and Platinum uses: Modern applications, Online)

Platinum is today the most valuable of precious metals because it is required in a number of industrial applications. It is estimated that one-fifth of everything we use either contains platinum or requires platinum in its manufactures. Among all the known modern uses of platinum, most of the annual production is consumed by two dominant categories: catalytic converters and fine jewelry. Together, these two applications consume more than 70% of the world's supply of platinum. The uses of platinum include medical apparatus (i.e. neurosurgery, drugs for cancer treatment, and dentistry) and computer equipments as well.

The best known use of platinum is in the catalytic converter (Figure 2.1), a part of the exhaust system in the automobile. Instead of spewing harmful gases such as carbon monoxide and nitric oxide into the atmosphere, autocatalyst converts these harmful emissions into harmless carbon dioxide and water. About half of newly mined platinum is used for this purpose. Increased concerns about environment protection has let to tougher emission standards being imposed by governments worldwide, which is further escalating the demand for platinum.

Moreover, platinum is now regarded as more prestigious than gold. Its rarity, hypoallergenic and tarnish resistant properties makes platinum the ideal choice for creating the finest of jewelry. Many diamond engagement rings are now fashioned out of platinum because its luster makes it far superior to gold in bringing out the brilliance of diamonds. As the color (or colorless) grading of diamonds affects its value, diamonds with lesser color grades tends to be slightly yellowish and much less expensive than colorless diamonds. So, unlike yellow gold, a platinum band is desirable for a diamond ring since it does not make the diamond look yellowish and less valuable. While rhodium-plated white gold may seem like a cheaper alternative to platinum, it needs to be replated every 12-18 months to retain its shine. Thus, platinum remains the metal of choice for the diamond engagement ring.

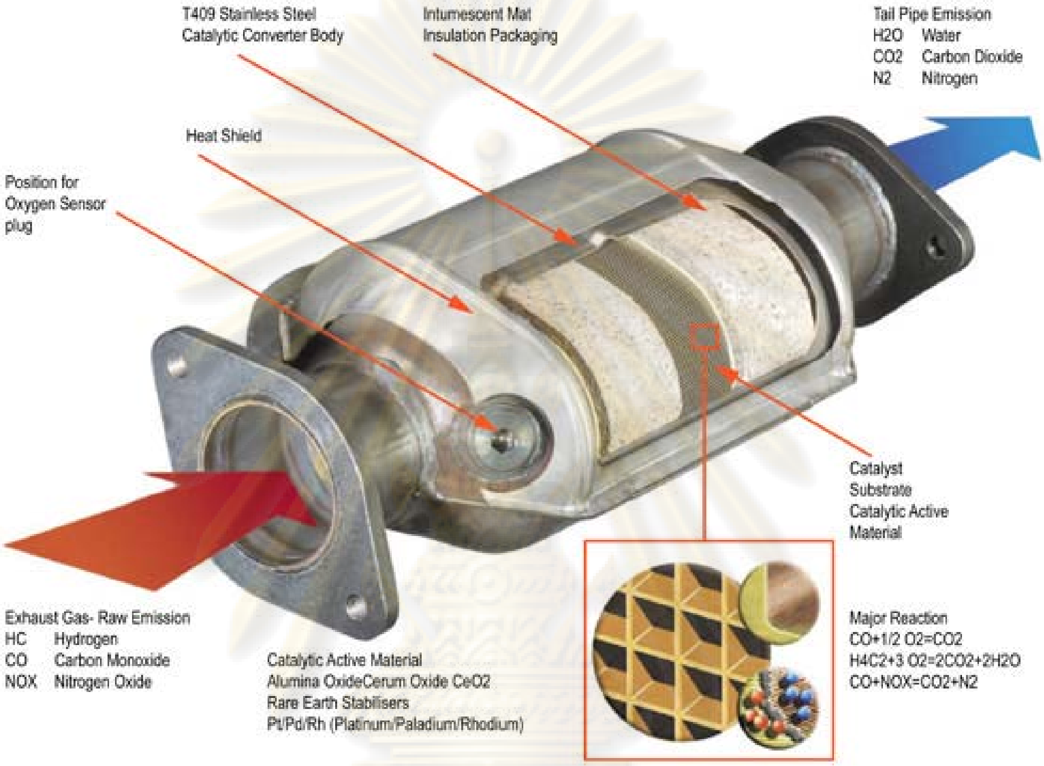


Figure 2.1 An automobile catalytic converter. Source: http://www.redbackmufflers.com.au

For catalytic functions, platinum catalyst is used in fuel cell as well. Fuel cells generate electrical power using hydrogen and oxygen as fuel. As they have no moving parts, a fuel cell generates power silently, emitting only pure water as a by-product. Hence, they do not contribute to either air or noise pollution and are a promising new breed of power source for the automobile industry. The most common type of fuel cell is the proton exchange membrane (PEM) fuel cell (Figure 2.2), which contains platinum catalysts. Besides being used to power automobiles, PEM fuel cells can also be used in power generation for buildings, instead of batteries or generators in portable equipment.

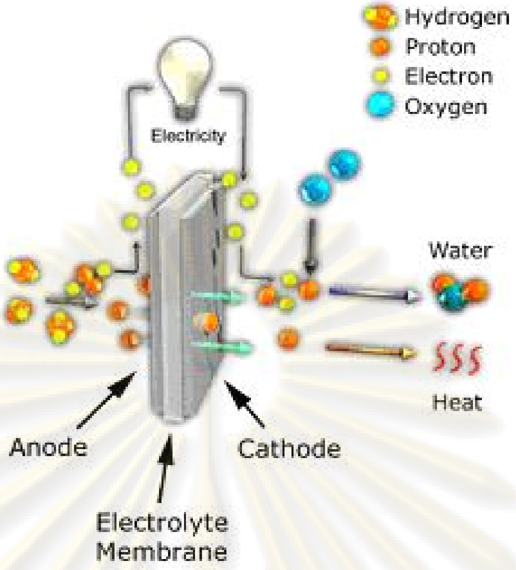


Figure 2.2 A proton exchange membrane (PEM) fuel cell.

Source: http://www.tkk.fi

In electronic industry, platinum is one of significant metals which are used in computer components. The hard drive is the component of the computer where data is stored. Each drive contains one or more platters or disks where data is stored on the magnetic surfaces. The amount of data that can be recorded on a given surface depends very much on the strength of the magnetic field generated by the surface layer. In 1957 when IBM first introduced the hard disk, storing just 5 megabytes of data require 50 disks, each measuring 24 inches in diameter. Sixty years later, a much smaller 3.5 inch disk drive is capable of storing over 500 gigabytes of data. An important process to achieving this remarkable increase in storage capacity is by adding platinum to the cobalt alloy to enhance its magnetic properties, allowing data to be stored at higher densities. With so much digital content being created (at higher and higher definitions) and then shared online by millions of people over high speed broadband internet, the strong demand for higher capacity disk drives has resulted in more platinum being used in the manufacture of hard disks to enhance their storage capacity. The proportion of platinum in the magnetic alloy has increased up from less than 10 percent in 2002 to 35 percent in 2007.

Beyond cleaning up the air, platinum’s excellent catalytic properties also extend to another important industry, the petroleum industry. Platinum mesh or gauze is used in cracking processes in oil refineries. Platinum catalysts play a critical role in extracting gasoline from crude oil and for making high octane fuels. However, platinum demand growth in this area can become static in the long run because of efficient platinum recycling processes built into the refineries.

2.1.3. Palladium (Palladium uses: Modern application, Online; and Stillwater palladium: Uses for palladium, Online)

As a member of PGMs, palladium exhibits many of the characteristics found in platinum, such as hardness, high melting point and excellent catalytic properties. As such, many of palladium's applications parallel that of platinum and palladium is often used as a lower cost alternative to its more famous sibling. Like platinum, palladium is used in pollution control, chemical processing and in electronics. Unlike platinum, its use in jewelry is mainly as a hardening agent in platinum alloy. Pure palladium is seldom seen in jewelry, despite efforts to promote the metal as a viable alternative to platinum. The proportions of palladium uses are as shown in Figure 2.3.

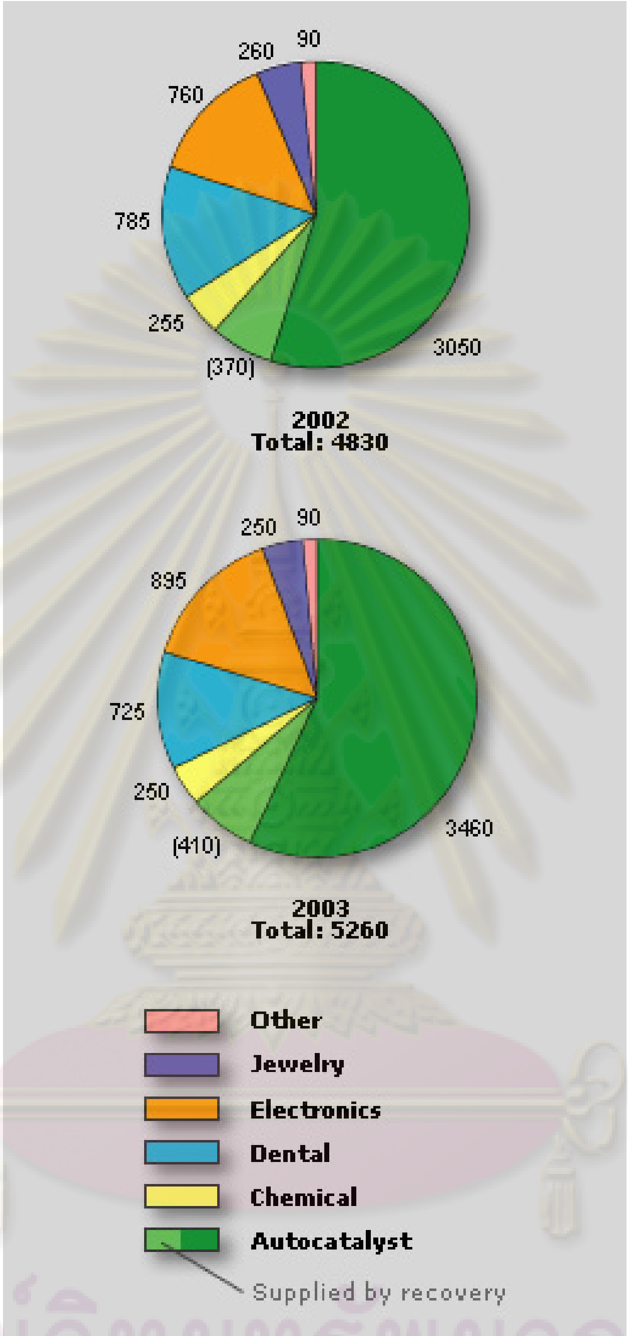


Figure 2.3 The proportions of palladium uses in 2002 and 2003 supplied by Johnson Matthey. Numbers indicate palladium consumption in thousands of ounces.

Source: http://www.stillwaterpalladium.com/uses.html

Softer than platinum, ductile and resistant to oxidation and high temperature corrosion, palladium is useful in eliminating harmful emissions produced by internal combustion engines. Autocatalysts are by far the largest user of palladium; autocatalysts convert over 90 percent of hydrocarbons, carbon monoxide and oxides of nitrogen produced in the exhaust from gasoline engines into carbon dioxide, nitrogen and water vapor.

Palladium has been used in a number of electronic applications. For example, palladium's chemical stability and electrical conductivity make it an effective and durable alternative to gold for plating in electronic components. Palladium-containing components are used in virtually every type of electronic devices, from basic consumer products to complex military hardware. Although each component contains only a fraction of a gram of metal, the sheer volume of units produced results in significant consumption of palladium. The largest area of palladium use in the electronics sector is in multi-layer ceramic (chip) capacitors (MLCC) (Figure 2.4). Smaller amounts of palladium are used in conductive tracks in hybrid integrated circuits (HIC) (Figure 2.5) and for plating connectors and lead frames.

For MLCC, capacitors are components that help to control the flow of an electric current through the various parts of a circuit by storing a charge of electricity until it is required. They consist of layers of conductive electrode material (usually palladium or palladium-silver) sandwiched between insulating ceramic wafers. In the early 1990s, MLCC manufacturers responded to the drive towards miniaturization of consumer goods by producing ever smaller capacitors using less palladium per unit. Soon afterwards came the development of technology to substitute palladium with nickel. This was not significant until 1997, when the increasing palladium price encouraged manufacturing of nickel-based capacitors on a much larger scale.

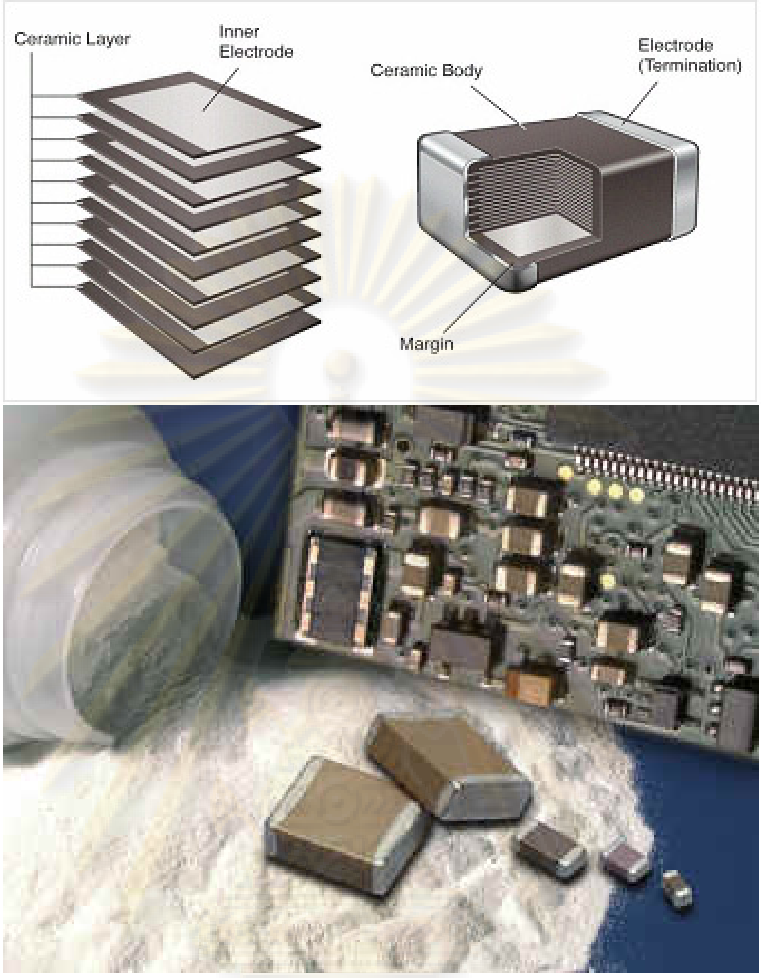


Figure 2.4 The multi-layer ceramic (chip) capacitors (MLCC). Sources: http://sem.samsung.co.kr and http://www.choe.cn

For HIC, a hybrid integrated circuit consists of a ceramic substrate on which are mounted a number of different electronic components, including integrated circuits and capacitors. They are linked by conductive silver-palladium tracks. The function of the palladium is to hold the silver in place, without which it would migrate. The automotive industry is the largest market for HIC.

Figure 2.5 The hybrid integrated circuits (HIC). Source: http://parts.digikey.com/1/parts/487849-ic-mpu-hybrid-dsp-32k-64-lqfp-mc56f8323vfbe.html

Components inside computers are linked by connectors plated with a conductive layer of precious metal. Palladium is used as an alternative plating material to gold for connectors as it has a lower density and so less weight of metal is required for a coating of similar thickness. Lead frames are used to connect integrated circuits to other electronic devices. Some manufacturers use palladium to plate the frames as an environmentally preferable alternative to tin-lead solder.

Moreover, palladium is an important part of the refining of nitric acid, and has important uses in developing raw materials for synthetic rubber and nylon. With the fall in palladium prices and the rise in platinum prices palladium's cost-effectiveness in chemical applications has become apparent. Various chemical applications use palladium, including the manufacture of paints, adhesives, fibers and coatings. Palladium is used in the production of purified terephthalic acid, which is a precursor to polyesters and to polyethylene terephthalate a plastic resin used in packaging of film and glass laminates. PGM catalysts for nitric acid production take the form of a gauze made out of fine wire. Palladium is used in the production of catchment gauze used in the making of nitric acid for the manufacture of nitrogen fertilizers. When nitric acid was first produced commercially in 1904, a platinum-only catalyst was used. Rhodium was later added for strength and to reduce the amount of platinum lost during conversion of the gas. Palladium-based "catchment" or "getter" gauze was introduced in 1968 to further reduce losses of platinum and rhodium, which can be as high as 300 mg per ton of acid produced. The catchment sits downstream of the gas flow and collects pgm vaporized from the catalyst. Ethanol is produced using palladium catalysts through the "Wacker Process". This process manufactures ethanol by oxidizing ethane, yielding 95% acetaldehyde which is converted to the ethanol. The process has good economics due to the abundance of ethylene. The reaction is catalyzed by $PdCl_2$ and $CuCl_2$. It involves the reaction of ethylene with palladium chloride in water. Palladium is thereby reduced to palladium black. To make the reaction catalytic, palladium is reoxidized by reaction with copper chloride and oxygen. The process is run in one vessel at slightly elevated temperatures and pressures (50-130 °C and 3-10 atm).

Furthermore, similar to platinum, palladium is used in fuel cells, oil refining, medication and jewelry. Also, palladium is used in manufacture of polyester, hydrogen purification, and water treatment.

Palladium-based alloys are actively being researched for applications in fuel cell technology, an area of future promise for the metal. Palladium and other PGM metals serve important functions in catalytic reactions that are used in various stages in the refining of petroleum. Palladium-103, a radioactive isotope of palladium, is seeing promising applications in the treatment of prostate cancer. A newly emerging added area of research is potential use in the treatment of breast cancer. Palladium-based alloys are used in dentistry for dental crowns and bridges. And palladium metal is also compatible with human tissue and is used, in a radioactive form, in the medical industry for the treatment of cancer. For jewelry, palladium is lighter than platinum having about the same density as silver, thus, palladium is a jewelry metal as well. Palladium in jewelry is primarily used as an alloy with platinum to optimize platinum's working characteristics and wear properties. Palladium is also used as an alloy in producing white gold.

Palladium is a unique and important catalyst being studied for use in removing a number of toxic and carcinogenic substances from groundwater. Palladium's ability to absorb and desorbed hydrogen depending on circumstances allows it to be an effective material to filter hydrogen from other gasses resulting in an ultra pure hydrogen gas.

2.2. Metallurgical process for precious metals recovery (State-of-the-art)

Precious metals recovery processes which have been academically developed can be categorized into three types based on metallurgical methods.

The pyrometallurgical recovery process involves refining, melting and smelting. The pyrometallurgical method is applied to recover the precious metals as bulk materials, either elements or compounds. An example of gold recovery by pyrometallurgical process is extraction of gold by chlorination (Ojeda et al., 2008). Gold presented in alluvial material was recovered by means of a chlorination process using chlorine as a reactive agent. The alluvial material contained gold was concentrated to remove the less dense material and to separate magnetite. By chlorination at 873K, gold was extracted as a binary complex of $AuCl_3.FeCl_3$ in gaseous phase due to the presence of Fe_2O_3.

Another precious metals recovery by pyrometallurgical process is combination of the recovery process to copper refining process (e.g., Toyo Smelter & Refinery, Online), which is nowadays popular in recovery of precious metals from electronic wastes. After preprocessing of gold containing wastes such as crushing or combustion, the processed material is introduced to flash furnace and the following copper refining process. In the process, crude copper is experienced electrowinning refining to produce pure copper and remain slime highly concentrating precious metals in anode mud. From the mud, precious metals are extracted by the following hydrometallurgical process. Advantage of using copper smelting process is to allow us to save any separation process and initial costs for obtaining concentrate of precious metals. On the other hand, copper smelting plant is not ubiquitous.

The hydrometallurgical recovery process involves precipitation, adsorption, cementation, solvent extraction and ion exchange. Each process has both merit and demerit. For example, solvent extraction can recover precious metals from even much diluted solution however; it requires much safety precaution as well. Adsorption often can save initial costs but include adsorption capacity problem or separation (refining) after adsorption problem. By a hydrometallurgical method, precious metals are recovered from solutions as metal powder, either elements or compounds.

The widely accepted process for recover gold is aqua regia leaching, cyaniding, and thiourea process then, applying cementation to reduce gold by zinc powder or hydrazine. An example is a study on selective extraction of Pd(II) over Au(III) and Pt (IV) by Shen and Xue (2007). The Pd(II) was extracted into organic phase, while the Au(III) and Pt(IV) were separated from HCl solution by using 2-hydroxy-4-sec-octanoyl diphenyl-ketoxime diluted in kerosene as an extractant. Each metal was reduced to metal powder and precipitated from the solutions.

The electrometallurgical recovery process involves electrowinning and electrolysis. Usually, an electrometallurgical method is applied subsequent to hydrometallurgical process such as leaching. Precious metals ions are recovered as elements by electrons transfer due to the applied current intensity and various types of cathodes. Mostly, this method is applied to the precious metals purification. An example of this process is gold electrowinning from aqueous–alcoholic thiourea solutions (Urbanski et al., 2000). Gold was recovered by electrowinning from acidic thiourea solutions containing alcohol admixture which was obtained by gold elution from activated carbon in the processing of gold-bearing raw materials. A high gold recovery (96%–100%) was obtained at elevated temperature of 60°C using a platinum mesh cathode. In general, electrometallurgical process costs high, but it is very effective recovery method from much lower concentration of precious metals.

2.3. Coprecipitation of precious metals with metal hydroxides

Coprecipitation of precious metals with metal hydroxides can spontaneously or naturally proceed at ambient temperature in which energy provision is unnecessary. The examples of research which introduced precious metals separation by coprecipitation with other metal compound carriers are as follow.

Yokoyama et al. (2001) reported the coprecipitation of Au (III) with aluminum hydroxide followed with spontaneous reduction to Au (0) on the surface of aluminum hydroxide without any addition of specific reducing agents. The presence of Au metallic particles was confirmed by XRD patterns. They deduced that reduction of

Au (III) to Au (0) is caused by the formation of Al-O-Au bond and its distortion of the coordination structure.

Uchida et al. (2002) reported that Au (III) was more effectively coprecipitated by ferric hydroxide than by aluminum hydroxide; however, the reduction mechanisms of Au (III) on the surface of Fe (III) hydroxide and Al hydroxide are the same as suggested by Yokoyama et al. (2001). Their interpretation is actually based on the geochemistry of gold concentration in nature.

Ohashi et al. (2005) reported that Au (III) was well-adsorbed on manganese dioxide, when compared with other metal oxides such as alumina, and then the adsorbed gold is spontaneously reduced to Au(0).

Kitamoto et al. (2007) focused well on practical recovery of gold from e-waste and reported that gold was effectively recovered by coprecipitation with cupric and ferric hydroxides from cellular phones. As Uchida et al. (2002) studied, ferric hydroxide could be good gold coprecipitation career. In this study, cupric and ferric ions primary contained in cellular phone were directly used for recovery of gold.

Parinayok et al. (2007) reported the results of platinum coprecipitation with various metal hydroxides: Al, Mg, Fe (III), and Fe (II) hydroxides. The most preferable coprecipitation carriers for platinum as mentioned in the study were both Fe (II) and Fe (III) hydroxides. Nevertheless, it is found that a part of reduction of Pt (IV) to Pt (0) only occurred by coprecipitation with Fe (II) hydroxide.

Yamashita et al. (2008) studied the formation of precursor of gold-supported manganese dioxide (MnO_2) in the preparation process of gold-supported MnO_2 catalyst of CO oxidation at low temperature. The precursor of gold-supported MnO_2 is manganese(II) hydroxide ($Mn(OH)_2$) coprecipitating Au(III) complex ions. The chemical state of gold $[AuCl_{4-n}(OH)_n]^-$ (n = 0–4) coprecipitated with $Mn(OH)_2$ was examined by Mössbauer spectroscopy. The study suggested that the amount of coprecipitated Au(III) complex ions increase linearly in Au:Mn atomic ratio range of 0.05-0.8 (14-70 %Wt. of Au). When Au:Mn atomic ratio was below 6:10, all Au(III) complex ions in the coprecipitates with %Wt. Au of 14, 30 and 60 were reduced to Au(0). But when Au:Mn atomic ratio was above 6:10, both Au(III) complex ions and Au(0) were present in the coprecipitates in which Au(III):Mn atomic ratio increased with increasing Au Wt.%. Moreover, the study indicated that Au(III) complex ions were reduced to Au(0) only when $Mn(OH)_2$ was precipitated. Mn(II) in $Mn(OH)_2$ was oxidized to Mn(IV) in conjunction with coprecipitation of $[AuCl_{4-n}(OH)_n]^-$ complex ions. Finally, it was concluded regarding previous researched (Yokoyama et al., 2001 and Uchida et al., 2002) and study by Yamashita et al. (2008) that the stoichiometric reduction of Au(III) to Au(0) as the formation of precursor of gold-supported MnO_2 was rapidly occurred due to electron transfer from Mn(II) ion in $Mn(OH)_2$ to Au(III) complex ion through Mn-O-Au bonds.

2.4. Personal computer CPU microprocessor

A major part of personal computer having precious metal constituents is motherboard. CPU microprocessor is one of motherboard components, which possibly contains precious metals such as gold. Although metal recovery from computers, especially computer printed circuit board, has been worldwide studied, recovery of valuable materials from microprocessors has not been yet well developed. Due to the presence of precious metals, recovery of precious metals from the CPU microprocessors can be beneficial.

A microprocessor is connected to motherboard via slot or socket. It thus works as computer processing unit (CPU). Typical assembly of a motherboard and a location of CPU microprocessor socket is shown in Figure 2.6.

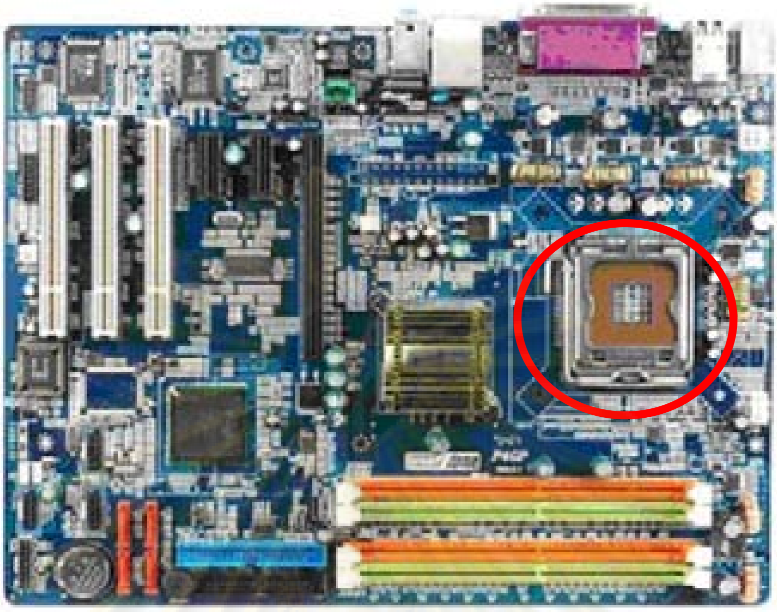


Figure 2.6 Assembly of 915G Motherboard 0119. “The location of CPU microprocessor socket is circled.” Source: http://www.lakewoodconferences.com/catalog/96/528/194925/sell_915g_motherboard_0119.html

The motherboard mainly consists of 1) chipsets; 2) computer processing unit (CPU) or microprocessor; 3) printed circuit board (PCB); 4) slots, sockets and connectors; 5) heat sink; 6) other peripheral components such as battery and capacitors.

Generally, there are two major groups of CPU widely used, based on how the processor is placed on motherboard (Sutherland Global Services, [n.d.]). One is socket type which mostly has various grid array structures. Another is slot type. Figure 2.7 shows the typical microprocessors recently found in the rejected computer yards.

The pin arrangement in the socket processors mostly found in the obsolete computers recently is known as *Pin Grid Array* (PGA). Apart from this, there are other grid array processors namely LGA (*Land Grid Array*), PPGA *(Plastic Pin Grid Array)* and OOI or “OLGA” (*Land Grid Array*) (Processors - Package Type Guide, Online).

The slot type processor consists of *Single Edge Processor (SEP)* and *Single Edged Contact Cartridge* (SECC). To connect to the motherboard, the processor is inserted into a slot. Instead of having pins, it uses goldfinger contacts, which the processor uses to carry its signals back and forth. Inside the S.E.C.C., most processors have a printed circuit board called the substrate that links together the processor.

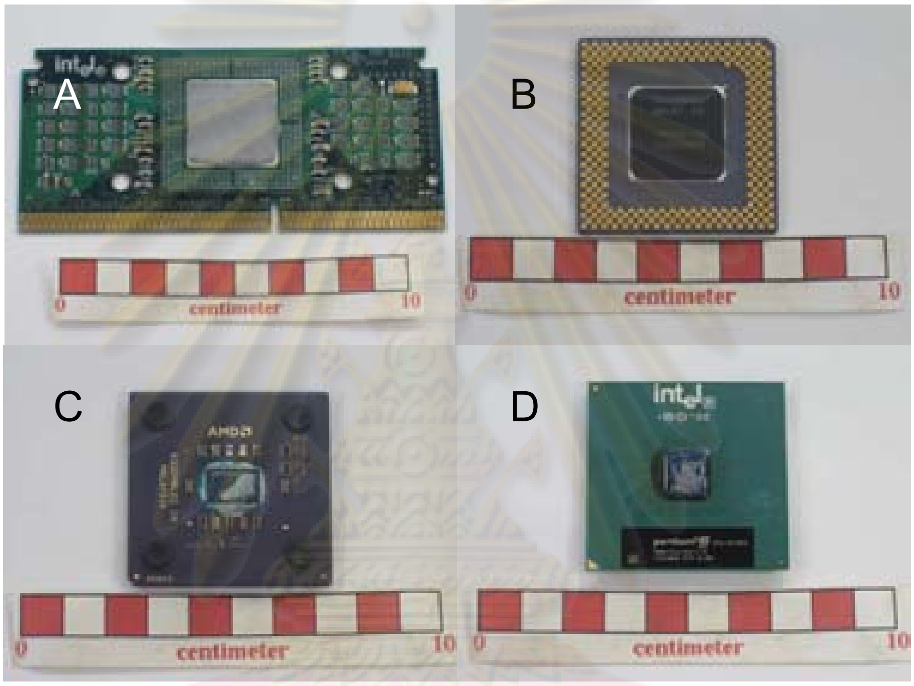


Figure 2.7 Typical microprocessors where (A) is SECC; (B) and (C) are PGA which their bodies are made of ceramic-like materials; and (D) is PGA which its body are made of plastic-like material.

Apparently, there are several kinds of CPUs; however, the study emphasizes on only PGA processors. The PGA microprocessor has three main components: (1) microprocessor body which is mainly made of plastic or ceramic-like materials; (2) pins which are inserted into a socket on motherboard when the CPU is used; (3) package, made of very strong materials (e.g., aluminum silicon carbide (AlSiC) composites, covering the important operating parts (i.e. silicon chip or “die” and bonding wires). Figure 2.8 illustrates components of a microprocessor sample. Precious metals are included in microprocessors as coating material or bonding wires or metal composite (Intel, 2000; and Integrated Circuit Engineering, (n.d.)).

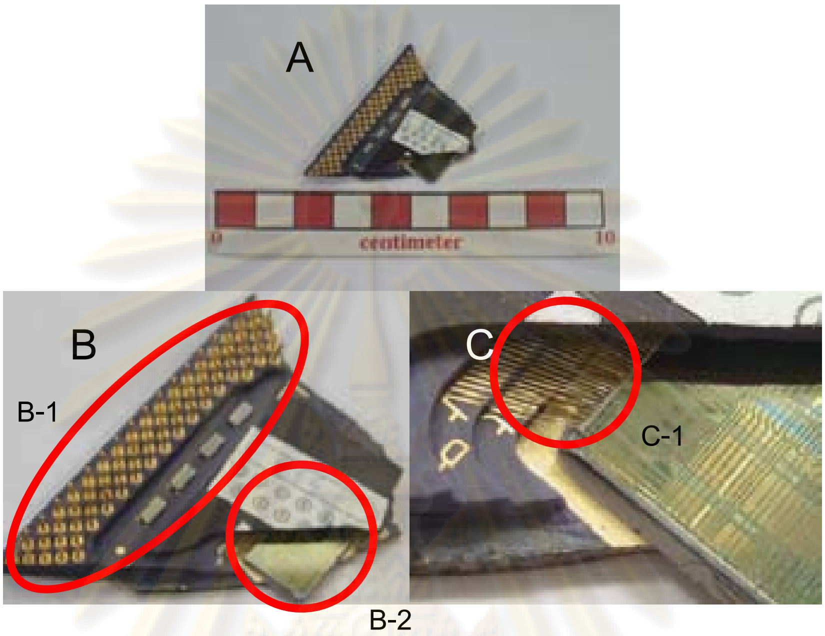


Figure 2.8 Images of a package-opened PGA microprocessor sample, (A); zoom images of the microprocessor sample, (B) and (C) in which pins (B-1), bonding wires (C-1) and die (B-2) are circled.

In this study, to focus only on recovery of metals, the ceramic PGA microprocessor is selected as the experimental sample to avoid the chemical reaction between other leachable parts on CPU and reagents. The ceramic PGA microprocessor samples were randomly collected from personal computer scraps.

CHAPTER III

COPRECIPITATION OF PRECIOUS METALS WITH MANGANESE HYDROXIDE

3.1. Introduction

3.1.1. Background

In chemistry, coprecipitation (CPT) or co-precipitation is the carrying down by a precipitate of substances normally soluble under the conditions employed. Coprecipitation is an important issue in chemical analysis in which it is often undesirable, but in some cases it can be exploited. On the other hand, in the analysis of trace elements, as is often the case in radiochemistry, coprecipitation is often the only way of separating an element. Since the trace element is too dilute (sometimes less than a part per trillion) to precipitate by conventional means, it is typically coprecipitated with *a carrier*, a substance that has a similar crystalline structure that can incorporate the desired element (Coprecipitation, Online).

There are generally three main mechanisms of coprecipitation: (1) inclusion (so-called mechanical entrapment: the process of random incorporation of comparatively small quantity of other phases such as water, dust, and particles in the bulk of a precipitate during its formation) (IUPAC Gold Book- mechanical entrapment, Online), (2) occlusion, and (3) adsorption. An inclusion occurs when the impurity occupies a lattice site in the crystal structure of the carrier, resulting in a crystallographic defect. This can happen when the ionic radius and charge of the impurity are similar to those of the carrier. An adsorbate is an impurity that is weakly bound (adsorbed) to the surface of the precipitate. An occlusion occurs when an adsorbed impurity gets physically trapped inside the crystal as it grows.

Besides applications of coprecipitation in chemical analysis and in radiochemistry, coprecipitation is also "potentially important to many environmental issues closely related to water resources, including acid mine drainage, radionuclide migration in fouled waste repositories, metal contaminant transport at industrial and defense sites, metal concentrations in aquatic systems, and wastewater treatment technology" (Zhu et al., 2003).

Since the coprecipitation can be applied for trace element analysis, it is expected to be applicable for recovery of trace-amounted precious metals from, for instance, aqueous solution of electronic wastes. For implication of the precious metals recovery, modeling experiments were performed in order to demonstrate effective recovery procedures and conditions. The modeling experiments were subsequently either applied or implied to practical precious metals recovery processing. In general, there are various metal components in electronic wastes, but the precious metals content is seemingly low. Therefore, the prospective recovery procedures should selectively separate trace-amounted precious metals from the complicated mixtures in electronic wastes.

To concentrate or separate precious metals from the sources with their low and complicated content, hydrometallurgical method is substantially considered to be one of the most effective ways because it possibly offers selectively-recovered product with minimum loss of the target elements. Coprecipitation is commonly known as one of the spontaneous hydrometallurgical methods to separate small-amounted metals as implied in many researches (e.g., Yokoyama et al., 2001; Uchida et al., 2002; Yonezu et al., 2006; Kitamoto et al., 2007; Parinayok et al., 2007; and Yamashita et al., 2008). In this study, coprecipitation of precious metals with $Mn(OH)_2$ was mainly focused due to its spontaneity and environmental friendliness according to precious metals concentration in marine manganese nodules in nature.

Manganese was found composed in marine manganese nodules in ocean, which is proved to be an effective substrate for many rare metals such as cobalt, molybdenum, tungsten, gold and PGMs. As predicted in previous studies that there is a possibility that those of metals probably concentrated in manganese nodules by coprecipitation with $Mn(OH)_2$ (Halbach et al, 1984; Halbach et al., 1989; and Jacinto and Van den berg, 1989), $Mn(OH)_2$ can be not only a good coprecipitation carrier but also selector during the coprecipitation or the subsequent processes. In addition, each metal has its own concentration behavior onto manganese nodules due to its particular properties. Therefore, concentration process of metals by coprecipitation with $Mn(OH)_2$ can be considered selective.

Generally, electronic wastes contain more than one precious metal. Thus, a technique which can recover several precious metals at the same time will be considered advantageous. In previous work, the coprecipitation has been developed to be a technique for recovery of single trace-amounted target metal. However, application of the coprecipitation technique as a selective separation method for multiple target metals to recover precious metals from electronic wastes is still ambiguous. Moreover, it is hypothesized that selective separation of multiple metals by coprecipitation with $Mn(OH)_2$ is possible according to natural concentration of metals onto marine manganese nodules. Therefore, in this chapter, recovery of two target precious metals (i.e. Au with Pt or Pd) by coprecipitation with $Mn(OH)_2$ was investigated emphasizing effectiveness of the method and changes in valence states of Au, Pt, and Pd in the coprecipitates.

3.1.2. Principles

The common coprecipitation reaction is the formation of at least two insoluble products or coprecipitates due to the changed conditions such as pH or temperature (Chang, 2002). In this study, it is expected that precious metals will be coprecipitated with the precipitation of $Mn(OH)_2$ to either elements or uncomplicated compounds. In the other words, $Mn(OH)_2$ is considered as a main coprecipitation carrier for recovery of precious metals

To demonstrate modeling experiments of precious metals recovery from electronic wastes, the experimental conditions are significant. Most precious metals are extracted from electronic wastes by strong leaching agents such as aqua regia and other strong acid before recovery process (e.g., Diamantatos, 1977; Oh et al., 2003; and Sheng and Etsell, 2007). In a strong acid solution with high chloride concentration (e.g., aqua regia), precious metals like gold, platinum, palladium, and also manganese are dissolved and some formed their stable chloride complex ions like $[AuCl_4]^-$ and $[PtCl_6]^{2-}$. Hence, gold, platinum, palladium, and manganese are in forms of $[AuCl_4]^-$; $[PtCl_6]^{2-}$; $[PdCl_4]^{2-}$; and Mn^{2+} before coprecipitation. Because NaOH solution is used for pH adjustment in all experiments, Na^+ and Cl^- ions are considerably presented in the experimental systems. Also, a constant concentration of electrolyte contributes to keeping the surface charge of manganese precipitate constant as well. Therefore, NaCl is added in initial solutions in order that the system will have high NaCl concentrations and the effect of formation of NaCl due to pH adjustment is negligible.

In case of gold in strong acid solution which include chloride, $[AuCl_4]^-$ complex ion is stable. However, hydrolysis of the $[AuCl_4]^-$ complex ion is continuously occurred as pH increasing, and gives sequential gold complexes in chloro-hydroxy forms (Murphy and LaGrange, 1998). The chloride ions are stepwise replaced by hydroxyl group as expressed in a general formula of $[AuCl_n(OH)_{4-n}]^-$, the new form of which depends on pH and chloride concentration. The behavior of $[AuCl_4]^-$ hydrolysis, which continuously changed, can be summarized in general equation shown below (Baes and Mesmer, 1976).

$$[AuCl_4]^- + n\ OH^- \Leftrightarrow [AuCl_{4-n}(OH)_n]^- + n\ Cl^-\ (n= 0\text{-}4) \qquad (1)$$

In the formation of gold coprecipitate with $Mn(OH)_2$ as a precursor of gold-supported MnO_2 (Yamashita et al., 2008), it is considered that Au(III) of $[AuCl_4]^-$ is rapidly reduced to Au(0) when coprecipitated with $Mn(OH)_2$. It is believed that the rapid stoichiometric reduction of Au(III) to Au(0) is caused by electron transfer from Mn(II) of $Mn(OH)_2$ to Au(III) complex ion through an Mn–O–Au bond, in which $Mn(OH)_2$ is oxidized to MnO_2 as shown below.

$$[AuCl_n(OH)_{4-n}]^- + 3e^- \rightarrow Au + n\ Cl^- + (4-n)\ OH^-\ (n= 0\text{-}4) \qquad (2)$$

$$Mn(OH)_2 + 2OH^- \rightarrow MnO_2 + 2H_2O + 2e^- \qquad (3)$$

$$3Mn(OH)_2 + 2[AuCl_n(OH)_{4-n}]^- \rightarrow 3MnO_2 + 2Au(0) + 6H_2O + 2nCl^- + (2- 2n)OH^- \qquad (4)$$

In case of platinum and palladium, as implied from the uptake mechanisms of platinum and palladium by iron and manganese oxide and hydroxide (Yamashita, 2007), Pt(IV) and Pd(II) ions coprecipitated with $Mn(OH)_2$ in the form of Pt(IV), Pt(II) and Pd(II), respectively. It is also considered that some adsorbed Pt(II) were oxidized to Pt(IV) on MnO_2, which was immediately oxidized to $Mn(OH)_2$ by dissolved oxygen in water. The reactions are shown below.

$$[PtCl_6]^{2-} + 2e^- \rightarrow 2Cl^- + [PtCl_4]^{2-} \qquad (5)$$

$$Mn^{2+} + 2H_2O \rightarrow MnO_2 + 4H^+ + 4e^- \qquad (6)$$

According to the calculation of standard redox potential (E^0) and standard Gibbs free energy (ΔG^0), oxidation of aqueous Pt(II) by δ-MnO_2 is a spontaneous process for species in their standard states. In case of palladium, the Pd(II) would be oxidized as well. However, its ΔG^0 indicates that oxidation of aqueous Pd(II) by δ-MnO_2 is not spontaneous. Regarding the existing of both Pt(IV), it was hypothesized that some of Pt(II) were uptaken by the isomorphous replacement between Pt(II) and Mn(IV). Palladium is not oxidized and concentrated on MnO_2 due to its different uptaking model.

3.1.3. Objectives

In this chapter, coprecipitation behaviors of Au, Pt and Pd with $Mn(OH)_2$ were described. Precipitation of $Mn(OH)_2$ was observed to attain an optimum pH to apply in coprecipitation of precious metals. Effects of reaction time and initial precious metals concentrations on the coprecipitation were examined. Effectiveness of the coprecipitation technique for recovery of precious metals was reported emphasizing recovery percentage, selectivity, and changes in valance states of precious metals.

3.2. Materials

3.2.1. Reagents

1. Manganese(II) chloride tetrahydrate ($MnCl_2.4H_2O$) analytical grade (Wako Pure Chemicals)
2. Tetrachloroauric acid ($HAuCl_4$) standard solution for atomic absorption spectrometry (AAS) (1000 mg dm^{-3} Au in 1 mol dm^{-3} hydrochloric acid) (Wako Pure Chemicals)
3. Hexachloroplatinic acid (H_2PtCl_6) standard solution for atomic absorption spectrometry (AAS) (1000 mg dm^{-3} Pt in 1 mol dm^{-3} hydrochloric acid) (Wako Pure Chemicals)
4. Palladium(II) chloride ($PdCl_2$) standard solution for atomic absorption spectrometry (AAS) (1000 mg dm^{-3} Pd in 1 mol dm^{-3} hydrochloric acid) (Wako Pure Chemicals)
5. Hydrochloric acid (HCl) analytical grade (Wako Pure Chemicals)
6. Sodium chloride (NaCl) analytical grade (Wako Pure Chemicals)
7. Manganese dioxide (MnO_2) powder ($203 m^2 g^{-1}$, CMD-200) supplied from Chuo Denki Kogyo Co., Ltd.
8. Sodium hydroxide (NaOH) analytical grade (Wako Pure Chemicals)
9. Ultra pure water

3.2.2. Instruments and equipments

1. Glass volumetric flasks
2. Glass beakers
3. Glass pipettes
4. Glass droppers
5. Magnetic stirrers
6. Horiba F-21 and D-52 pH meters
7. Vacuum filtration system with pumping speed of 5/6 $dm^3 min^{-1}$ and ultimate pressure of 24.0 kPa

8. Adventec 0.45 μm 47mm membrane filters
9. Nippon Jarrell Ash AA-835 flame atomic absorption spectrophotometer (AAS)
10. Seiko and Varian Instruments VISTA- MPX CCD Simultaneous Inductively coupled plasma- atomic emission spectrometer (ICP-AES)
11. Shimadzu KRATOS AXIS-165 X-ray photoelectron spectroscope (XPS)

3.3. Experimental procedures

3.3.1. Precipitation of $Mn(OH)_2$

Mn(II) stock solution was prepared by dissolving manganese(II) chloride tetrahydrate ($MnCl_2.4H_2O$) in 0.1 mol dm^{-3} hydrochloric acid. NaCl was dissolved to solution and prepared to 1 mg dm^{-3}. A 500 cm^3 Mn(II) (0.005 mol dm^{-3}) sample solution containing 0.12 mol dm^{-3} NaCl was prepared just before the precipitation experiment. An original pH of sample solution was measured. Then, the sample solution was gradually adjusted to pH 4, 5, 6, 7, 8, 9, and 10 respectively, by dropping NaOH solution. The time interval for maintaining each pH was 1 hour. 5 cm^3 aliquots were taken at each ends of time interval. Every aliquot were filtered to get their filtrates for Mn(II) concentration measurement. All solutions were prepared with ultra pure water. All experiments carried out at ambient temperature. Manganese dioxide powder (203m^2g^{-1}, CMD-200) as a standard material for X-ray photoelectron spectroscopy (XPS) was supplied from Chuo Denki Kogyo co., ltd.

3.3.2. Coprecipitation of precious metals with $Mn(OH)_2$

The stock solutions of Au(III), Pt(IV) and Pd(II) complexes were prepared from standard solutions of tetrachloroauric acid ($HAuCl_4$), hexachloroplatinic acid (H_2PtCl_6), and palladium(II) chloride ($PdCl_2$)solution for atomic absorption spectrometry (AAS) (1000 mg dm^{-3} as Au, Pt and Pd, respectively in 1 mol dm^{-3} hydrochloric acid). Coprecipitation experiments divided into five systems according to combination of precious metals (Table 3.1).

Table 3.1 Five systems of coprecipitation experiments divided according to the precious metal combination

Experimental Systems	Combination of initial metal ions in sample solutions			
	Mn(II) 0.005 mol dm^{-3}	Au(III) 5, 50, or 100 mg dm^{-3}	Pt(IV) 5, 50, or 100 mg dm^{-3}	Pd(II) 5, 50, or 100 mg dm^{-3}
(I) Au	✓	✓	✗	✗
(II) Pt	✓	✗	✓	✗
(III) Au-Pt	✓	✓	✓	✗
(IV) Pd	✓	✗	✗	✓
(V) Au-Pd	✓	✓	✗	✓

Each sample solution (500 cm^{3}) containing Mn (0.005 mol dm^{-3}), Au (5 5, 50 and 100 mg dm^{-3}), and/or Pt (5, 50 and 100 mg dm^{-3}), and/or Pd (5, 50 and 100 mg dm^{-3}) was prepared just immediately before each batch experiment. NaCl solution was also added in sample solutions for ionic strength adjustment. All solutions were prepared with ultra pure water.

The solutions were adjusted and maintained at pH 9±0.1 by dropping NaOH solution to form $Mn(OH)_2$. All experiments were carried out at ambient temperature with magnetic stirring. At the designated time, aliquots were taken from the suspension, and filtered by 0.45 μm membrane filter to estimate the amount of gold, platinum and palladium coprecipitated with $Mn(OH)_2$. Au, Pt and Pd concentrations in filtrates were measured by AAS and ICP-AES. After 24 hours, the suspended solutions were filtered to collect solid sample for characterization by XPS as described later.

In addition, effects of Pt:Mn initial mole ratio and Au:Pt:Mn initial mole ratio on coprecipitation of platinum were examined. Experiments to determine effect of Pt:Mn initial mole ratio was carried out by varying Mn(II) chloride initial concentrations (0.001, 0.005 and 0.1 mol dm^{-3}). Experiments to determine effect of Au:Pt:Mn initial mole ratio was conducted by varying Au:Pt initial mole ratio (1:1; 1:2; 1:4 and 1:6) in which the initial concentration of $MnCl_2$ was maintained at 0.005 mol dm^{-3}. Consequently, the optimum Au:Pt:Mn ratio giving yield percentage of coprecipitated gold and platinum was introduced.

3.4. Analytical methods

3.4.1. Atomic absorption spectrometry (AAS) and inductively coupled plasma-atomic emission spectrometry (ICP-AES)

The concentration of gold, platinum, palladium and manganese in filtrate were determined by Nippon Jarrell Ash AA-835 flame atomic absorption spectrophotometer (AAS) and Seiko and Varian VISTA- MPX CCD Simultaneous Instruments inductively coupled plasma- atomic emission spectrometer (ICP-AES).

3.4.2. X-ray photoelectron spectrometry (XPS)

All residues and coprecipitates were dried for at least 24 hours. The valence state of gold, platinum, palladium and manganese was examined by XPS (Shimadzu KRATOS AXIS-165). Powder sample of the coprecipitates were adhered to the carbon tape, and placed in an evacuated chamber (10^{-10} Torr). The XPS spectra were acquired using a monochromatic Al K_α X-ray source (1,486.94 eV) operated at 30 W (15 kV, 2 mA). In all cases, the photoelectron takeoff angle was 45°. The XPS spectra were acquired for C1s, Mn2p, Au4f, Pt4f and Pd3d using pass energy equal to 40 eV. The XPS spectra were collected internally using C1s (284.6 eV) because of the peak shift due to sample charging. The spectra were acquired by a 0.1 eV step and 298 ms point^{-1}. Shirley method was applied to correct the background of all spectra. Curve fitting was subsequently achieved by XPSPEAK 4.1.

3.5. Results and discussion

3.5.1. Precipitation of $Mn(OH)_2$

Manganese(II) ions started to partly precipitated at pH 7, and abruptly completely precipitated to $Mn(OH)_2$ from pH 9. Figure 3.1 shows the precipitation percentage of $Mn(OH)_2$ at each increasing pH. The range of precipitation pH of $Mn(OH)_2$ in the experiment corresponds with that of $Mn(OH)_2$ theoretically indicated in Monhemius (1977) (Figure 3.2). Therefore, all following coprecipitation experiments in this chapter will be conducted at pH 9 at ambient temperature.

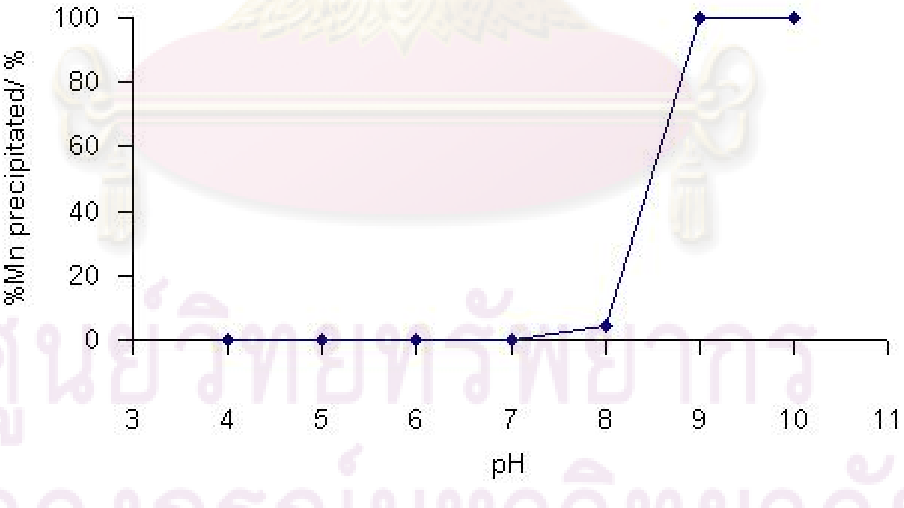


Figure 3.1 Effect of pH on precipitation of $Mn(OH)_2$. Reaction time interval: 1 hour. Volume: 500 cm^3. Initial Mn concentration: 0.005 mol dm^{-3} (274.7 mg dm^{-3}).

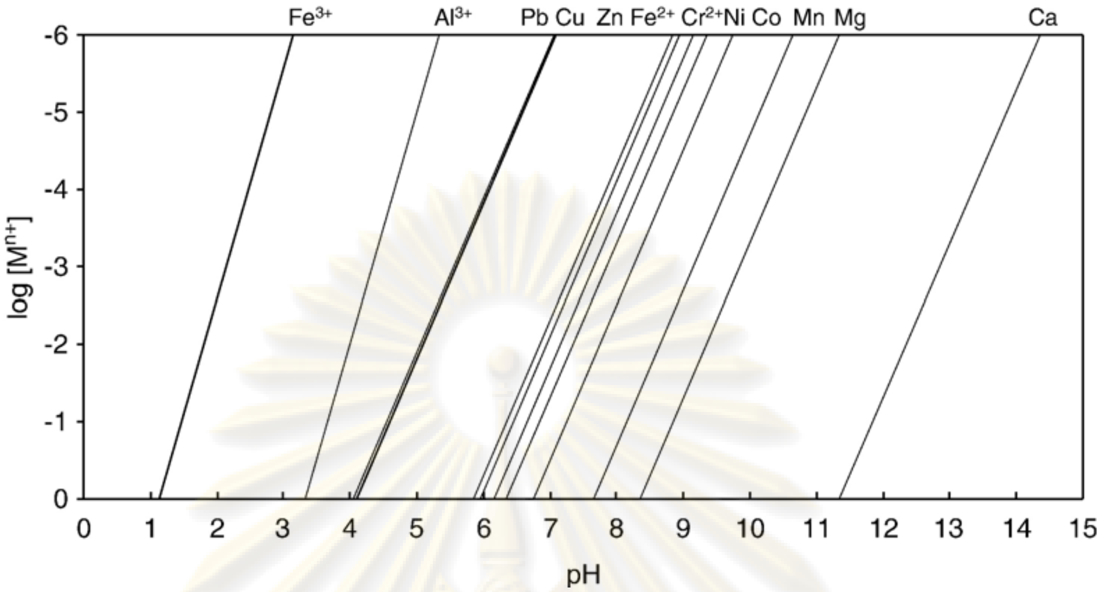


Figure 3.2 A solubility diagram of metal hydroxides at 25°C (Monhemius, 1977 cited in Zhang and Cheng, 2007).

3.5.2. Coprecipitation behaviors of Au(III), Pt(IV) and Pd(II) complex ions with $Mn(OH)_2$

The coprecipitation experiments were divided into five systems: Au(III) with Mn(II); Pt(IV) with Mn(II); Au(III) and Pt(IV) with Mn(II); Pd(II) with Mn(II); Au(III) and Pd(II) with Mn(II) according to Table 3.1. The recovery effectiveness was discussed regarding the precious metals coprecipitation percentages. In all systems, the coprecipitation percentage are not directly measured, but calculated from the amount of precious metals removed from sample solutions after adjusted to pH 9 at a given time as the amount of precious metals coprecipitated. Every calculation considered the initial concentrations of precious metals in sample solution as 100% of the precious metals contained in systems or 0% of coprecipitated precious metals.

The results of Au coprecipitation are as reported in Table 3.2. Figure 3.3 shows that gold was immediately and completely coprecipitated with $Mn(OH)_2$ at pH 9 within an hour regardless of Au(III) concentration. The coprecipitation rates were constant even after 24 hours.

Table 3.2 Results of the experiments on Au coprecipitation with $Mn(OH)_2$.

Samples	Amounts of coprecipitated Au at various reaction time (h)											
	0 h		1 h		3 h		6 h		12 h		24 h	
	Wt.	%C	Wt.	%C	Wt.	%C	Wt.	%C	Wt.	%C	Wt.	%C
Au 5 ppm (2.5 mg)	0	0	2.48	99.2	2.48	99.2	2.46	98.4	2.5	100	2.48	99.2
Au 50 ppm (25 mg)	0	0	2.49	99.8	2.49	99.8	2.49	99.8	2.49	99.8	2.49	99.8
Au 100 ppm (50 mg)	0	0	2.48	99.5	2.48	99.5	2.48	99.5	2.48	99.5	2.48	99.5

Note: Wt. is calculated weight of coprecipitated Au (mg). %C is coprecipitation percentage of Au.

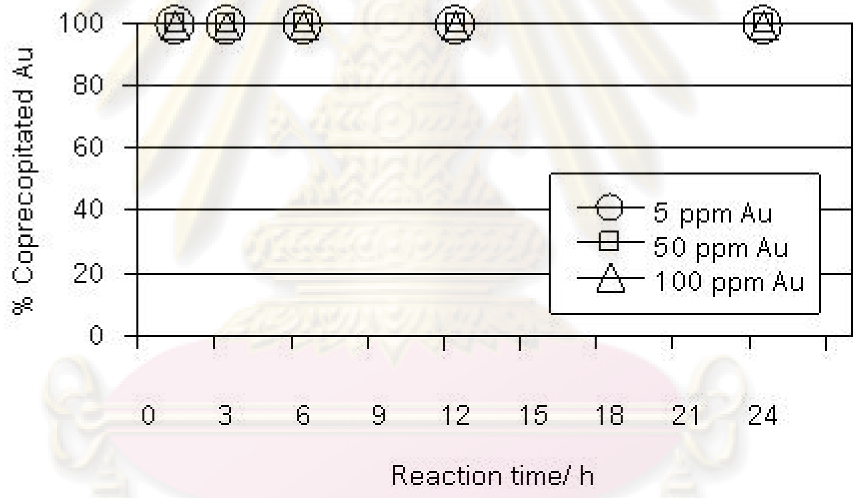


Figure 3.3 Percentages of gold coprecipitated with $Mn(OH)_2$ as a function of time. [Experiment conditions: pH 9, volume 500 cm^3, initial Au concentration 5, 50, and 100 mg dm^{-3} (Au 2.5, 25 and 50 mg, respectively)].

The results of Pt coprecipitation are as reported in Table 3.3. Platinum, as shown in Figure 3.4, was gradually coprecipitated with $Mn(OH)_2$ upon reaction time. The reaction almost tended to reach equilibrium after 24 hours, since the amount of coprecipitated platinum was not increased afterward. Moreover, the percentage of Pt coprecipitated after 24 hours has the similar values regardless of the initial concentrations of Pt.

Table 3.3 Results of the experiments on Pt coprecipitation with $Mn(OH)_2$.

Samples	Amounts of coprecipitated Pt at various reaction time (h)											
	0 h		1 h		3 h		6 h		12 h		24 h	
	Wt.	%C	Wt.	%C	Wt.	%C	Wt.	%C	Wt.	%C	Wt.	%C
Pt 5 ppm (2.5 mg)	0	0	0.17	6.8	0.26	10.6	0.37	14.9	0.79	31.7	1.0	40.3
Pt 50 ppm (25 mg)	0	0	3.75	15.0	4.45	17.8	4.95	19.8	5.85	23.4	6.74	27.0
Pt 100 ppm (50 mg)	0	0	6.86	13.7	8.65	17.3	11.4	22.9	14.9	29.8	19.3	38.6

Note: Wt. is calculated weight of coprecipitated Pt (mg). %C is coprecipitation percentage of Pt.

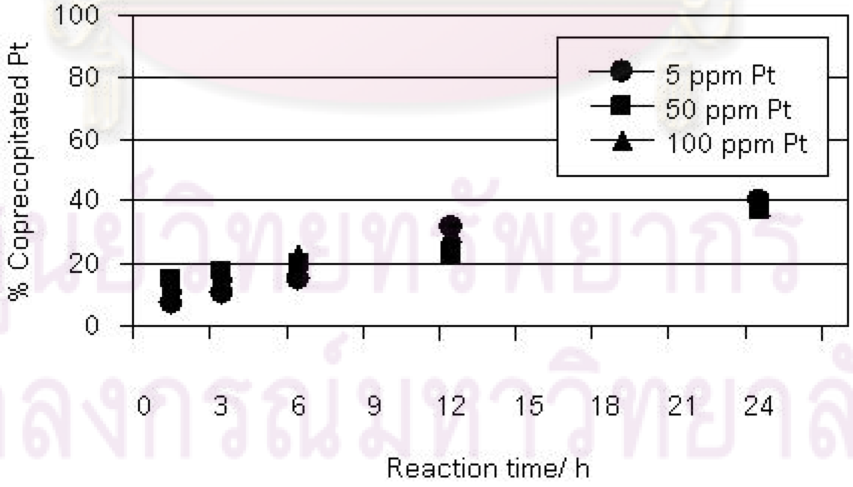


Figure 3.4 Percentages of platinum coprecipitated with $Mn(OH)_2$ as a function of time.

[Experiment conditions: pH 9, volume 500 cm^3, initial Pt concentration 5, 50, and 100 mg dm^{-3} (Pt 2.5, 25 and 50 mg, respectively)].

The results of Au and Pt coprecipitation are as reported in Table 3.4. Figure 3.5 shows that in the system containing both gold and platinum, gold was completely coprecipitated, whereas platinum was still gradually coprecipitated with increasing reaction time. The reaction did not reach equilibrium within 24 hours. In addition, it is observed that the percentages of coprecipitated Pt were enhanced in the presence of Au, when compared with Figure 3.4.

Table 3.4 Results of the experiments on Au-Pt coprecipitation with $Mn(OH)_2$.

Samples	Amounts of coprecipitated Au and Pt at various reaction time (h)											
	0 h		1 h		3 h		6 h		12 h		24 h	
	Wt.	%C	Wt.	%C	Wt.	%C	Wt.	%C	Wt.	%C	Wt.	%C
Au 5 ppm (2.5 mg)	0	0	2.5	100	2.5	100	2.5	100	2.5	100	2.5	100
Au 50 ppm (25 mg)	0	0	25	99.9	25	99.9	25	99.9	25	99.9	25	99.9
Au 100 ppm (50 mg)	0	0	49.9	99.8	49.9	99.8	49.9	99.8	49.9	99.8	49.9	99.8
Pt 5 ppm (2.5 mg)	0	0	0.41	16.4	0.86	34.5	1.01	40.5	1.3	52	1.62	64.7
Pt 50 ppm (25 mg)	0	0	7.23	29.3	9.52	38.1	10.7	42.9	12.9	51.7	14.6	58.5
Pt 100 ppm (50 mg)	0	0	15	30.0	19	37.9	21.0	42.1	25.3	50.6	29	58

Note: Wt. is calculated weight of coprecipitated Au or Pt (mg). %C is coprecipitation percentage of Au or Pt.

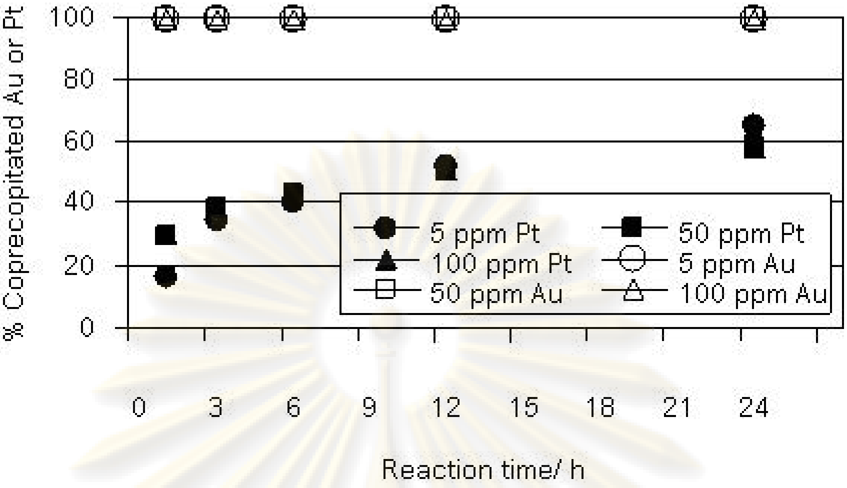


Figure 3.5 Percentages of gold and platinum coprecipitated with $Mn(OH)_2$ as a function of time. [Experiment conditions: pH 9, volume 500 cm^3, initial Au and Pt concentration 5, 50, and 100 mg dm^{-3}. (Au and Pt 2.5, 25 and 50 mg, respectively)].

For palladium, Pd(II) was completely coprecipitated with $Mn(OH)_2$ within an hour in which the presence of Au did not quantitatively affect coprecipitation rates of palladium as reported in Table 3.5 and 3.6. The coprecipitation rates of palladium with $Mn(OH)_2$ are as shown in Figure 3.6, and the coprecipitation rates of gold and palladium with $Mn(OH)_2$ in the Au-Pd coexisting system are as shown in Figure 3.7.

Regarding recovery percentages of precious metals by the coprecipitation technique, the results suggest that coprecipitation with $Mn(OH)_2$ is capable to yield almost 100% of gold, 100% of palladium, 40% of platinum, and almost 60% of platinum when Au(III) and Pt(IV) are coexisting. This indicates that the presence of Au(III) plays an important role in enhancing the amount of coprecipitated Pt with gold and $Mn(OH)_2$. Nevertheless, the changes in valance states of precious metals due to coprecipitation with $Mn(OH)_2$ are later reported. The coprecipitation mechanisms of precious metals with $Mn(OH)_2$ are then discussed.

Table 3.5 Results of the experiments on Pd coprecipitation with $Mn(OH)_2$.

Samples	Amounts of coprecipitated Pd at various reaction time (h)											
	0 h		1 h		3 h		6 h		12 h		24 h	
	Wt.	%C	Wt.	%C	Wt.	%C	Wt.	%C	Wt.	%C	Wt.	%C
Pd 5 ppm (2.5 mg)	0	0	2.5	100	2.5	100	2.5	100	2.5	100	2.5	100
Pd 50 ppm (25 mg)	0	0	24.7	98.8	24.7	98.8	24.7	98.8	24.7	98.8	24.7	98.8
Pd 100 ppm (50 mg)	0	0	2.49	99.8	2.49	99.8	2.49	99.8	2.49	99.8	2.49	99.8

Note: Wt. is calculated weight of coprecipitated Pd (mg). %C is coprecipitation percentage of Pd.

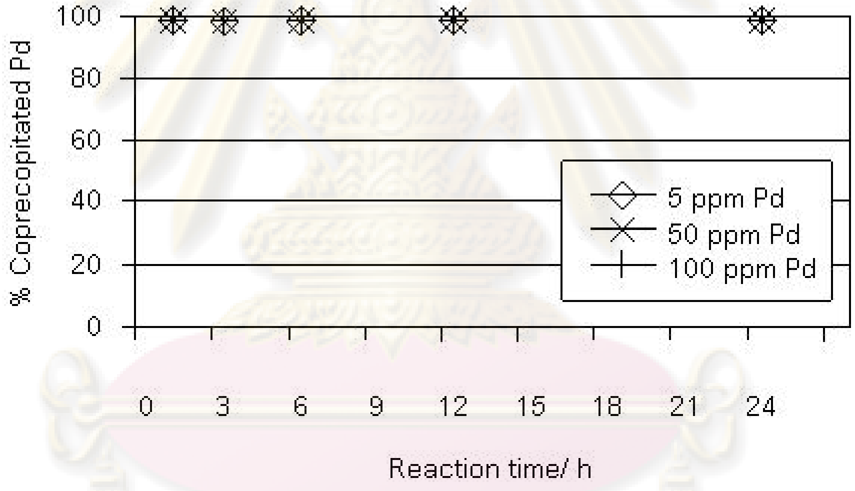


Figure 3.6 Percentages of palladium coprecipitated with $Mn(OH)_2$ as a function of time. [Experiment conditions: pH 9, volume 500 cm^3, initial Pd concentration 5, 50, and 100 mg dm^{-3} (Pd 2.5, 25 and 50 mg, respectively)].

Table 3.6 Results of the experiments on Au-Pd coprecipitation with $Mn(OH)_2$.

Samples	Amounts of coprecipitated Au and Pd at various reaction time (h)											
	0 h		1 h		3 h		6 h		12 h		24 h	
	Wt.	%C	Wt.	%C	Wt.	%C	Wt.	%C	Wt.	%C	Wt.	%C
Au 5 ppm (2.5 mg)	0	0	2.5	100	2.5	100	2.5	100	2.5	100	2.5	100
Au 50 ppm (25 mg)	0	0	25	99.9	25	99.9	25	99.9	25	99.9	25	99.9
Au 100 ppm (50 mg)	0	0	2.5	99.8	2.5	100	2.5	100	2.5	100	2.5	100
Pd 5 ppm (2.5 mg)	0	0	2.5	100	2.5	100	2.5	100	2.5	100	2.5	100
Pd 50 ppm (25 mg)	0	0	2.5	100	2.5	100	2.5	100	2.5	100	2.5	100
Pd 100 ppm (50 mg)	0	0	2.5	99.9	2.5	99.9	2.5	99.9	2.5	99.9	2.5	99.9

Note: Wt. is calculated weight of coprecipitated Au or Pd (mg). %C is coprecipitation percentage of Au or Pd.

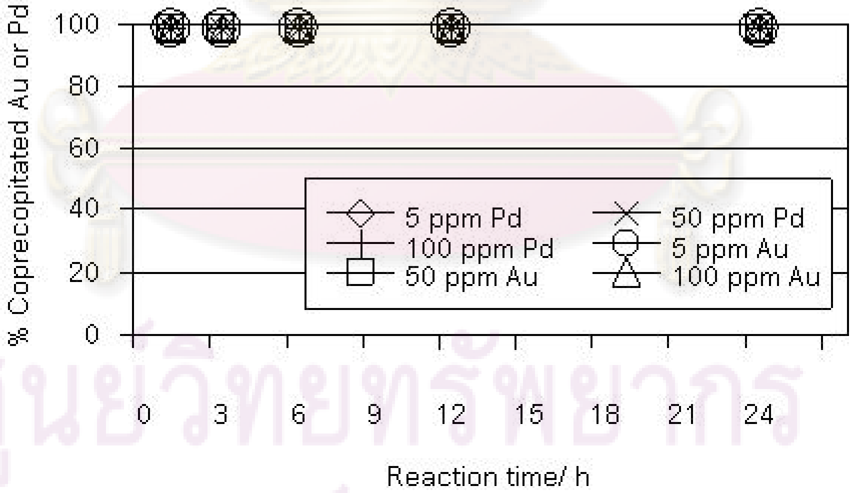


Figure 3.7 Percentages of gold and palladium coprecipitated with $Mn(OH)_2$ as a function of time. [Experiment conditions: pH 9, volume 500 cm^3, initial Au and Pd concentration 5, 50, and 100 mg dm^{-3} (Au and Pd 2.5, 25 and 50 mg, respectively)].

3.5.3. Effect of initial Pt:Mn mole ratio and initial Au:Pt:Mn mole ratio on coprecipitation of platinum

Regarding capability of $Mn(OH)_2$ for coprecipitation of Au and Pt, Au(III) complex ions was thoroughly stoichimetric coprecipitated to Au(0) when Au:Mn atomic ratio was lower than 0.6:1 (Yamashita et al., 2008). For Pt, the following experiment was fundamentally achieved by increasing Mn concentration. As shown in Table 3.7 and Figure 3.8, the percentages of coprecipitated Pt were not change even the initial Mn(II) concentration was twenty times higher than the former experiment. This result suggests that the maximum coprecipitation percentage of Pt is around 40%. The optimum Pt:Mn ratio giving 100% coprecipitated Pt might be examined by either increasing initial Mn(II) concentrations to conduct manganese-riched coprecipitating environment or varying such factors as initial valence states of Pt. Nonetheless, the optimum conditions for recovery of 100% platinum by coprecipitation with $Mn(OH)_2$ was not conducted in this study.

Table 3.7 Results of the experiments on Pt coprecipitation with varied initial Mn(II) concentration.

Mn initial concentration (mol dm^{-3})	Amounts of coprecipitated Pt at various reaction time (h)											
	0 h		1 h		3 h		6 h		12 h		24 h	
	Wt.	%C	Wt.	%C	Wt.	%C	Wt.	%C	Wt.	%C	Wt.	%C
0.001	0	0	8.45	16.9	8.77	17.1	10.2	20.3	10.8	21.7	12.2	24.4
0.005	0	0	6.86	13.7	8.65	17.3	11.4	22.9	14.9	29.8	19.3	38.6
0.1	0	0	6.71	13.4	8.09	16.2	12	23	14	27	17.3	34.6

Note: Wt. is calculated weight of coprecipitated Pt (mg). %C is coprecipitation percentage of Pt.

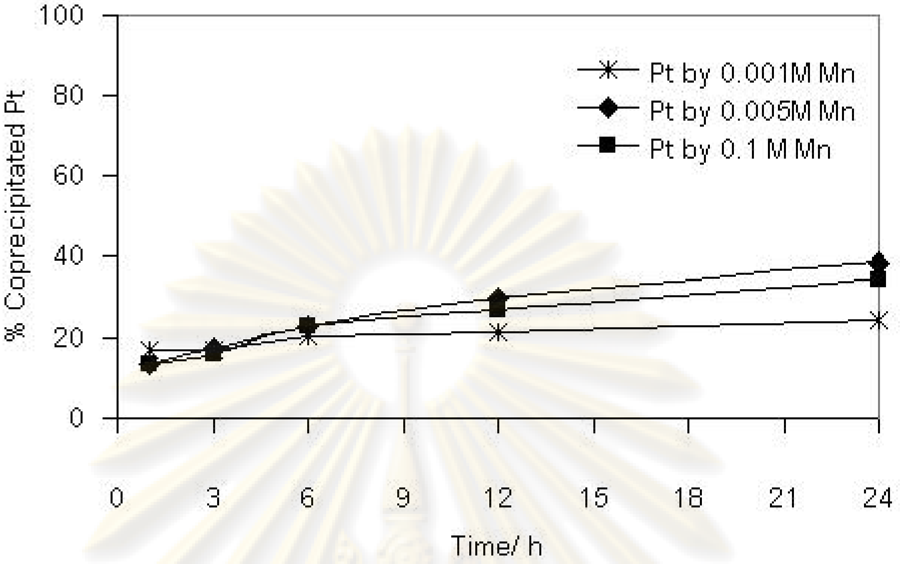


Figure 3.8 Effect of initial concentration of Mn on Pt coprecipitation with $Mn(OH)_2$. [Experiment conditions: pH 9. Volume 500 cm^3. Initial Pt concentration: 100 mg dm^{-3}, Initial Mn concentration: 0.001, 0.005, and 0.1 mol dm^{-3}]

Concerning effect of initial Au:Pt:Mn mole ratio on coprecipitation of platinum, it was found that the amount of coprecipitated Pt was enhanced in the presence of Au. Thus, we hypothesized that if the concentration of initial Au(III) increased, coprecipitation rate of platinum with $Mn(OH)_2$ in the presence of Au(III) will be increased. The results of coprecipitated Pt percentages as a function with time are as shown in Table 3.8 and Figure 3.9.

Table 3.8 Results of the experiments on Pt coprecipitation with varied initial Au:Pt mole ratio in sample solution.

Au:Pt initial mole ratio	Amounts of coprecipitated Pt at various reaction time (h)											
	0 h		1 h		3 h		6 h		12 h		24 h	
	Wt.	%C	Wt.	%C	Wt.	%C	Wt.	%C	Wt.	%C	Wt.	%C
0.5:1	0	0	15	30	16	32	21	42.1	23.6	47.2	30.2	60.5
1:1	0	0	15	30	19	37.9	21.0	42.1	25.3	50.6	29	58
2:1	0	0	23.5	47	24.4	48.9	27.9	55.8	29.7	59.4	35.7	71.4
4:1	0	0	n/a	n/a	32.4	64.8	34.4	68.7	36	72.1	36.9	73.8
6:1	0	0	n/a	n/a	37.4	74.8	40.3	80.6	43.4	86.8	46.4	92.8

Note: Wt. is calculated weight of coprecipitated Pt (mg). %C is coprecipitation percentage of Pt

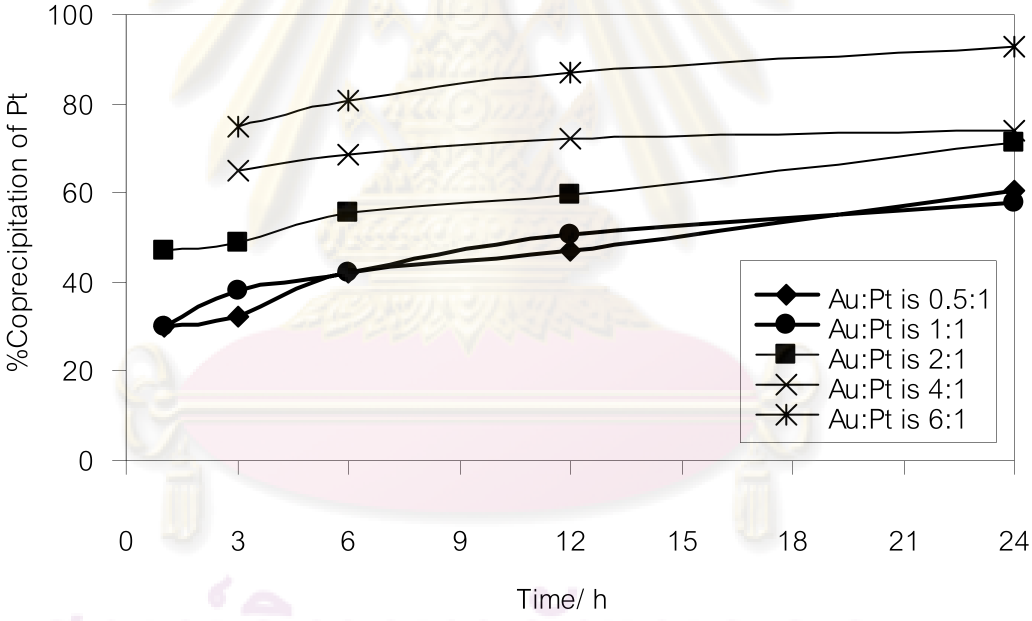


Figure 3.9 Effect of initial Au concentration on Percentage of Pt coprecipitation. [pH:9. Volume: 500 cm^3. Initial Pt concentration: 50 mg dm^{-3}, Initial Au concentration: 50, 100, 200, 400 and 600 mg dm^{-3}, Initial Mn concentration: 0.005 mol dm^{-3}]

The percentages of coprecipitated platinum were increased as the initial Au:Pt mole ratio increased, although the Au:Pt mole ratio of 0.5:1 and 1:1 resulted in the similar percentage. At the initial Au:Pt mole ratio of 6:1, platinum was effectively coprecipitated in which platinum was around 90% yielded. As the maximum initial Au:Mn mole ratio which Au(III) could be thoroughly coprecipitated as Au(0) was 0.6:1 (Yamashita et al., 2008), the most effective Au:Pt:Mn initial mole ratio for simultaneous recovery of gold and platinum by coprecipitation with $Mn(OH)_2$ is 6:1:10.

3.5.4. Valence states of coprecipitated precious metals and manganese

According to X-ray photoelectron spectrometry (XPS), chemical states or valence states of gold, platinum, palladium and manganese in coprecipitates were identified.

The chemical states of gold in coprecipitates is Au(0) as shown in Figure 3.10. Though Mn3s broad peak is quite closely located with Au4f peak, the Au4f doublets are successfully assigned and fitted. The peak positions of Au4f spectra shown for Au, Au-Pt and Au-Pd systems in Figures 3.10 are 84.1, 84.0 and 83.8 eV, respectively. Those of positions agree with the metallic state of gold (Ikeo et al., 1991).

Figure 3.11 shows Pt4f spectra for residues after coprecipitation with $Mn(OH)_2$. Two doublets in the upper figure refer to the existence of both Pt(II) and Pt(IV) species based on the binding energy of 72.5 and 74.7 eV (Ikeo et al., 1991). The lower figure in Figure 3.11 also shows the similar peak positions of two doublets, suggesting that Pt (II) and Pt (IV) species were also presented in the coprecipitates in the presence of Au. This indecates that the existence of Au did not affect the chemical states of Pt from coprecipitation with $Mn(OH)_2$, but only enhance the amount of coprecipitated platinum. Here, we can deduce that the existence of Au increased the amount of coprecipitated Pt, but did not result in the changing way of chemical states of coprecipitated Pt.

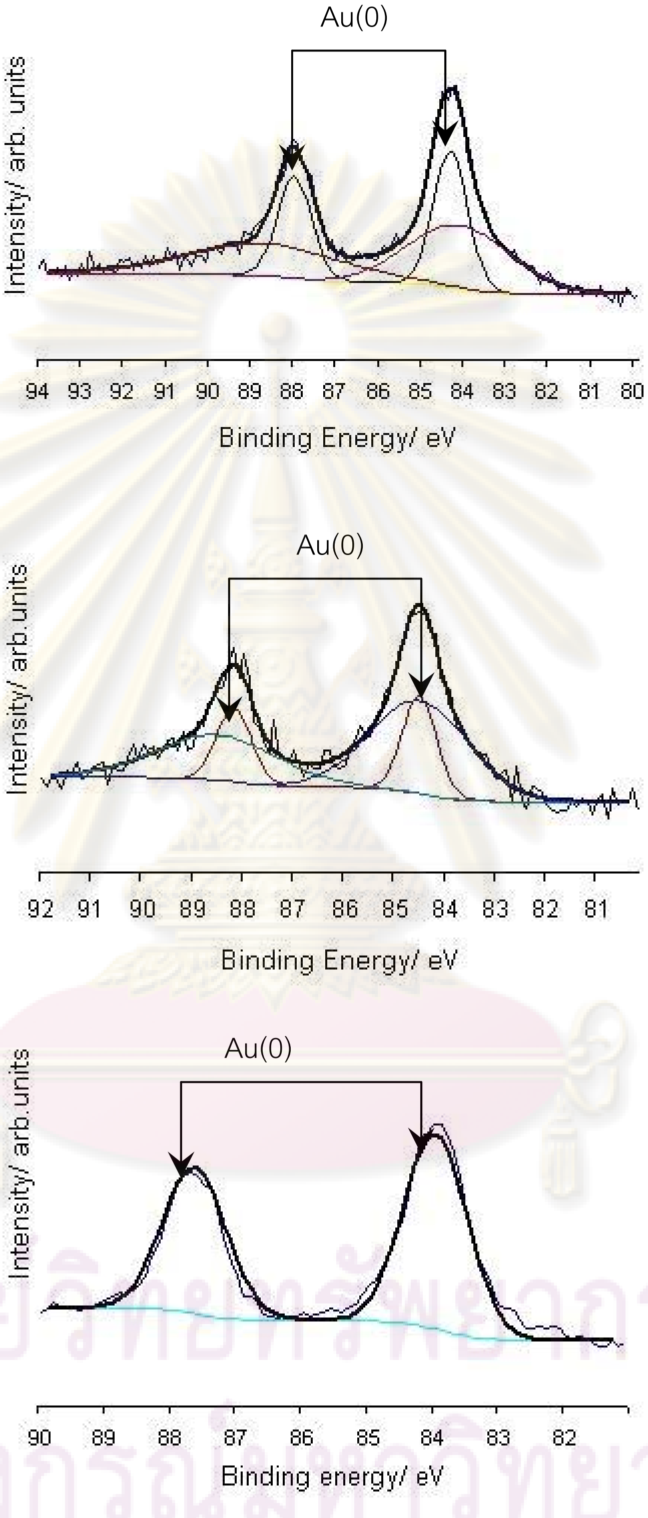


Figure 3.10 Au4f XPS spectra for coprecipitates. Au in upper figure is from Au-Mn system and Au in lower figure is Mn-Au-Pt system.

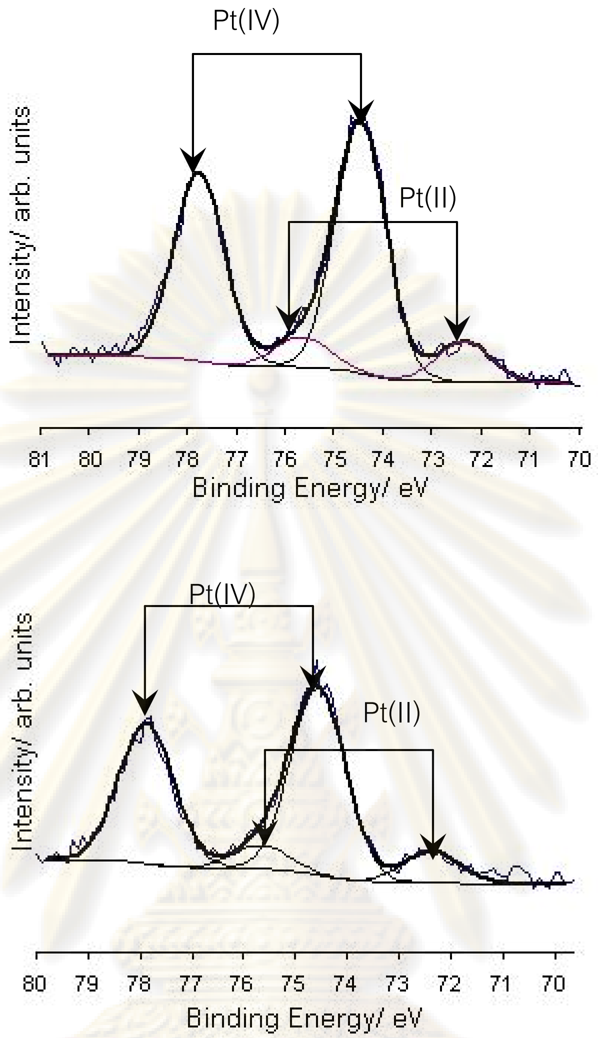


Figure 3.11 Pt4f XPS spectra for coprecipitates in which Pt in the upper figure is from Pt-Mn system and Pt in the lower figure is from Mn-Au-Pt system.

Figure 3.12 represents Pd3d XPS spectra for Pd after coprecipitation with $Mn(OH)_2$ in the presence and absence of Au. In the upper figure, the peak position of the doublet was assigned to 337.1 eV, which can be infer to the presence of Pd(II) (Fleisch and Mains, 1986). Since there is only one doublet could be assigned on the spectrum, it is implied that Pd after coprecipitation with $Mn(OH)_2$ is only in form of Pd(II). In the lower figure, two doublets were assigned their peak positions to 335 and 337 eV, which are inferred to the presence of Pd(0) (Kim et al., 1974) and Pd(II) (Shyu et al., 1988), respectively.

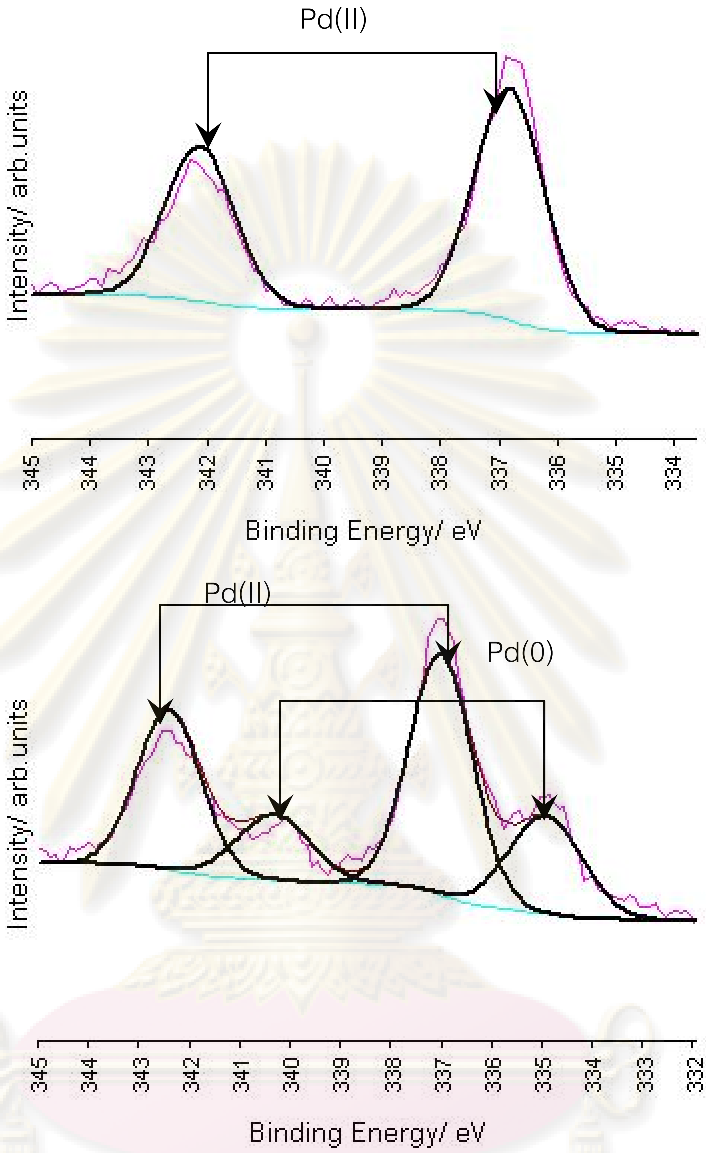


Figure 3.12 Pd3d XPS spectra for coprecipitates in which Pd in the upper figure is from Pd-Mn system and Pd in the lower figure is from Mn-Au-Pd system.

Figure 3.13 represents Mn2p spectra of coprecipitating $Mn(OH)_2$ with precious metals, precipitated $Mn(OH)_2$, and MnO_2. It is noted that the spectra of MnO_2 is a representative for Mn(IV) species from the MnO_2 standard powder ($203 m^2 g^{-1}$, CMD-200) supplied from Chuo Denki Kogyo Co., Ltd. The upper figure of Figure 3.13 shows Mn2p peak of MnO_2 suggesting binding energy around 642.0 eV, which agrees with the chemical shift of MnO_2 introduced by Ikeo et al. (1991). The middle figure of Figure 3.13

shows Mn2p spectra for precipitated $Mn(OH)_2$ with the peak position around 641 eV, corresponding with Mn(II) species (Ikeo et al., 1991; and Yamashita et al., 2008). The lower figure of Figure 3.13 shows the representative of Mn2p spectra for Mn coprecipitating gold and platinum from Mn-Au system, Mn-Pt system, and Mn-Au-Pt system. The spectra from each system show the similar position around 642.0 eV, which is the same as Mn2p spectra for MnO_2 as mentioned before. Therefore, we can deduce that coprecipitating Mn from all system was oxidized to the higher valance states including Mn(IV). However, Yamashita et al. (2008) also reported that the peak position for coprecipitates from coprecipitation of low concentration Au(III) complexes (30 wt% Au) with $Mn(OH)_2$ slightly shifted to higher-energy side from 642.0 eV, indicating a part of Mn(II) in $Mn(OH)_2$ converted to higher valance states such as Mn(III) and Mn(IV).

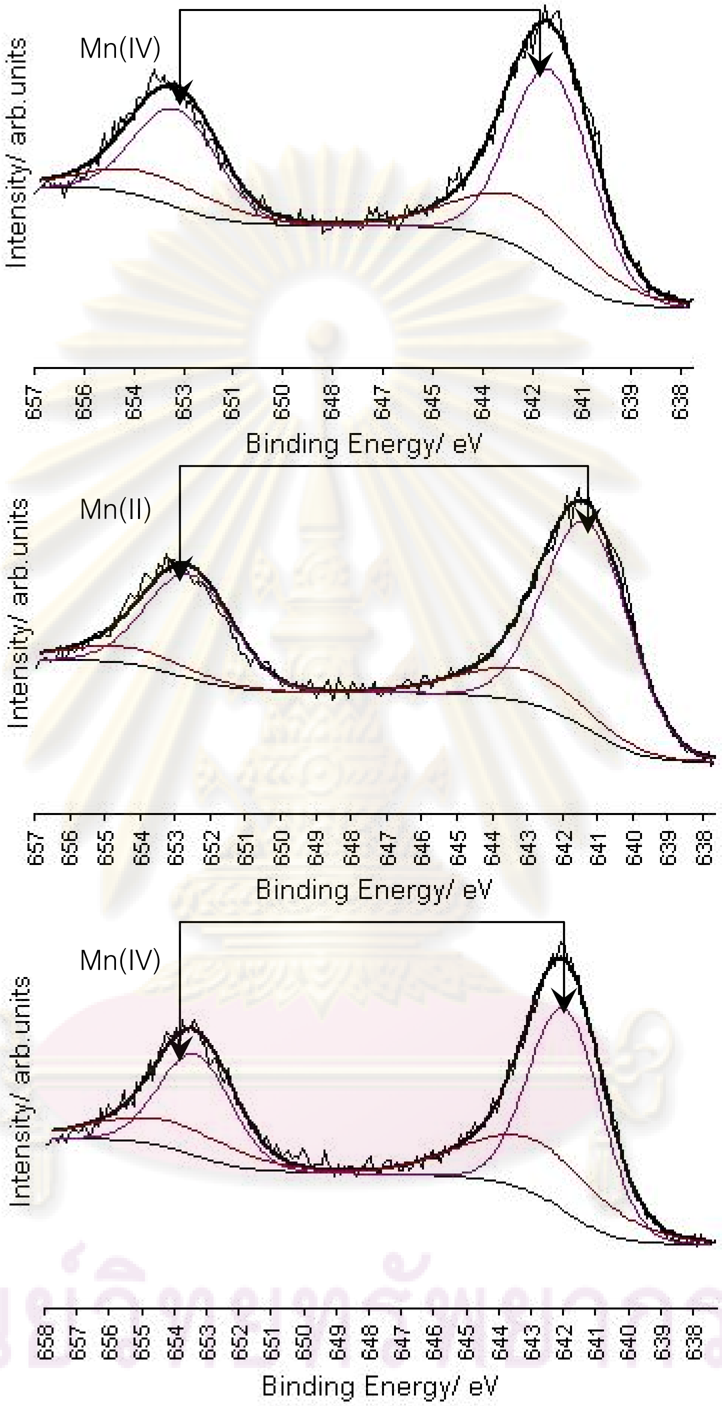


Figure 3.13 Mn2p XPS spectra for standard samples and coprecipitates in which Mn in the upper figure is from standard powder MnO_2, Mn in the center figure is precipitated $Mn(OH)_2$, and Mn in the lower figure is the representative of coprecipitated Mn.

3.5.5. Coprecipitation mechanisms of precious metals complex ions with $Mn(OH)_2$

According to comparison Mn2p spectra, it is clear that the XPS spectra for coprecipitating Mn and MnO_2 powder are quite similar, indicating that $Mn(OH)_2$ was oxidized to MnO_2 by Au(III) and/or dissolved oxygen in the solution for 24 hours. However, the average valence state for manganese in coprecipitating Mn sample is lower than that of Mn(IV), suggesting that a part of $Mn(OH)_2$ may still remain. The proportion of remained $Mn(OH)_2$ depends on the initial precious metals/Mn atomic ratio.

Au(III) complex ions were coprecipitated with $Mn(OH)_2$ effectively and rapidly at pH 9. The Au(III) complex ions coprecipitated were reduced to elemental gold (Au(0)) within an hour (Yamashita et al., 2008). In this study, the amount of gold coprecipitated (almost 100%) was constant for at least 24 h. According to Au4f XPS spectra of gold coprecipitated in each system, it is clearly suggested that most of gold coprecipitated with $Mn(OH)_2$ existed as Au(0) even after 24 h. According to previous study (Yokoyama et al., 2001 and Uchida et al., 2002), the coprecipitation mechanisms of Au(III) proceeded as follows. When $Mn(OH)_2$ was formed at pH 9, $[AuCl_n(OH)_{4-n}]^-$ complex ion are predominantly existed as $[AuCl_2OH)_2]^-$ in the solution. Yokoyama et al. (2001) and Uchida et al. (2002) suggested that a form of $[AuCl_2OH)_2]^-$ is suitable for strong adsorption, especially bidendate coordination as shown in Figure 3.14. The adsorbed $[AuCl_2OH)_2]^-$ on the surface of $Mn(OH)_2$ in which Au-O-Mn bond was formed as the unstable asymmetry structure (Figure 3.14).

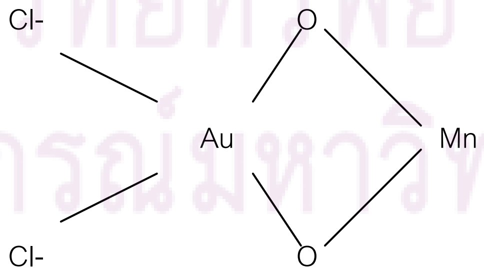


Figure 3.14 The unstably distorted asymmetry Au-O-Mn bonding.

The unstable structure is proved by combination of Mössbauer spectroscopy for the presence of two different Au-O-metal bonding and X-ray absorption fine structure (XAFS) for the two different coordination distance of Au-O (Yokoyama et al., 2009 to be submitted). Au(III) was then immediately reduced to Au(0) by electron transfer through Au-O-Mn bond. As Au-O-Mn bonding was unstable due to asymmetry or distorted structure, it leads to bond breaking and, thus, Au was successfully reduced to metallic state. In addition, it was observed that the color of the coprecipitates rapidly changed from light brown to dark brown during pH adjustment. Therefore, it was reasonable to deduce that oxidation of Mn(II) to Mn(IV) occurred by Au(III) or dissolved oxygen. The stoichiometric redox reaction for coprecipitation of gold with $Mn(OH)_2$ can be written as follow:

$$3\ Mn(II) + 2\ Au(III) \longrightarrow 3\ Mn(IV) + 2\ Au(0) \qquad (7)$$

According to Pt4f XPS spectra, the coprecipitated Pt has two chemical states, mainly Pt(IV) and Pt(II). The existence of Pt(IV) is probably resulted from the incorporation of Pt(IV) into Mn oxides structure or substitution between Pt(IV) and Mn(IV) due to their similar atomic radius during the coprecipitation process. Thus, Pt(IV) was uptake together with insoluble MnO_2. The existence of Pt(II) might be caused by the reduction of Pt(IV) to Pt(II) due to the oxidation of Mn(II) to Mn(IV). The reduction and oxidation might be possible up on calculation of standard potentials (E^0) as shown in equations below.

$[PtCl_6]^{2-} + 2e^- \leftrightarrow 2Cl^- + [PtCl_4]^{2-}$ ($E^0 = +0.68$) (Weast, 1988) (5)

$MnO_2 + 2H_2O + 2e^- \leftrightarrow Mn(OH)_2 + 2OH^-$ ($E^0 = -0.05$) (Yamashita et al., 2007) (8)

The stoichiometric redox reaction can be written as follow:

$[PtCl_6]^{2-} + Mn(OH)_2 + 2OH^- \leftrightarrow [PtCl_4]^{2-} + 2Cl^- + MnO_2 + 2H_2O$ ($E^0 = +0.73$) (9)

In case of gold and platinum coexisting system, without Au(III) complex ions Pt(IV) was coprecipitated and incorporation of Pt(II) into Mn oxides structure occurred. According to XPS analysis results for manganese and Yamashita et al. (2008), the oxidation of $Mn(OH)_2$ is accelerated by the presence of Au(III) species and their stoichiometrical reduction to Au(0). Thus, the increased coprecipitation rates of Pt(IV) was caused by accelerated increase of Mn oxides produced by the reduction of Au(III).

In case of palladium, the changes of chemical states of Pd due to coprecipitation of palladium with $Mn(OH)_2$, both in the presence or absence of Au(III) have the same direction as those of platinum, although palladium was completely coprecipitated whereas platinum is only effectively coprecipitated in the presence of gold. According to Pd3d XPS spectra for coprecipitates, Pd(II) was unchanged by coprecipitation with $Mn(OH)_2$. The coprecipitation mechanism of Pd can be described as the mechanic entrapment, or incorporation of Pd(II) into MnO_2 structure, or substitution of Pd(II) with Mn(IV) in MnO_2 due to the similar atomic radius of Pd(II) and Mn(IV), or just adsorption on the surface of manganese precipitates. In contrast, in the presence of Au, some of Pd was reduced to Pd(0). This is probably resulted from oxidation of Mn(II) to Mn(IV) which is accelerated by the reduction of Au(III) to Au(0). It may imply that the reduction rate of Pd(II) to Pd(0) is quite low then the reduction of Pd(II) could not be observed within 24 hours in Pd-Mn system. The The reduction of Pd(II) was also found possible according to the calculation of standard potentials (E^0) as shown in chemical equations below.

$Pd^{2+} + 2e^- \leftrightarrow Pd$ ($E^0 = +0.951$) (Weast, 1988) (10)

$MnO_2 + 2H_2O + 2e^- \leftrightarrow Mn(OH)_2 + 2OH^-$ ($E^0 = -0.05$) (Yamashita et al., 2007) (8)

The stoichiometric redox reaction can be written as follow:

$$Pd^{2+} + Mn(OH)_2 + 2OH^- \rightarrow Pd + MnO_2 + 2H_2O \ (E^0 = +1.001) \qquad (11)$$

In this chapter, we can describe the possible coprecipitation mechanisms with $Mn(OH)_2$ for both platinum and palladium either in the presence or absence of Au(III). The entrapment of Pt(IV) and Pd(II) into Mn oxides structures and reduction to Pt(II) and elemental Pd were discussed. Each coprecipitation behavior is substantially different and these coprecipitation mechanisms of gold, platinum and palladium with $Mn(OH)_2$ are found advantageous for their selective recovery and implication to recovery of precious metals from electronic wastes as described in next chapters.

CHAPTER IV

SELECTIVE SEPARATION OF PRECIOUS METALS AFTER COPRECIPITATION WITH MANGANESE HYDROXIDE

4.1. Introduction

4.1.1. Background

In general, a complete precious metals recycling consists of two main processes. The first process is extraction and separation of precious metals from scraps. The second process is recovery (i.e. separation, concentration and purification) of precious metals. The purification methods include, for example, thermal purification and parting by acids (e.g., Kitamoto et al., 2007; and Okabe et al., 2003). In this study, precious metals recovered by coprecipitation methods in the previous chapter were either independently or simultaneously recovered. To attain each precious metal separately, the subsequent selective separation is necessary. In this study, selective separation of precious metals after coprecipitation with $Mn(OH)_2$ by HCl was studied.

4.1.2. Principles

Each metal, element or compound, has different solubility or dissolution behavior. Precious metals in coprecipitates after coprecipitation with $Mn(OH)_2$ are expected to be selectively separated due to those of differences. Table 4.1 shows solubility of metals composed in coprecipitates.

Table 4.1 A solubility of metals contained in precious metals coprecipitates after coprecipitation with $Mn(OH)_2$ (Weast, 1988).

Name	Formulae	Solubility, in grams per 100 cm^{-3}		
		Acids	Alkali	Other solvents
Gold	Au	aqua regia, hot in H_2SO_4	KCN	insoluble in acids
Manganese(II) hydroxide	$Mn(OH)_2$	acids	insoluble in alkali	NH4 salts
Manganese(II,III) oxide	Mn_3O_4	HCl		
Manganese dioxide	MnO_2	HCl; insoluble in HNO_3		insoluble in acetone
Palladium	Pd	aqua regia, hot in H_2SO_4 and HNO_3; slightly soluble in HCl		
Platinum	Pt	aqua regia, fused alkali		

4.1.3. Objectives

Purposes of this chapter study are to discuss the selective separation method for precious metals which were simultaneously coprecipitated with $Mn(OH)_2$; to describe the unusual dissolution behavior of Au(0) with HCl, and to report an advantage of gold recovered by coprecipitation with $Mn(OH)_2$ as the possible catalyst for CO oxidation.

4.2. Materials

4.2.1. Samples

1. Coprecipitates of gold, platinum and palladium with $Mn(OH)_2$ from previous chapter

4.2.2. Reagents

1. Hydrochloric acid (HCl) analytical grade (Wako Pure Chemicals)
2. Ultra pure water

4.2.3. Instruments and equipments

1. Glass volumetric flasks
2. Glass beakers
3. Glass pipettes
4. Glass droppers
5. Magnetic stirrer
6. Laboratory mortar and pestle
7. Vacuum filtration system with pumping speed of 5/6 dm^3min^{-1} and ultimate pressure of 24.0 kPa
8. Adventec 0.45 μm 47mm membrane filters
9. Nippon Jarrell Ash AA-835 flame atomic absorption spectrophotometer (AAS)
10. Seiko and Varian Instruments VISTA- MPX CCD Simultaneous Inductively coupled plasma- atomic emission spectrometer (ICP-AES)
11. Shimadzu KRATOS AXIS-165 X-ray photoelectron spectroscope (XPS)
12. Shimadzu UV-2200 UV-Visible spectrometer
13. FEI Tecnai-F20 transmitted electron microscope

4.3. Experimental procedure

4.3.1. Preparation of dissolution experiments

All reagents used were of analytical grade (Wako pure chemical industry). All solutions were prepared with ultra pure water. All coprecipitates used in experiments were prepared by coprecipitation of precious metals with $Mn(OH)_2$ as mentioned in chapter 3. The initial concentrations of Au(III) or Pt(IV) or Pd(II) complex ions for coprecipitates preparation was 100 mg dm^{-3}. The initial Mn(II) concentration was 0.005 mol dm^{-3}. Therefore, it was expected that coprecipitates from each system contain precious metals 50 mg. All coprecipitates were dried for at least 24 hours. In some cases, coprecipitates were grinded by mortar for laboratory before dissolution. All experiments were carried out at ambient temperature by batch method. All acids were prepared immediately before each experiment.

4.3.2. Coprecipitates dissolution

The dried coprecipitates samples were immersed in HCl solutions (0.01-1 mol dm^{-3} or conc., 50 ml). At given time, the aliquots were taken and filtered with 0.45 μm membrane filter. The concentrations of Au, Pt and Pd in filtrates were determined by AAS or ICP-AES to estimate the amount of precious metals dissolved by acids. The residues after dissolution tests were examined for their changes by XPS.

4.4. Analytical methods

4.4.1. UV-Visible absorption spectrometry

In order to examine the chemical state of gold in HCl in filtrates after dissolution, the absorption spectra were measured by UV-Visible spectrometry (Shimadzu UV-2200). The analysis was conducted at Department of Chemistry, Faculty of Sciences, Kyushu University, Japan.

4.4.2. Transmission electron microscopy (TEM)

In order to observe gold particles in/on the coprecipitates, high-resolution transmission electron microscopy (HRTEM), analytical electron microscopy (AEM) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) were conducted using a FEI Tecnai-F20. Spherical coefficient Cs is 1.2 mm. In STEM mode, the probe size was 1.0 nm and the collection angle of the HAADF detector was 50-110 mrad. The size of condenser aperture was 20 μm. TEM specimens were prepared by dispersing powder sample on holey carbon mesh covering Cu grid.

4.4.3. X-ray photoelectron spectrometry (XPS)

All residues and coprecipitates were dried for at least 24 hours. The valence state of gold, platinum, palladium and manganese was examined by XPS (Shimadzu KRATOS AXIS-165). Powder sample of the coprecipitates were adhered to the carbon tape, and placed in an evacuated chamber (10^{-10} Torr). The XPS spectra were acquired using a monochromatic Al K_α X-ray source (1,486.94 eV) operated at 30 W (15 kV, 2 mA). In all cases, the photoelectron takeoff angle was 45°. The XPS spectra were acquired for C1s, Mn2p, Au4f, Pt4f and Pd3d using pass energy equal to 40 eV. The XPS spectra were collected internally using C1s (284.6 eV) because of the peak shift due to sample charging. The spectra were acquired by a 0.1 eV step and 298 ms point^{-1}. Shirley method was applied to correct the background of all spectra. Curve fitting was subsequently achieved by XPSPEAK 4.1.

4.4.4. Catalytic activity measurement for CO oxidation

All the catalytic activity measurements for CO oxidation were performed by using a conventional fixed-bed flow reactor and by passing the reactant gas. A powder sample (150 mg) sieved between 70 and 120 mesh (212–125 μm) was placed on a ceramic wool plug in a quartz tube with an inner diameter of 6 mm. Before and after the pretreatment of the catalyst samples calcined at 573K for 4 hours and in an air stream at 523K for 30 minutes, the reactant gas (1 vol.% CO in the air) was passed through the catalytic bed at a flow rate of 33 ml min^{-1} (SV = 20,000 h^{-1} ml g^{-1} catalyst).

The catalyst temperature was monitored with a quartz-tube covered thermocouple in contact with the inlet part of the catalyst bed. It was raised or lowered stepwise and maintained at each temperature for more than 40 minutes until steady state conversions were obtained. Oxygen, nitrogen and carbon monoxide in the inlet and the outlet were analyzed by a gas chromatograph (Shimadzu GC-8A) with a thermal conductivity detector (TCD) and with a column of molecular sieve 13 x 5m at 333 K. Calibration was done with a standard gas containing known concentrations of the components.

4.5. Results and discussion

4.5.1. Dissolution test of gold and platinum coprecipitated with $Mn(OH)_2$ by HCl

As a test to examine separation of gold and platinum, the coprecipitates were thereafter dissolved with 1 mol dm^{-3} HCl.

Figure 4.1 suggests that, most of gold was unexpectedly dissolved by HCl. In addition, the amount of dissolved gold was increased with time. This remarkably contrasts to the dissolution behaviors of bulk gold that is not dissolved by acids.

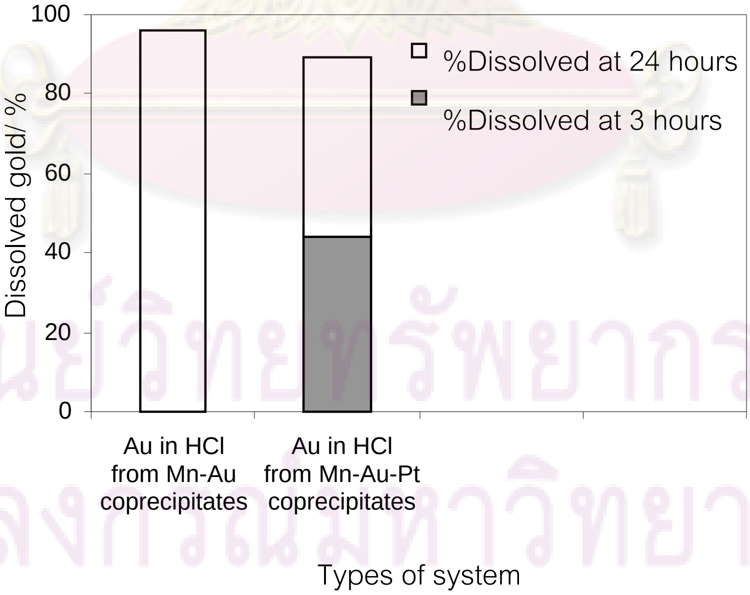


Figure 4.1 The percentage of Au dissolved with HCl. Volume: 50 cm^3.

HCl concentration: 1 mol dm^{-3}.

Figure 4.2 indicates Pt was slightly dissolved with HCl. However, compared with dissolution of gold in Figure 4.1, the percentages of dissolved Pt were much less than those of gold.

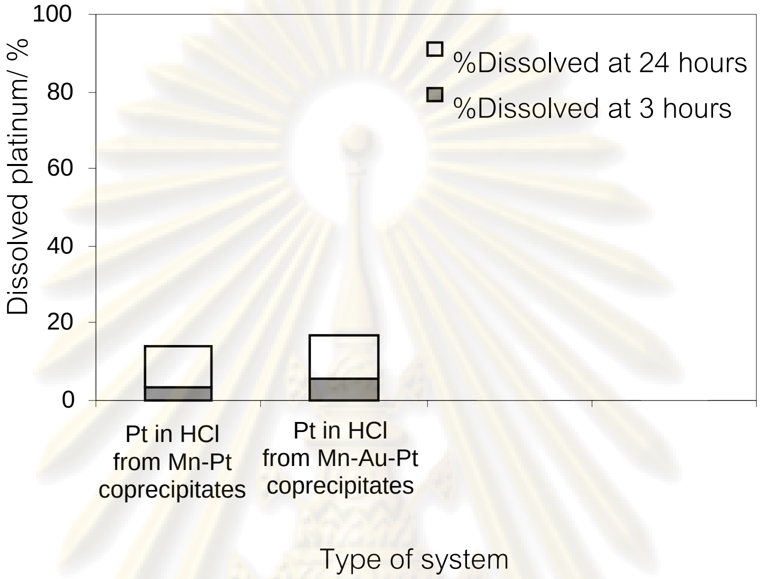


Figure 4.2 The percentage of Pt dissolved with HCl. Volume: 50 cm^3.
HCl concentration: 1 mol dm^{-3}.

As shown in Figure 4.3, Mn was also well-dissolved in HCl. As mentioned in XPS for coprecipitates in chapter 3 that although the Mn2p spectra for coprecipitates from all system agreed with that of MnO_2 reference sample, coprecipitates were not only composed of MnO_2 but also Mn in other forms or species. Generally, MnO_2 is insoluble in nitric acid (Weast, 1987). Besides, Mn precipitated as $Mn(OH)_2$ is slowly oxidized to a mixture of hydrated Mn oxides in the presence of air (Zhang and Cheng, 2007). Thus, Mn in coprecipitates from all system includes MnO_2, other oxidized form of Mn(IV) and other species such as Mn(III).

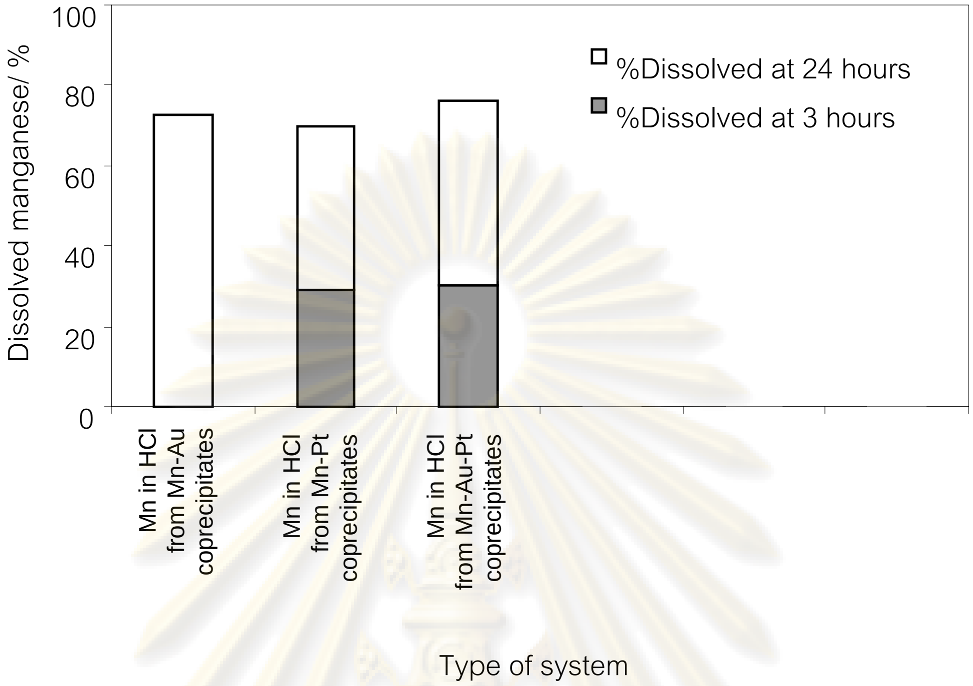
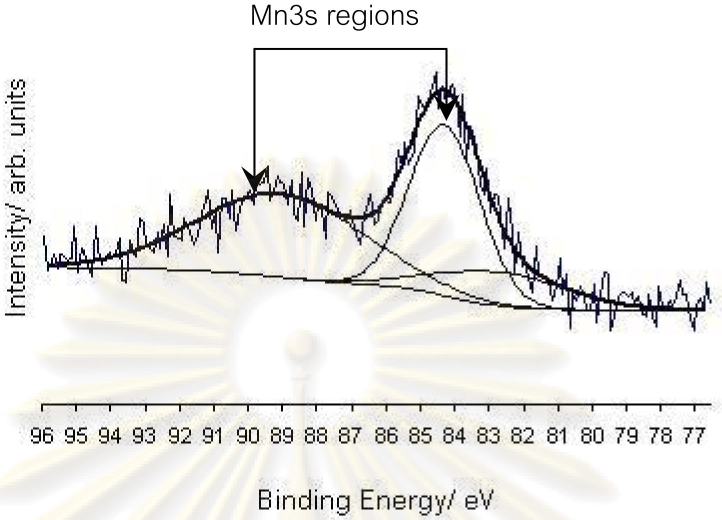


Figure 4.3 The percentage of Mn dissolved with HCl. Volume: 50 cm^3.
HCl concentration: 1 mol dm^{-3}.

Figure 4.4 shows the result of XPS analysis for chemical state of Au in residues from Mn-Au and Mn- Au-Pt systems after leaching by HCl. Both spectra show only the regions of Mn3s. Hence, gold was almost completely leached out, as supported by dissolution results in Figure 4.1.

Figure 4.5 shows the chemical state of Pt from residues after dissolution by HCl from Mn-Pt and Mn-Au-Pt system. Each spectrum shows two doublets, suggesting that both Pt (II) and Pt (IV) species were still presented in the residue. Their similar binding energy of 72.5 and 74.6 eV represented the existence of Pt (II) and Pt (IV) species, respectively (Ikeo et al., 1991).



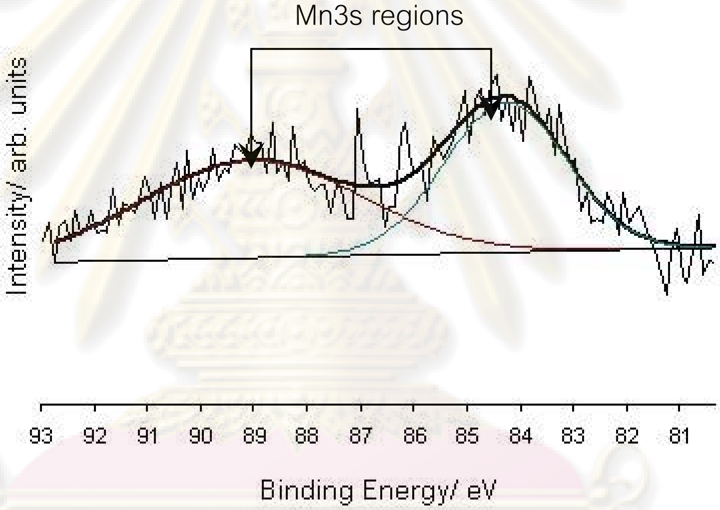


Figure 4.4 Au4f XPS spectra for residues after dissolution by HCl in which the upper figure is from Au-Mn system and the lower figure is from Mn-Au-Pt system.

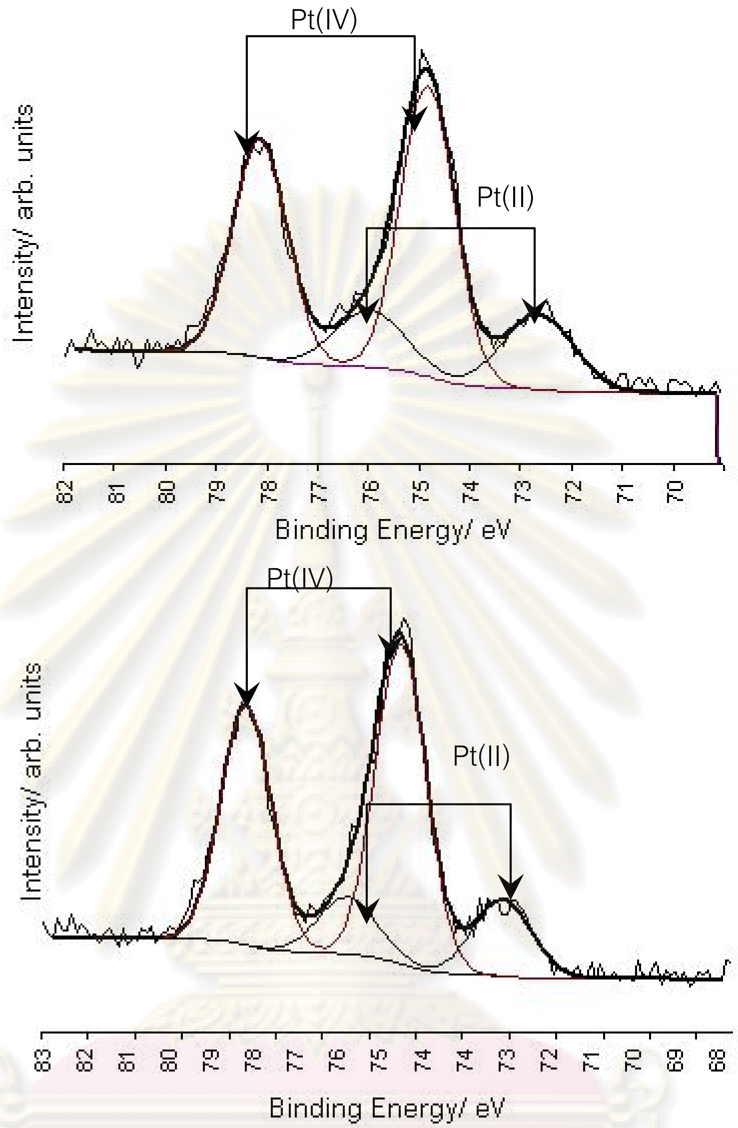


Figure 4.5 Pt4f XPS spectra for residues after dissolution by HCl in which the upper figure is from Pt-Mn system and the lower figure is from Mn-Au-Pt system.

4.5.2. Formation of gold nanoparticles by coprecipitation with $Mn(OH)_2$ and incorporation of Pt(IV) into Mn oxides structures

According to XPS spectra for residues after leaching by HCl, gold was unexpectedly dissolved in HCl, whereas Pt was slightly leached. It was hypothesized that gold was dissolved because gold was formed as nanoparticles in coprecipitates.

Shi et al. (2000) reported that the optical Plasmon absorption due to gold nanoparticles in pores of mesoporous silica disappeared when gold nanoparticles were immersed in concentrated HCl. The result suggests that the gold nanoparticles may be dissolved with concentrated HCl in contrast to bulk gold metal.

In this study, according to TEM results, gold coprecipitated with $Mn(OH)_2$ was exactly present as nanoparticles (Figure 4.6). A unit of a gold particle was around 10 nm. Moreover, the UV-Visible absorption spectra for the dissolved gold in HCl and gold standard solutions (Figure 4.7) indicate the existence of gold in leachate after dissolution of gold coprecipitates. These spectra indicated that the dissolved gold is present as $[AuCl_4]^-$ complex ions and gold nanoparticles taken up in the coprecipitates can be considerably dissolved in HCl. The amount of gold dissolved from the measurement of the UV-Visible absorption spectra coincided with the gold concentration from dissolution tests measured by AAS.

Although generally the bulk gold cannot be dissolved with single HCl, it can be dissolved with aqua regia. At the surface of nanoparticles, in contrast to bulk gold particles, a huge number of dangling bonds (unsaturated bonds) exists. This results in high surface energy and, in turn, high chemical activity. When the nanoparticles contact with HCl, gold atoms located at the surfaces of the particles dissolve in HCl, forming $[AuCl_4]^-$ complex ions. Gammons et al. (1997) proposed the following reaction concerning the dissolution of bulk gold in HCl:

$$Au(s) + 3H^+ + 4Cl^- + 3/4\ O_2 = [AuCl_4]^- + 3/2\ H_2O \qquad (12)$$

At 25°C, the equilibrium constant (K) of Equation (12) is estimated to be $10^{10.61}$. Under oxidizing and acidic condition, the equilibrium shifts right side, that is, $[AuCl_4]^-$ complex ion is more stable than Au(s). For gold nanoparticles, gold atom located at the surface may rapidly interact with HCl to form $[AuCl_4]^-$ because of the high chemical reactivity and huge surface area.

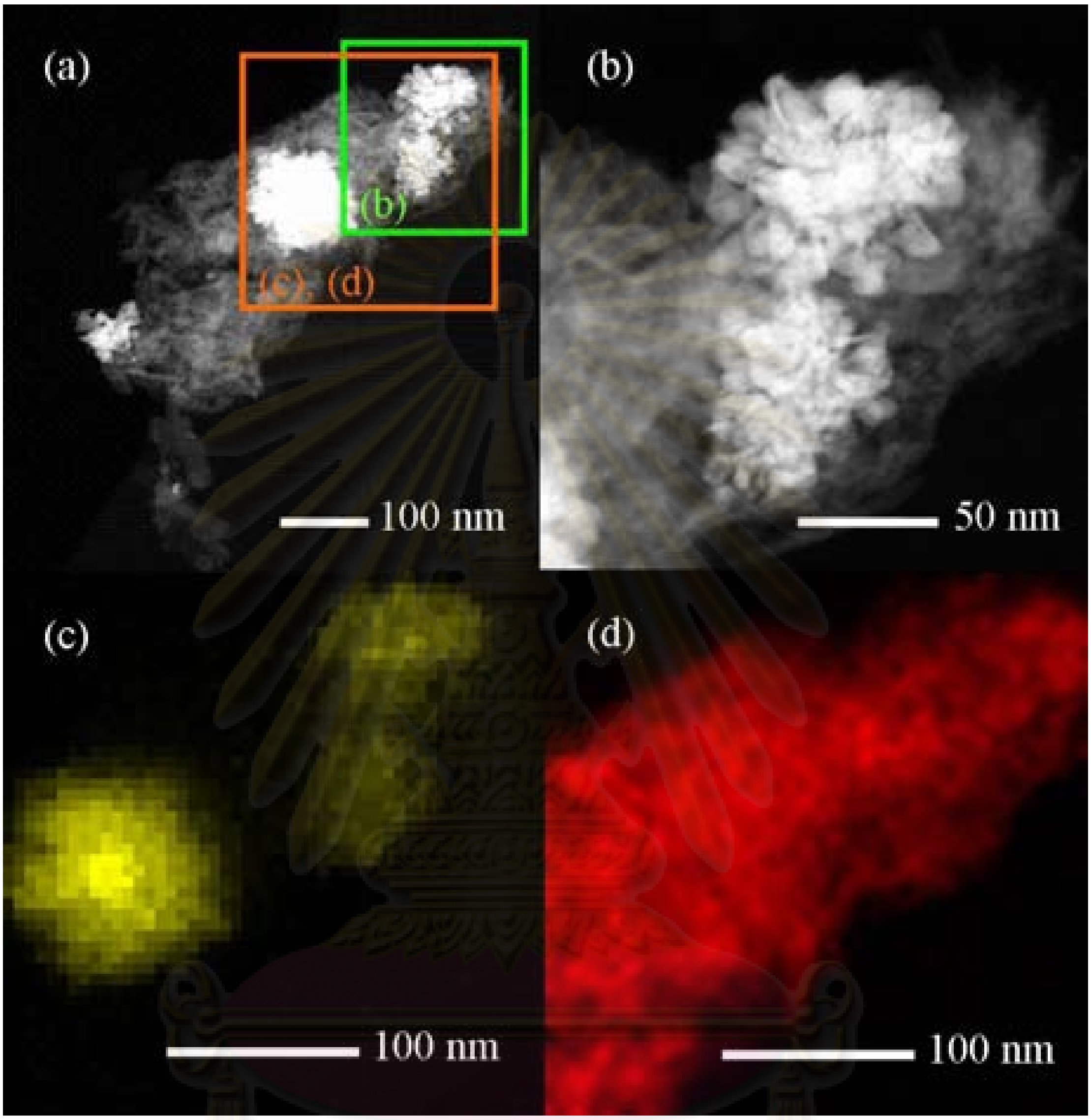


Figure 4.6 The TEM (a) backscattered and (b) zoomed backscattered electron image for gold nanoparticles. (c) Characteristic X-ray image of Au and (d) Mn in coprecipitates. Initial Au/Mn atomic ratio: 1/4.

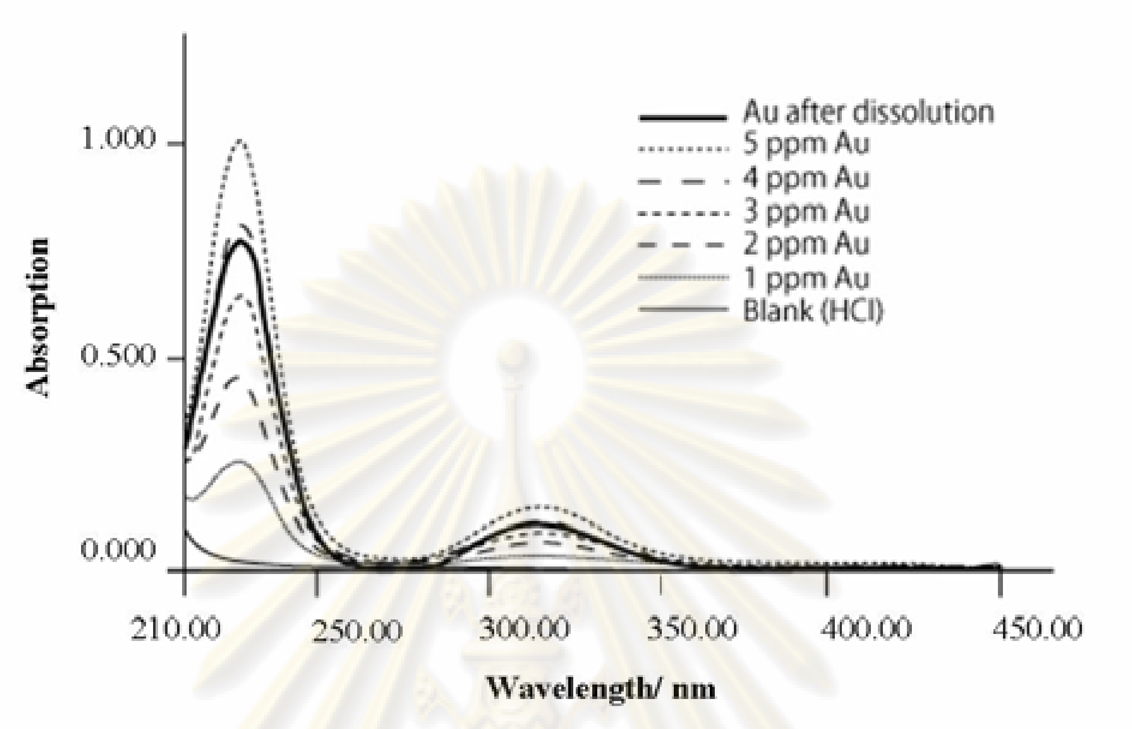


Figure 4.7 The UV-Visible absorption spectra for gold dissolved from gold nanoparticles in coprecipitate by HCl. HCl concentration: 1 mol dm^{-3}.
Initial Au/Mn atomic ratio is 1/10.

In case of platinum, a very small part of platinum dissolved in acid. Nevertheless, as coprecipitated Pt was in non-metallic states and did not well-dissolved in acid media, Pt was reasonably strongly bonded or incorporated into MnO_2 or Mn oxides structure. This dissolution results coincide with the hypothesis made in chapter 3 that Pt(IV) was coprecipitated with $Mn(OH)_2$. Then, Pt(IV) was either entrapped in Mn oxides structure or replaced Mn(IV) which was oxidized from Mn(II) by dissolved oxygen or coexisting gold. This phenomena can be, in the other word, described that the incorporated structure is resulted from the substitution between Mn(IV) and Pt(IV) in their coordination structure.

4.5.3. Selective separation of gold from platinum group metals by dissolution with HCl

In this study, it was found that coprecipitated gold with $Mn(OH)_2$ was leached completely from coprecipitates, whereas only a part of platinum dissolved in HCl. Gold was formed as nanoparticles resulting in the unique dissolution property. Pt(II) was seemingly absorbed on the surface of MnO_2, and Pt(IV) incorporated in MnO_2 structure. Therefore, Pt(II) was slightly leached in acid solution, while Pt(IV) was tightly substituted to Mn(IV) in MnO_2. According to the difference in solubility for gold nanoparticles and coprecipitated platinum in acid, separation of gold from platinum by HCl leaching is possible. To investigate the selective separation of gold and platinum, the dissolution of gold and platinum in various concentrations of HCl was conducted.

Figure 4.8 show the variation of dissolved gold percentage as a function of time and the initial concentration of HCl. Gold was well dissolved when HCl concentration rose to 0.1 mol dm^{-3}. Although the dissolution rates of gold were quite different from the beginning of reaction, dissolution rates became similar after 18 hours and were thereafter constant.

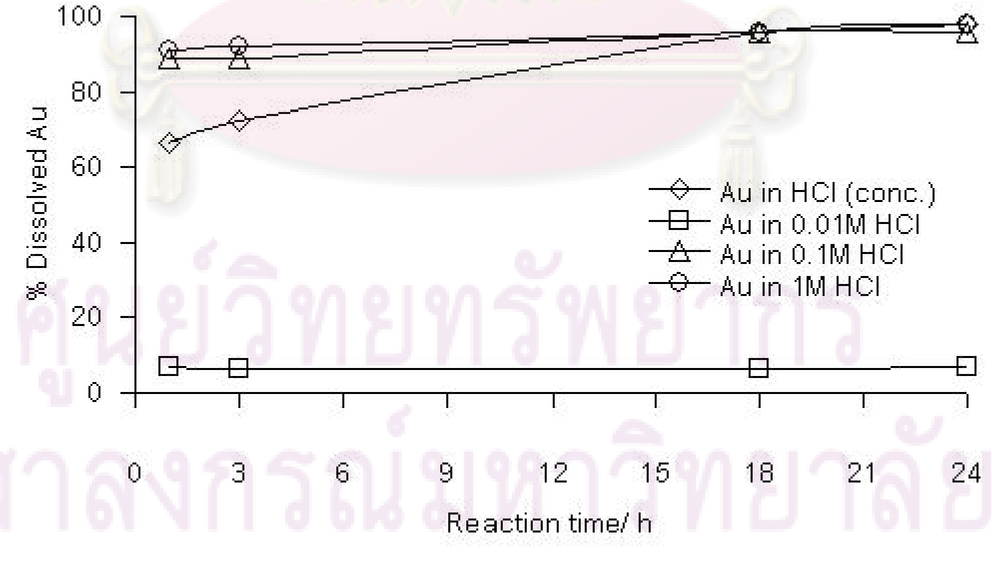


Figure 4.8 The variation of dissolved gold percentage as a function of time and the initial concentration of HCl. Initial weight of Au: 50 mg. Initial Au/Mn mole ratio: 1/10. Reaction time: 24 h.

The different dissolution behaviors of gold nanoparticles probably resulted from the different behaviors of coprecipitation or drying process which probably cause the different location of gold supported on coprecipitates or different gold particle sizes. Otherwise, the different dissolution behaviors are because gold particles enter in the tunnel structure of MnO_2 (Ohashi et al., 2005). Due to slow diffusion of HCl into the tunnel structure, the dissolution rate of gold is varied.

Figure 4.9 shows the variation of dissolved platinum percentages as a function of time and the initial concentration of HCl. Coprecipitated platinum was hardly dissolved by HCl even such high concentration of HCl as 1 mol dm^{-3} was applied.

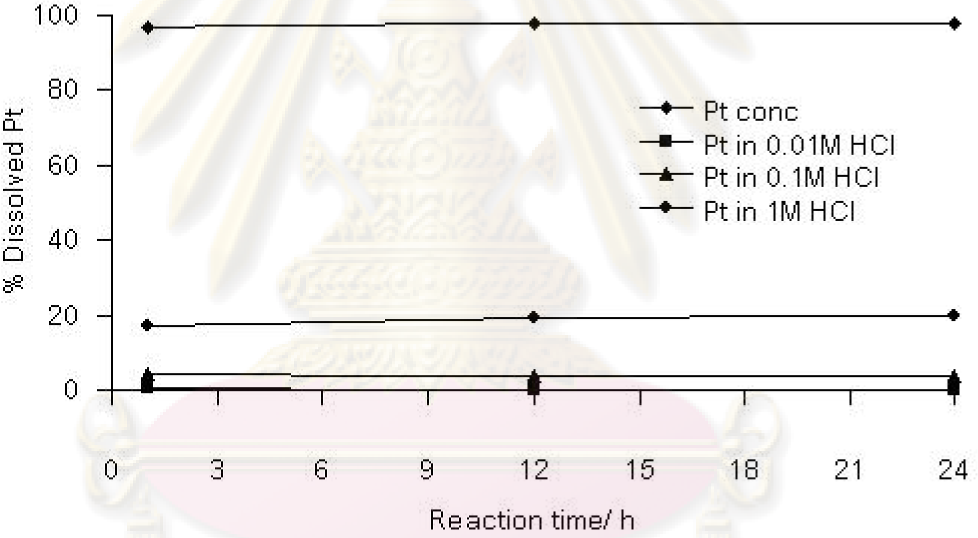


Figure 4.9 The variation of dissolved platinum percentage as a function of time and the initial concentration of HCl. Initial weight of Pt: 50 mg. Initial Pt/Mn mole ratio: 1/10. Reaction time: 24 h.

According to the difference solubility of coprecipitated gold nanoparticles and platinum as shown in Figure 4.8 and 4.9, the most effective HCl concentration for selective separation of gold and platinum coprecipitated with $Mn(OH)_2$ was 0.1 mol dm^{-3} since it is the lowest HCl concentration that can effectively dissolve coprecipitated gold, is the highest HCl concentration in which coprecipitated platinum is seldom dissolved. Furthermore, the most effective Mn:Au:Pt mole ratio for gold and platinum simultaneous recovery was 10:6:1. As a result, the separation procedure can be summarized as a flowsheet (Figure 4.10) as follow:

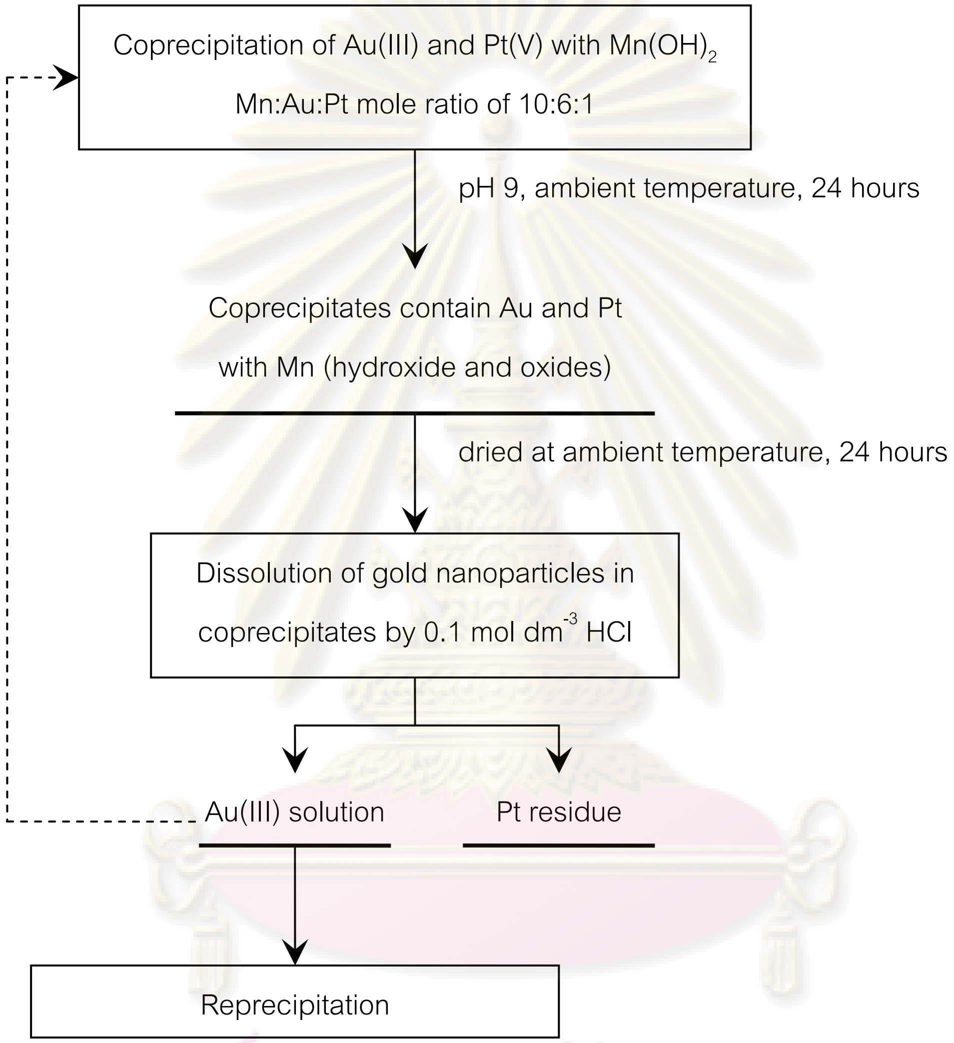


Figure 4.10 Schematic flowsheet for selective recovery of gold and platinum by coprecipitation Au(III) and Pt(V) with Mn(OH)$_2$ and selective separation by dissolution with 0.1 mol dm^{-3} HCl.

In addition, the variation of dissolved palladium percentages as a function of time and the initial concentration of HCl is as shown in Figure 4.11. Coprecipitated palladium was effectively dissolved by HCl. The dissolution rates are high and quite similar to those of gold. Therefore, it is implied that, according to the similar dissolution of Pd and Au and the different dissolution of Pd and Pt, the selective separation of Pd and Pt by 0.1M HCl is possible as well. Moreover, it is noticed that after dissolution and preparation of dissolved Pd samples by dilution with ultra pure water, the dissolved Pd was automatically reprecipitated in acidic conditions. This unique reaction or phenomenon which could observe only Pd included systems might be advantageous for recovery of Pd as will be studied in the future. As expected, using this specific property for Pd, Pd may be separated from other precious metals. Nevertheless, although possible, further investigation on the strategy of selective separation of palladium is necessary.

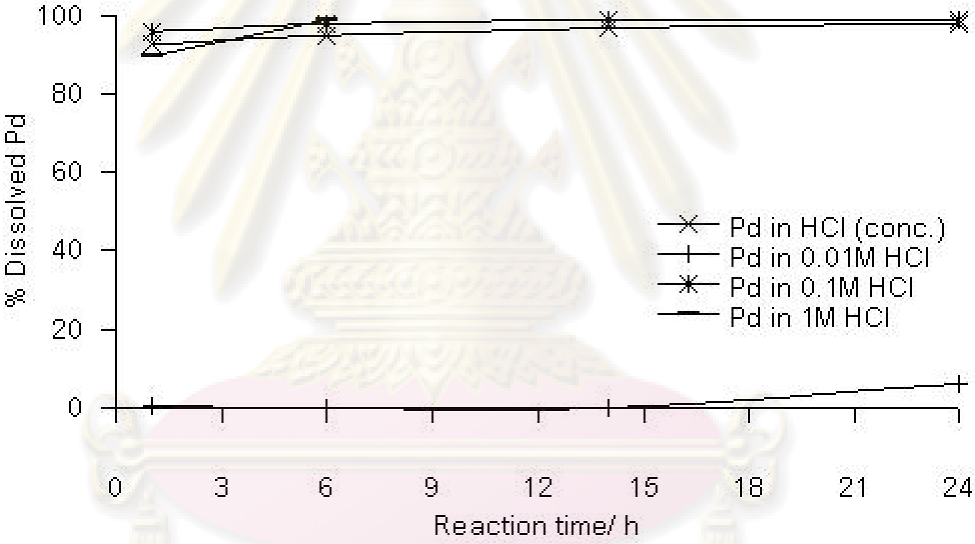


Figure 4.11 The variation of dissolved palladium percentage as a function of time and the initial concentration of HCl. Initial weight of Pd: 50 mg. Initial Pd/Mn mole ratio: 1/10. Reaction time: 24 h.

4.5.4. Catalytic properties of gold and platinum coprecipitates

The catalytic activity measurements of Au and Pt coprecipitates for CO oxidation were performed. The samples were either directly tested or calcined at 573K before tested. The catalytic activities of Au coprecipitates are as shown in Figure 4.12

The result showed half conversion temperature ($T_{1/2}$) of CO oxidation of the gold coprecipitate was around 80°C which calcination prior to the test was regardless.

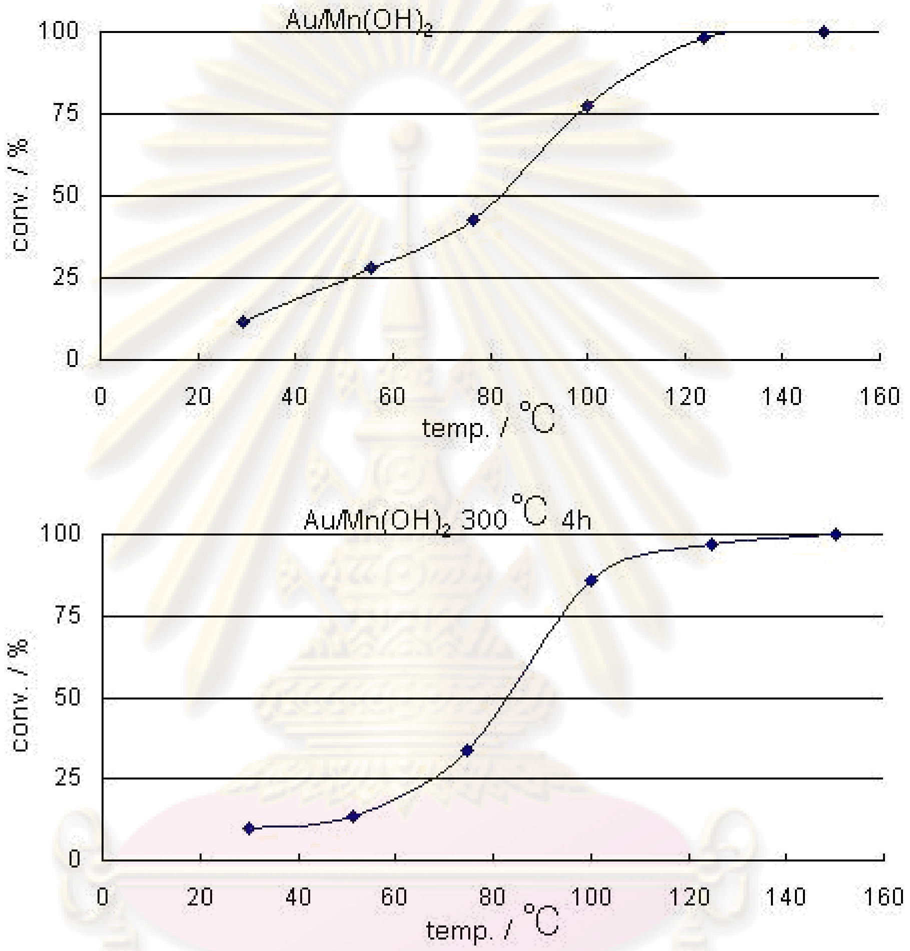


Figure 4.12 The catalytic activities of gold coprecipitates in which the upper figure is for the direct test and the lower figure is for the calcined sample.

Sample weight: 0.27 g. Initial Au %Wt.: 18%

Figure 4.13 shows the results of catalytic activity tests for platinum coprecipitates. The half conversion temperature ($T_{1/2}$) of CO oxidation of the platinum coprecipitate without calcination was around 130°C. $T_{1/2}$ was decreased to around 125°C due to calcination prior to the test.

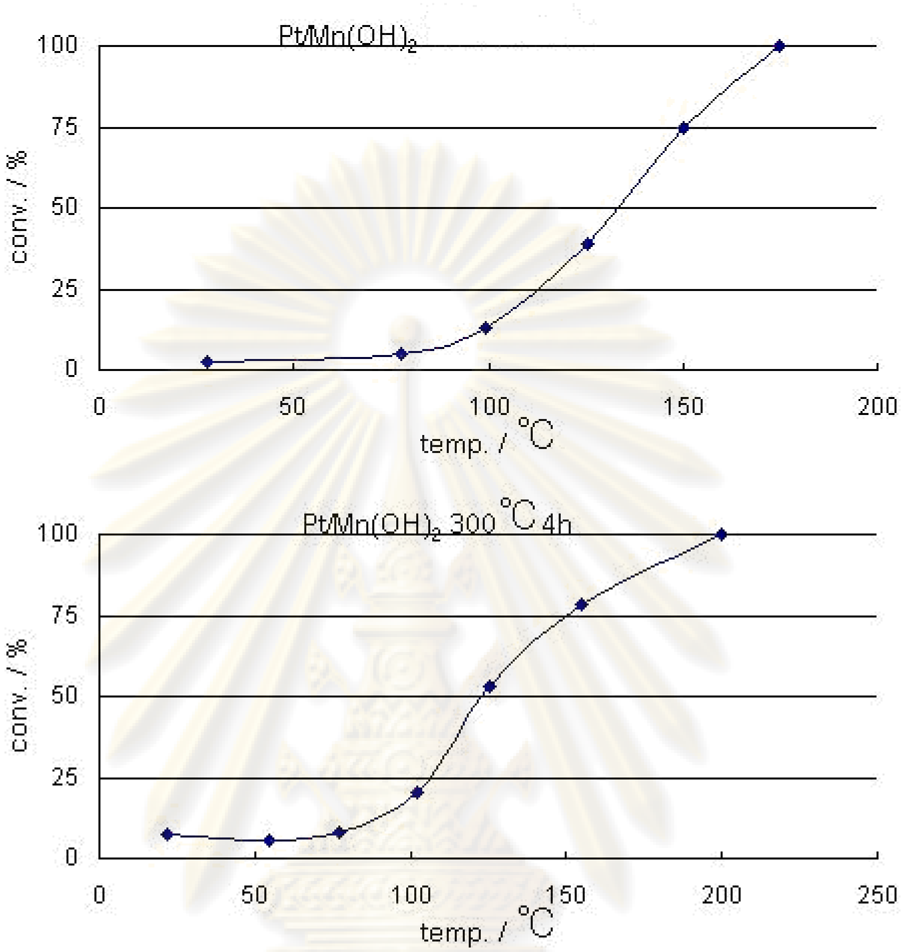


Figure 4.13 The catalytic activities of platinum coprecipitates in which the upper figure is for the direct test and the lower figure is for the calcined sample.

Sample weight: 0.27 g. Initial Pt %Wt.: 18%

Figure 4.14 presents the results of catalytic activity tests for coexisting gold and platinum coprecipitates. The half conversion temperature ($T_{1/2}$) of CO oxidation of the platinum coprecipitate was around 100°C regardless of calcination prior to the test. As compared to the gold coprecipitates, the coprecipitate could show the better catalytic property for CO oxidation without platinum.

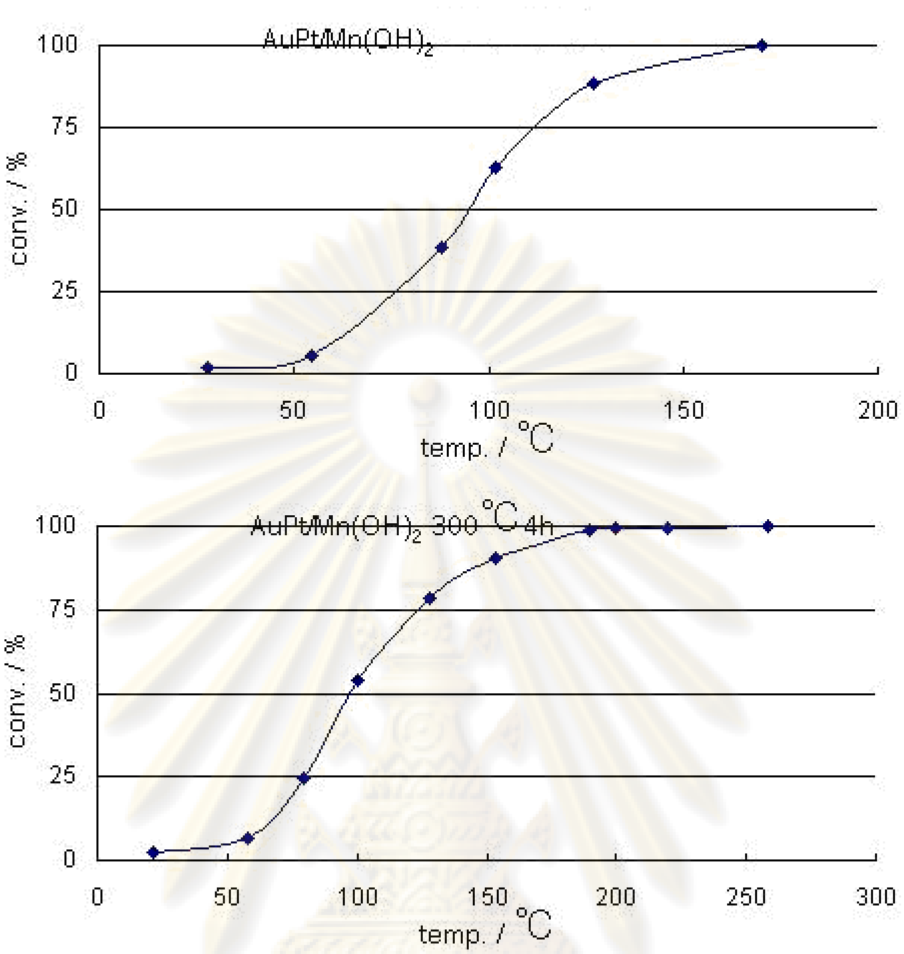


Figure 4.14 The catalytic activities of gold and platinum coprecipitates in which the upper figure is for the direct test and the lower figure is for the calcined sample. Sample weight: 0.32 g. Initial Au %Wt.: 15.5%. Initial Pt %Wt.: 15.5%.

In addition, the Mn(OH)$_2$ precipitate was also tested for catalytic activity after calcination (Figure 4.15). The $T_{1/2}$ of CO oxidation for the manganese precipitate after calcination was 150°C.

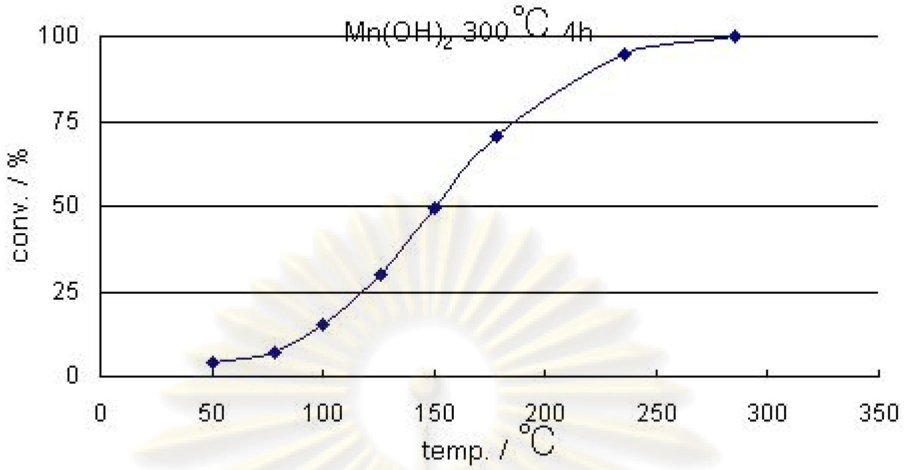


Figure 4.15 The catalytic activities of manganese coprecipitates after calcination.

Sample weight: 0.22 g.

According to all catalytic measurement, gold coprecipitates showed the most effective performance to convert CO to CO_2 at 80°C regardless of calcination. All precious metals coprecipitates regardless of calcination showed their CO oxidation performance at fewer temperatures than that of manganese precipitate. Thus, the presence of precious metals supported on manganese, says, hydroxide, could enhance CO oxidation performances. However, coexisting gold and platinum did not present its remarkable catalytic behavior like it was in the coprecipitation process.

CHAPTER V

RECOVERY OF GOLD FROM COMPUTER CPU MICROPROCESSOR SCRAP AS GOLD NANOPARTICLES BY COPRECIPITATION WITH MANGANESE HYDROXIDE

5.1. Introduction

5.1.1. Background

Used personal computer is one of major electronic wastes considered as a significant secondary source of valuable materials for recycling. Its amount has been drastically increased recent years due to the progressive development of information technology leading to the rapid devices rejection. In many countries, landfill and incineration are the common ways to handle a large amount of computer wastes. However, they caused several environmental pollution including toxic substances and heat emission. Since the used personal computer is one of the significant secondary sources of precious metals including gold, silver, platinum and palladium (Kang and Schoenung, 2005; and Shirahase and Kida, 2008), such valuable metals should be extracted and recycled in order to create sustainable uses of precious metals resources.

Personal computer parts which generally contain precious metals are motherboard and CPU microprocessor. The microprocessor is connected to motherboard through a slot or a socket. It works as computer processing unit (CPU). Precious metals are presented on microprocessors as coating material or bonding wires or metal composite. Although metals recovery from computer parts has been worldwide studied, recovery of valuable materials from microprocessors is seldom found, and consequently, has not been well developed. Due to the presence of precious metals and the sustainability in the uses of resources, recovery of precious metals from the microprocessors can be beneficial.

5.1.2. Principles

The relatively small amount of precious metals is effectively concentrated by coprecipitation method. In some cases, the precious metal was transformed from its complex ions to element (Yokoyama et al., 2001; Uchida et al., 2002; Kitamoto et al., 2007; and Yamashita et al., 2008).

Our model experiments in previous chapters aimed to examine coprecipitation of precious metals with $Mn(OH)_2$ as a simultaneous and selective separation method. By coprecipitation with $Mn(OH)_2$, Au(III) and some of Pd(II) complex ions were reduced to metallic state, whereas Pt(IV), Pt(II) and some of Pd(II) were trapped in Mn oxides structure. Furthermore, Au was coprecipitated as nanoparticles which are soluble in hydrochloric acid (HCl) and showed a good catalytic activity for CO oxidation. Due to the advantageous properties of Au coprecipitated with $Mn(OH)_2$, recovery of precious metals from CPU microprocessors by coprecipitation with $Mn(OH)_2$ was studied and discussed in this chapter.

5.1.3. Objectives

In this study, metals composition of CPU microprocessor scrap samples was determined. Recovery of gold and palladium from CPU microprocessors by coprecipitation technique was studied. According to the advantage of gold nanoparticles supported on Mn hydroxide and oxides prepared by coprecipitation method in the previous chapters, recovery of gold nanoparticles from CPU microprocessor was reported. Preliminary study on the new process for recovery of precious metals from microprocessors was introduced.

5.2. Materials

5.2.1. Samples

1. Computer CPU microprocessor scrap samples

5.2.2. Reagents

1. Manganese(II) chloride tetrahydrate ($MnCl_2.4H_2O$) (Wako Pure Chemicals)
2. Hydrochloric acid (HCl) (Wako Pure Chemicals)
3. Sodium chloride (NaCl) (Wako Pure Chemicals)
4. Sodium hydroxide (NaOH) (Wako Pure Chemicals)
5. Ultra pure water

5.2.3. Instruments and equipments

1. Glass volumetric flasks
2. Glass beakers
3. Glass pipettes
4. Glass droppers
5. Magnetic stirrers
6. Horiba F-21 and D-52 pH meters
7. Vacuum filtration system with pumping speed of 5/6 dm^3min^{-1} and ultimate pressure of 24.0 kPa
8. Adventec 0.45 μm (diameter 47mm) membrane filters
9. Nippon Jarrell Ash AA-835 flame atomic absorption spectrophotometer (AAS)
10. Seiko and Varian Instruments VISTA- MPX CCD Simultaneous Inductively coupled plasma- atomic emission spectrometer (ICP-AES)
11. Shimadzu KRATOS AXIS-165 X-ray photoelectron spectroscope (XPS)
12. Shimadzu Superscan SS-550 Scanning electron microscope and

energy dispersive X-ray spectroscope (SEM-EDX)

13. Horiba XGT-5000 X-ray analytical microscopy (XGT)

5.3. Experimental procedure

5.3.1. Characterization of computer CPU microprocessors

Computer microprocessor samples were randomly collected from personal computer wastes. All microprocessor samples used in this study are the PGA package (Figure 5.1). The microprocessor samples were characterized for their metals distribution and location by SEM-EDX and XGT. Their metals composition was determined by AAS and ICP-AES, in which the samples were crushed and leached by aqua regia prior to analysis to attain metal solution.

Figure 5.1 Examples of computer CPU microprocessor scrap used in this study.

5.3.2. Crushing and leaching of computer CPU microprocessor scrap

Initially, the samples were manually crushed to break the microprocessor package in order to allow the leaching agent (i.e. aqua regia) to reach the internal surface of samples. An example of roughly-crushed computer CPU microprocessor sample is as shown in Figure 5.2. Next, the samples were leached in aqua regia for 24 hours. All initial sample solution prepared from leachate was adjusted to 500 cm^3 before coprecipitation experiments.

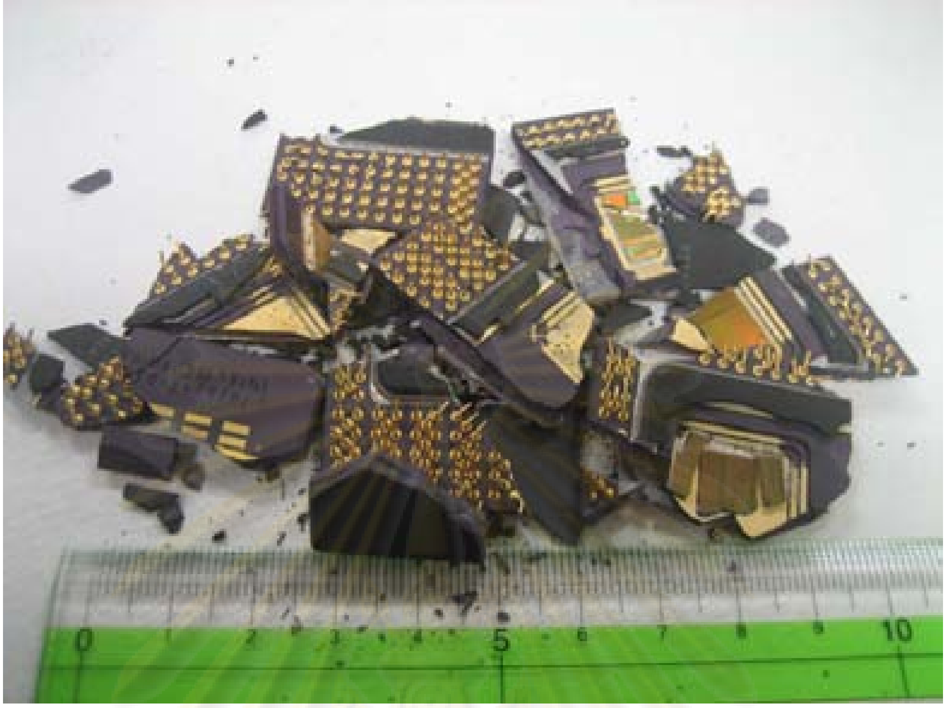


Figure 5.1 An example of crushed computer CPU microprocessor scrap before aqua regia leaching.

5.3.3. Recovery of precious metals from computer CPU microprocessor scraps by coprecipitation technique

All batch experiments were conducted at ambient temperature regarding the previous modeling experiments. All chemicals used were of analytical grade (Wako pure chemical industry). All solutions were prepared with ultra pure water. Mn(II) stock solution was prepared by dissolving manganese(II) chloride tetrahydrate ($MnCl_2.4H_2O$) in 0.1 mol dm^{-3} HCl.

Effect of pH and the presence of Mn on the coprecipitation of precious metals with metal hydroxides were examined. To determine the effect of pH, each of 500 cm^3 sample solution was adjusted and continually increased the pH from pH 3 to 10 with the pH interval of 1. The solution was maintained at each pH for one hour. The aliquots were immediately taken as sample solutions to determine metal concentrations. To determine effect of Mn on coprecipitation of precious metals, two of initial sample solutions were prepared (with or without adding Mn(II) chloride solution, Au:Mn mole ratio 6:10). The solutions were immediately adjusted to pH 9 at. At the time interval of 1, 3, 6, 12 and 24 hours, aliquots were taken and filtered to determine precious metals concentration.

Recovery of precious metals by coprecipitation with $Mn(OH)_2$ was investigated. Mn(II) chloride solution was added (Au:Mn mole ratio: 6:10) to the microprocessor sample leachate. Then, volume of the sample solution was adjusted to 500 cm^3. The prepared solution was then immediately adjusted to pH 9 by dropping NaOH solution and maintained for an hour. An aliquot was taken as sample solution to determine Au, Pd and Mn concentrations. The sample solution was finally filtered to collect the coprecipitate. The coprecipitate was dried for one day, and analyzed for valance states of, mainly, Au, Pd and Mn by XPS.

According to all result, a new process to selectively recover precious metals from CPU microprocessor and a new process to recover gold from CPU microprocessor as gold nanoparticles supported on metal (i.e. Mn and Fe) oxides using coprecipitation technique were demonstrated and introduced.

5.4. Analytical methods

5.4.1. X-ray analytical microscopy (XGT) and scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM-EDX)

The composition of elements on the CPU microprocessor samples were determined by X-ray analytical microscopy (XGT: Horiba XGT-5000), and scanning electron microscopy and energy dispersive X-ray detection (SEM-EDX: Shimadzu Superscan SS-550).

5.4.2. X-ray photoelectron spectroscopy (XPS)

All residues and coprecipitates were dried for at least 24 hours. The valence state of gold, platinum, palladium and manganese was examined by XPS

(Shimadzu KRATOS AXIS-165). Powder sample of the coprecipitates were adhered to the carbon tape, and placed in an evacuated chamber (10^{-10} Torr). The XPS spectra were acquired using a monochromatic Al K_{α} X-ray source (1,486.94 eV) operated at 30 W (15 kV, 2 mA). In all cases, the photoelectron takeoff angle was 45°. The XPS spectra were acquired for C1s, Mn2p, Au4f, Pt4f and Pd3d using pass energy equal to 40 eV. The XPS spectra were collected internally using C1s (284.6 eV) because of the peak shift due to sample charging. The spectra were acquired by a 0.1 eV step and 298 ms point^{-1}. Shirley method was applied to correct the background of all spectra. Curve fitting was subsequently achieved by XPSPEAK 4.1.

5.5. Results and discussion

5.5.1. Characterization of computer CPU microprocessor scrap

The microprocessor is divided into three main parts: body of microprocessor or package; pins; and chip (or die). Figure 5.3 shows the characteristic and transmitted X-ray image of a microprocessor from top view by XGT. The microprocessor die located inside of the microprocessor package was mainly composed of Si. Pins attached on the surface of a microprocessor were composed of several metals including Au, Co, Cu, Fe and Ni. The distribution of Au, Co, Fe and Ni was clearly presented on pins while Cu was probably present surrounding pins as the bond pad or connecting material between pins and body. Since pins were most likely to be composed of valuable materials among three parts, SEM-EDX observation was subsequently carried out to investigate the detailed distribution of each metal.

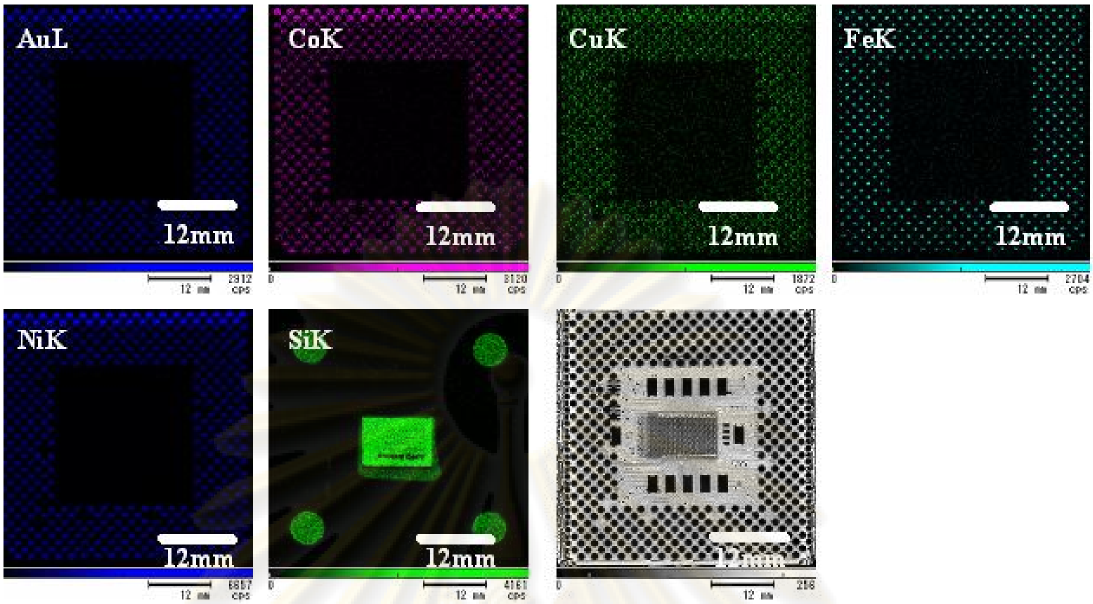


Figure 5.3 Characteristic X-ray image of Au-L, Co-K, Cu-K, Fe-K, Ni-K and Si-K, and transmitted X-ray image for the microprocessor.

Figure 5.4 represents SEM images of a pin on microprocessor. The EDX spectrum was also obtained and quantitatively analyzed by ZAF method. Figure 5.4 (a) focused on the normal surface on the pin, whereas Figure 5.4 (b) focused on the coating-removed area. On the normal surface, Au was detected as a main component. However, on the area where the coating material was removed, Ni was detected as a main component. In addition, the cross sectional image for the pin sample (Figure 5.4 (c)) shows that Fe, Ni and Co existed in which Fe was the major components among those of metals. These results suggest that pins on microprocessor were at least composed of two layers: Fe, Co and Ni composite coated by Au. Figure 5.5 illustrates the structure and chemical composition of the internal part of the microprocessor body. Au existed as Au wires attached onto the internal surface of microprocessor body which consisted of Al.

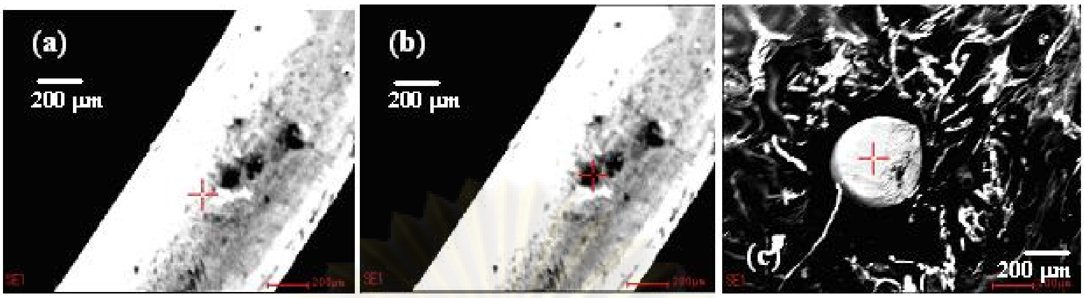


Figure 5.4 SEM images of a pin for (a) the normal surface, (b) the coating-removed surface, and (c) the cross section of a pin.

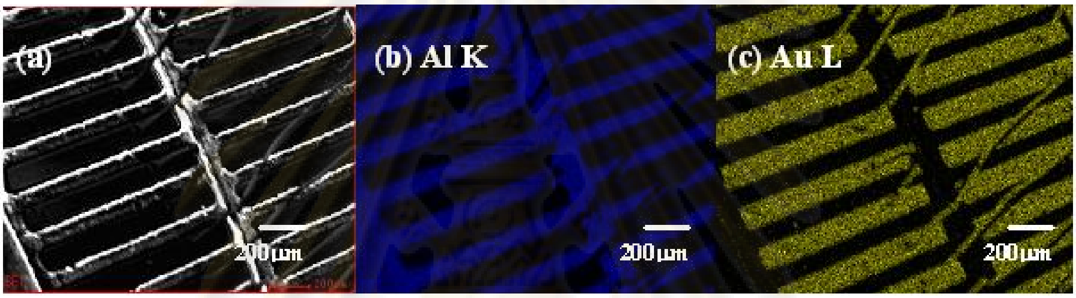


Figure 5.5 The surface inside the package on (a) SEM image, (b) characteristic X-ray images for Al-K and (c) Au-L.

5.5.2. Metal composition of computer CPU microprocessor scrap

The metal composition was determined by dissolving materials on CPU microprocessor by aqua regia. The leachate was then analyzed for amounts of metals in the solution by AAS or ICP-AES. It was found that the metal composition of each microprocessor is varied due to its manufacturing process and its specification. Although the amounts of each metal contained in microprocessor samples are different, it was found upon determination of metal composition of various samples that the metals which were presented in common are Au, Pd, Ag, Mn, Cu, Ni, Fe, W, and Co. The metal composition of microprocessor samples is as shown in Table 5.1. As majorly presented in CPU microprocessors, Au and Pd were considered as target precious metals to recover in this study.

Table 5.1 Metal composition of random CPU microprocessor samples.

Metals	*Sample I (28.8 g)*		*Sample II (17.3 g)*		*Sample III (38.6 g)*	
	Wt. (mg)	*%*	*Wt. (mg)*	*%*	*Wt. (mg)*	*%*
Au	6.5	3.5	40	1.7	59	3.1
Pd	0.6	0.3	1	<0.1	1	<0.1
Ag	2.3	1.2	15	0.6	15	0.8
Mn	0.6	0.3	12.5	0.5	2.7	0.1
Cu	6.0	3.2	72.5	3.2	568	29.7
Ni	45.6	24.1	721.5	31.4	238.9	17.2
Fe	48.1	25.5	768.7	33.5	396.2	20.7
W	2.2	1.1	5.5	0.2	5	0.3
Co	19.2	10.2	n/a	n/a	n/a	n/a
Other metals	57.6	30.6	660.1	28.8	537.3	28
Total	188.7	100	2,296.8	100	1,823.1	100

Note: the weight of parts insoluble in aqua regia (i.e. packaging material) on each CPU microprocessor sample are about 28.6, 15.0 and 36.7 g for sample I, II and III, respectively.

5.5.3. Preliminary studies on recovery of gold and palladium from computer CPU microprocessor scrap

According to results from previous chapters and literature reviews of precious metals recovery by coprecipitation technique, two preliminary studies on recovery of gold and palladium from computer CPU microprocessor scrap by coprecipitation were conducted as follow.

Firstly, as reported in the few previous researches (Chairaksa, 2005; Yonezu et al., 2006; and Kitamoto et al., 2007), precious metals coprecipitation with metal hydroxides was applied to recover precious metals from scraps (i.e. jewelry secondary slag and used mobile phone). As there are a number of metals existed in CPU microprocessor scrap, recovery of precious metals by coprecipitation with metal hydroxides was hypothesized possible. Therefore, a preliminary study of gold and palladium recovery by coprecipitation with existing metals hydroxides in CPU microprocessor scrap was investigated. In this research, effect of pH on coprecipitation of gold and palladium with metal hydroxides was examined. The fundamental recovery process of gold and palladium from computer CPU microprocessors by coprecipitation with metal hydroxides was introduced.

Secondly, a preliminary study of gold and palladium recovery by coprecipitation with $Mn(OH)_2$ was examined. Previous chapters reported that gold and palladium were effectively recovered from solution by coprecipitation with $Mn(OH)_2$. Gold was coprecipitated as gold nanoparticles and palladium was coprecipitated as Pd(II) incorporated into Mn oxides structure. Especially in the presence of gold, palladium was coprecipitated as elemental Pd (Pd(0)). In this chapter, effect of the presence of Mn on coprecipitation of metals including gold and palladium was examined. Those of coprecipitation with $Mn(OH)_2$ technique from previous chapters were applied to recover gold and palladium. Recovery of gold and palladium from computer CPU microprocessors by coprecipitation with $Mn(OH)_2$ was demonstrated. The fundamental process for recovery of gold from computer CPU microprocessor scrap as gold nanoparticles by coprecipitation with $Mn(OH)_2$ was introduced.

5.5.4. Effect of pH on coprecipitation of metals

After extracted from computer CPU microprocessor scrap, a sample solution prepared from the leachate was gradually adjusted to various pH from 3 to 10. It was found that metals were coprecipitated at various pH as shown in Figure 5.6.

Au was found completely coprecipitated at pH above 4, the same as Fe. Coprecipitation percentage of Pd was almost constant at pH 3 – 6, then gradually coprecipitated with the increasing pH and almost completely separated from the solution at pH 10. The coprecipitation trend of Pd is harmonious with the precipitation of Mn, Co, and Ni. The coprecipitation rate for Ag was quite slow and became constant at pH 8 upward. Therefore, according to effect of pH as shown in Figure 5.6, it is summarized that there are four groups of metals which were separately coprecipitated at four different pH: (1) Au and Fe at pH 4; (2) Cu at pH 6; (3) Ni, Co, Mn, Pd at pH 9; and (4) Ag at pH above 10.

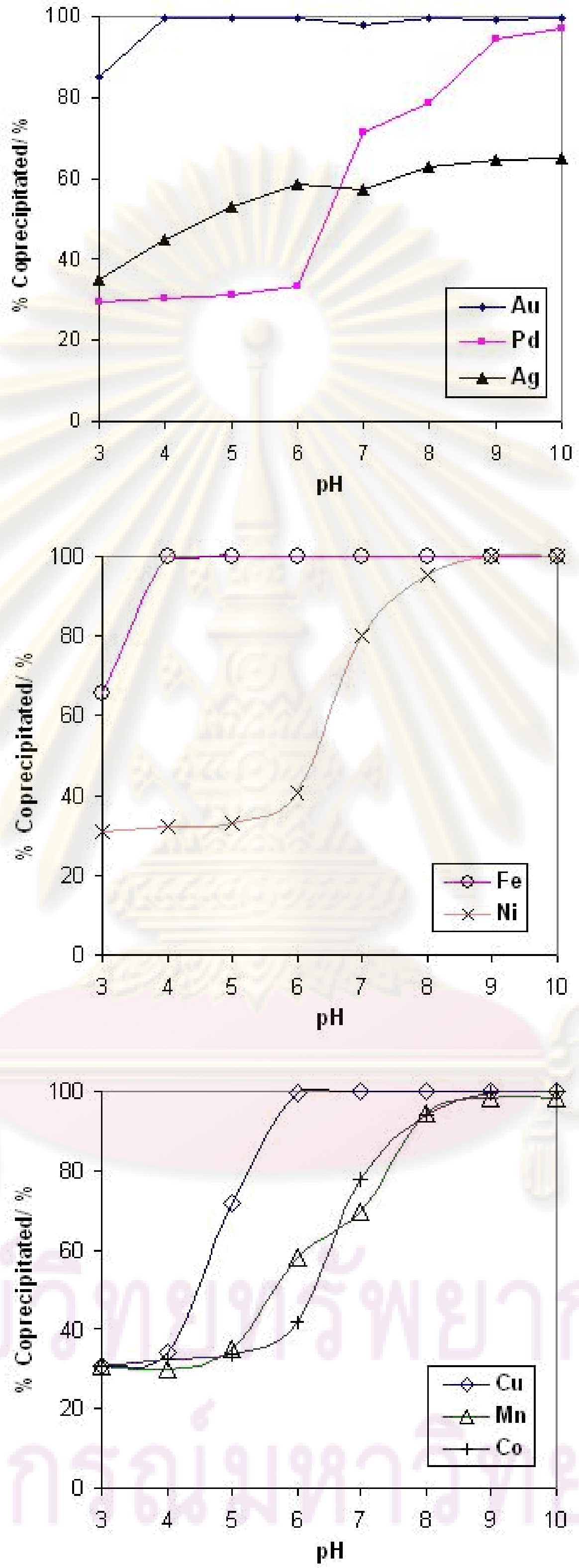


Figure 5.6 Variation of coprecipitated percentage with pH of: (a) Au, Ag and Pd. Initial Au concentration: 57 mg dm^{-3}. Initial Pd concentration: 1.3 mg dm^{-3}; (b) Cu, Mn and Co; (c) Fe and Ni. Volume: 500 cm^{3}. Reaction time on each pH: 1h.

5.5.5. The fundamental process for recovery of gold and palladium from computer CPU microprocessor scraps by coprecipitation with metal hydroxides

Since the coprecipitation behavior of metals at pH is different from each other, gold and palladium are selectively recovered using the change in pH.

For gold, $[AuCl_4]^-$ complex ions is stable in strong acid solution such as aqua regia. However, hydrolysis of the $[AuCl_4]^-$ complex ion is continuously occurred as pH increasing, and gives sequential gold complexes in chloro-hydroxy forms (Murphy and LaGrange, 1998). The chloride ions are stepwise replaced by hydroxyl group as expressed in a general formula of $[AuCl_n(OH)_{4-n}]^-$, the new form of which depends on pH and chloride concentration. According to Baes and Mesmer (1976 cited in Chairaksa, 2005), $[AuCl_4]^-$ is certainly hydrolyzed to form hydrolysis products (i.e. $[AuCl_3(OH)]^-$, $[AuCl_2(OH)_2]^-$, and $[AuCl(OH)_3]^-$,) with increasing pH (Figure 5.7).

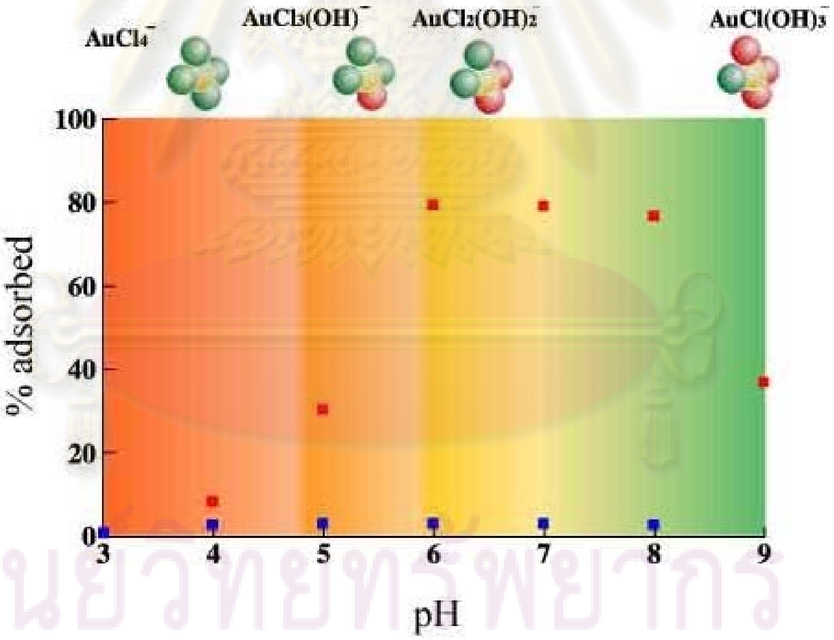


Figure 5.7 The effect of pH on adsorption of gold complex ions on Fe hydroxide and the predominant gold species in solution at increasing pH (Baes and Mesmer, 1976 cited in Uchida et al., 2002).

According to Figure 5.6, gold was effectively coprecipitated with iron which is considered to be formed as iron(III) hydroxide ($Fe(OH)_3$) (Monhemius, 1977 and Kitamoto et al., 2007) at pH 4. However, gold is still in form of $[AuCl_3(OH)]^-$ (Figure 5.7). Although Figure 5.7 indicates that $[AuCl_3(OH)]^-$ is seldom adsorbed on $Fe(OH)_3$, $[AuCl_3(OH)]^-$ was adsorbed onto precipitated $Fe(OH)_3$ due to the iron-riched condition in the sample solution by its single bonding by its monodentate form. As a result, to recover metallic gold, it is suggested that the sample solution should be adjusted to pH 6 in which gold will be effectively coprecipitated with Fe and Cu hydroxides (Chairaksa, 2005; Yonezu et al., 2006; and Kitamoto et al., 2007)

For palladium, as shown in Figure 5.6, it could be separately separated from gold and coprecipitated with metal (e.g., Ni, Mn and Co) hydroxides.

In addition, instead of being recovered by coprecipitation method, silver can be extracted by nitric acid parting prior to aqua regia leaching. Silver ions in nitric acid parting solution can be recovered by adding NaCl to precipitate all silver in form of silver chloride (AgCl). The silver chloride is separated by filtration and is reduced to metallic silver (Ag(0)) by heat and a reducing flux (Chairaksa, 2005).

Consequently, a new recovery process of gold and palladium from computer CPU microprocessors by coprecipitation with metal hydroxides is introduced as follow (Figure 5.8).

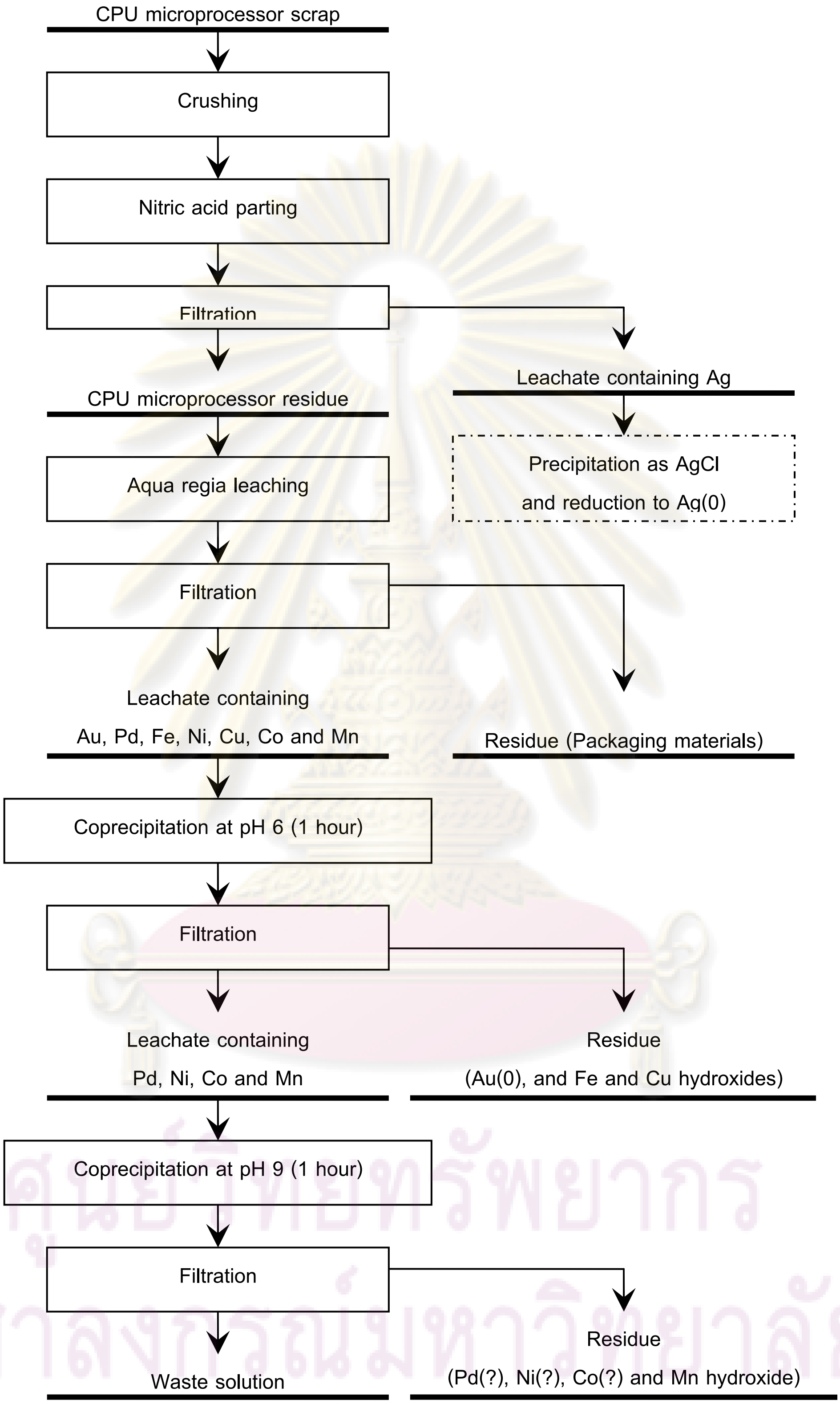


Figure 5.8 A fundamental recovery process of gold and palladium from computer CPU microprocessors by coprecipitation with metal hydroxides.

5.5.6. Effect of the presence of Mn on coprecipitation of metals

The effect of the presence of Mn on coprecipitation of metals including gold and palladium was studied. Two sample solutions (i.e. with or without adding Mn(II) chloride solution for Au:Mn ratio of 6:10 prior to volume adjustment to 500 cm^3) were prepared. Figure 5.9 illustrates the results of the precipitation behavior of metals from the leachate of aqua regia after adjusted to pH 9. Without adding Mn, metals especially Au and Pd were gradually coprecipitated with the reaction time. In contrast, Au and Pd were effectively coprecipitated at pH 9 after one hour in the system which Mn was added. This suggests that Mn assisted the coprecipitation of Au and Pd. Au and Pd could be rapidly separated from solution by the formation of $Mn(OH)_2$. Without Mn, Au and Pd were probably coprecipitated with other metal hydroxides as studied in 5.5.4.

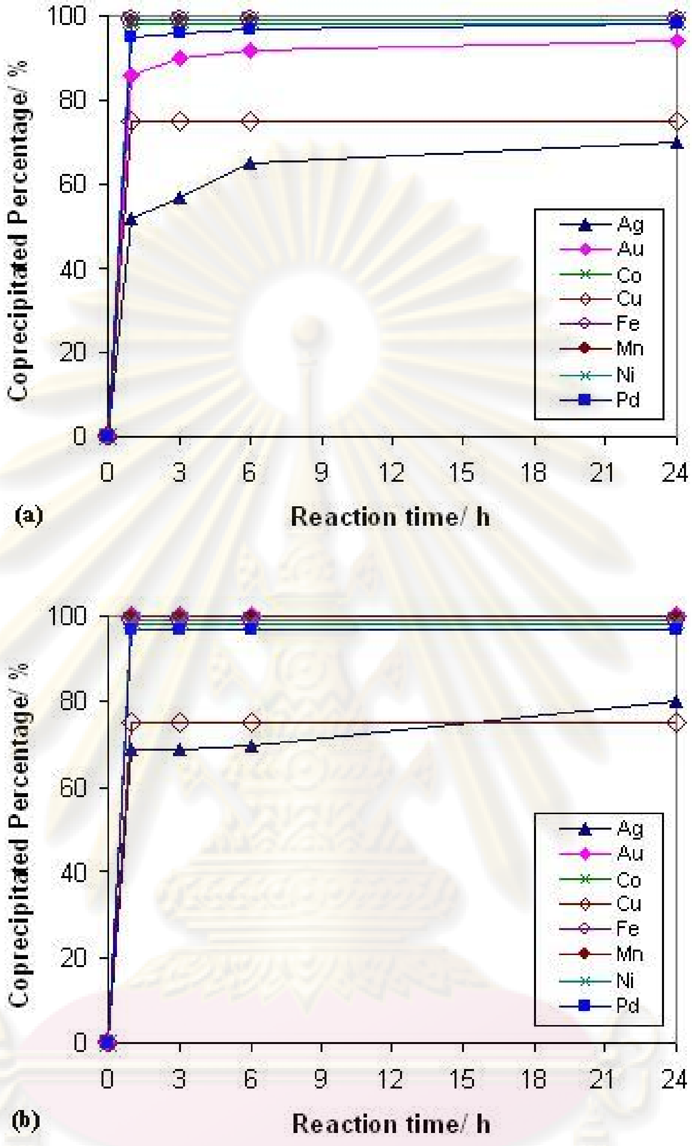


Figure 5.9 Variation of coprecipitated percentage of: (a) metals without adding Mn; (b) metals with Mn addition. [Volume: 500 cm^3, pH: 9. Initial Au concentration: 340 mg dm^{-3}].

5.5.7. The fundamental process for recovery of gold from computer CPU microprocessor scrap as gold nanoparticles by coprecipitation with $Mn(OH)_2$

As gold was coprecipitated with $Mn(OH)_2$ as gold nanoparticles (Previous chapters) and gold supported on MnO_2 or metal oxides showed the catalytic activity (Haruta, 2003 and 2004), recovery of gold as gold nanoparticles by coprecipitation with $Mn(OH)_2$ is worth studied here as a promising option to recycle gold as gold supported on Mn and Fe oxides catalyst from electronic wastes.

According to 5.5.5., gold could be effectively adsorbed on $Fe(OH)_3$ at pH 4 in form of $[AuCl_3(OH)]^-$ due to the iron-rich condition in the sample solution. $[AuCl_3(OH)]^-$ is a predominant species (continues to be hydrolyzed) and thus is unstable. Consequently, it was designed that, in order to recover gold as gold nanoparticles and in order to avoid a large amount of interfering mechanisms of base metal precipitation at the higher pH, the sample solution freshly prepared from leachate was first adjusted to pH 4. Then, the coprecipitate containing $[AuCl_3(OH)]^-$ adsorbed on $Fe(OH)_3$ was filtered from the pH 4 solution. The fresh gold coprecipitate was immediately dissolved again in 0.01 mol dm^{-3} HCl for an hour (500 cm^3, pH 2) in which Mn(II) ions was already added with Au:Mn mole ratio of 6:10. The $[AuCl_3(OH)]^-$ complex ions were expected to be reduced to $[AuCl_4]^-$ complex ions (Figure 5.7). Next, the new suspension containing Au(III), Mn(II) and $Fe(OH)_3$ was immediately adjusted to pH 9 and maintain its conditions for an hour. It is expected that gold could be then coprecipitated with $Mn(OH)_2$ and $Fe(OH)_3$ which were subsequently oxidized to Mn and Fe oxides such as MnO_2 and Fe_2O_3. Finally, gold could be recovered from computer CPU microprocessor scraps as gold nanoparticles supported on MnO_2 and Fe_2O_3. The designed fundamental process for recovery of gold as gold nanoparticles is as illustrated in Figure 5.10.

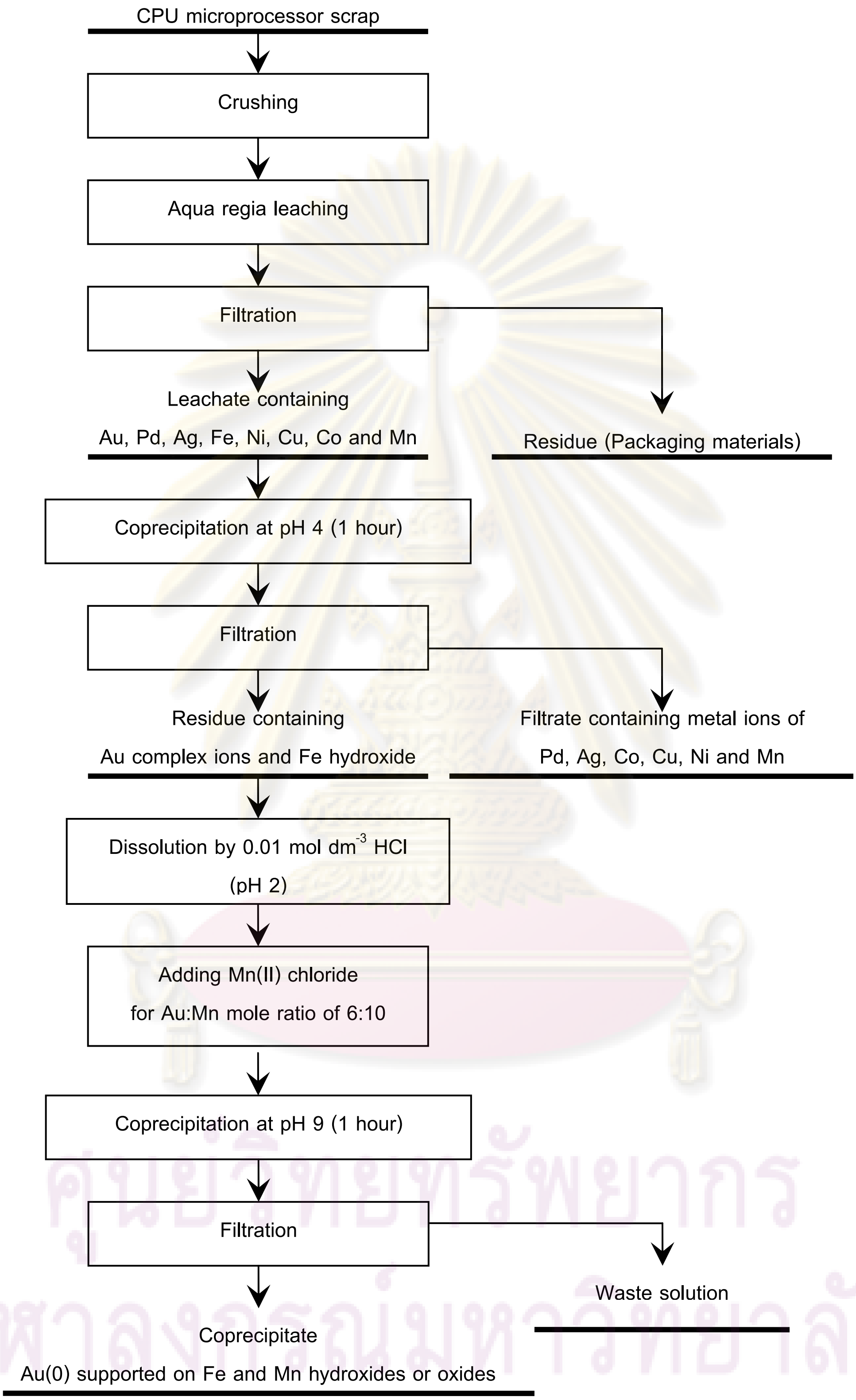


Figure 5.10 The new process for recovery of gold as gold nanoparticles supported on Mn and Fe oxides by coprecipitation with $Fe(OH)_3$ and $Mn(OH)_2$.

To determine the amount of gold yielded in each step and entire process, the aliquot were taken at each step, before and after pH adjustment and filtration. The aliquots were analyzed for their gold concentrations. According to the measurement of gold concentration in each step, the gold weight yielded in the process was implied. At the final stage, gold coprecipitate was dried for one day and analyzed for chemical states of Au, Fe and Mn by XPS to confirm their chemical states.

The results of experiment on recovery of gold from computer CPU microprocessor by coprecipitation with $Mn(OH)_2$ is shown in Table 5.2. The yielded percentage of gold is implied to the comparison of amount of gold recovered from the each step to gold in aqua regia leachate in which we considered amount of gold in aqua regia leachate as the original amount of gold in the CPU microprocessor sample.

Table 5.2 Results of the experiments on recovery of gold from computer CPU microprocessor by coprecipitation with $Mn(OH)_2$.

Procedures	Au concentration (mg dm^{-3})	Weight of Au (mg)
Aqua regia leaching (1)	69.2 in 500 cm^3 solution	34.6
Remained in solution (2)	19.2 in 500 cm^3 solution	1.0
In coprecipitate after coprecipitation at pH 4 (3)=(1)-(2)	n/a	33.6
In solution after dissolution of coprecipitate by 0.01 mol dm^{-3} HCl (4)	64.3 in 500 cm^3 solution	32.2
Loss during transferring solid after filtration to dissolve in HCl (4): (5)=(3)-(4)	n/a	1.4
Remained in solution after coprecipitation at pH 9 (6)	10.3 in 500 cm^3 solution	5.2
In coprecipitate after coprecipitation at pH 9 (7)=(4)-(6)	n/a	27.0

Note: [Experimental condition: Initial Au concentration: 692 mg dm^{-3} in 50 cm^3 solution].

Gold yielded from each recovery step was determined. 97% of Gold was separated from the solution after adjustment to pH 4. There was little loss of gold during filtration to separate the coprecipitate from solution. The residue containing gold was immersed in 0.01 mol dm^{-3} HCl and completely dissolved. $MnCl_2$ solution was added to the suspension and then adjusted to pH 9. Within an hour, gold was separated with 81% yield in this stage, of which the total recovery for gold of this new method was 78%. The mass balance of gold yielded from the recovery process is summarized in Figure 5.11.

For palladium, since the amount of Pd in CPU microprocessors was very low, the exact efficiency of this recovery method of Pd has not yet examined. However, the fundamental separation of Pd from Au was substantially possible because Au was separated in solid form and Pd still remained in the solution which can be later recovered as solid form with other metal hydroxides.

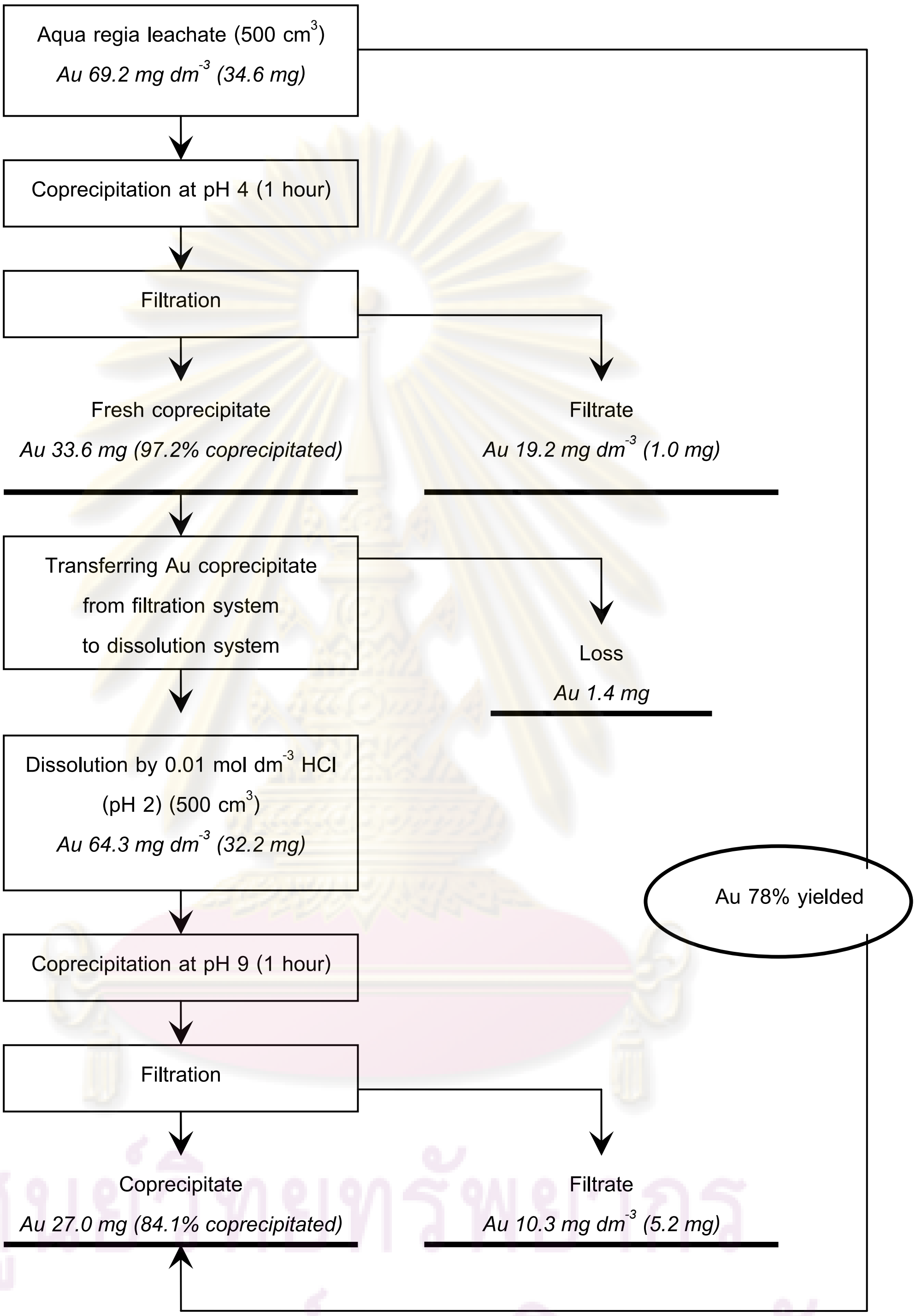


Figure 5.11 The mass balance diagram of new process for recovery of gold supported on Mn and Fe oxides by coprecipitation with $Fe(OH)_3$ and $Mn(OH)_2$.

5.5.8. Valence states of gold, iron and manganese from recovery of gold from computer CPU microprocessor scrap by coprecipitation with Mn(OH)$_2$

The valence states of gold, iron and manganese were confirmed by XPS spectra for gold, iron and manganese on coprecipitates recovered from computer CPU microprocessor. Gold presented as Au(0) as shown in Figure 5.12 with the peak position of 83.8 eV. In addition, the presence of Fe(III) could be observe in this Au4f region.

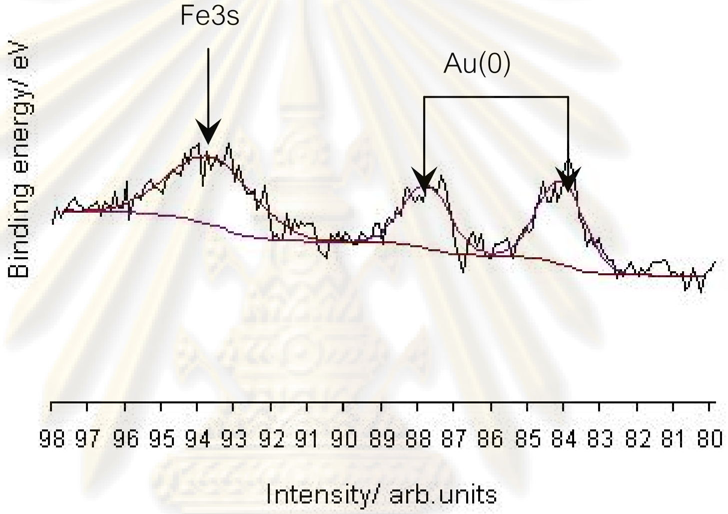


Figure 5.12 Au4f XPS spectra for coprecipitates from CPU microprocessor.

For iron and manganese supporting gold, it was found that iron presented as Fe(III) and Mn(IV) assigned and fitted. The peak positions of Au4f spectra shown for Au, Au-Pt and Au-Pd systems in Figures 3.10 are 84.1, 84.0 and 83.8 eV, respectively. Those of positions coincide with the metallic state of gold (Ikeo et al., 1991).

Figure 5.13 and 5.14 represents Fe2p and Mn2p XPS spectra for coprecipitates from acid solution of CPU microprocessor scrap, respectively The peak position of Fe doublet was assigned to 711.3 eV indicating that Fe presented as Fe(III) (Ikeo et al., 1991). Meanwhile, the peak position of Mn was assigned to 642.0 eV, indicating the presence of Mn(II) (Ikeo et al., 1991).

According to valence states of Au, Fe and Mn from the coprecipitate, it was confirmed that Au was effectively coprecipitated as metallic Au(0) with Fe(III) and Mn(II) hydroxides. Since the very thick coprecipitate was naturally dried in the room temperature and environment after fresh coprecipitation, Mn had not yet been oxidized to Mn(IV). However, it is expected that Mn(II) will be gradually oxidized to Mn(IV) to give MnO_2 when the coprecipitate is dried in a longer time.

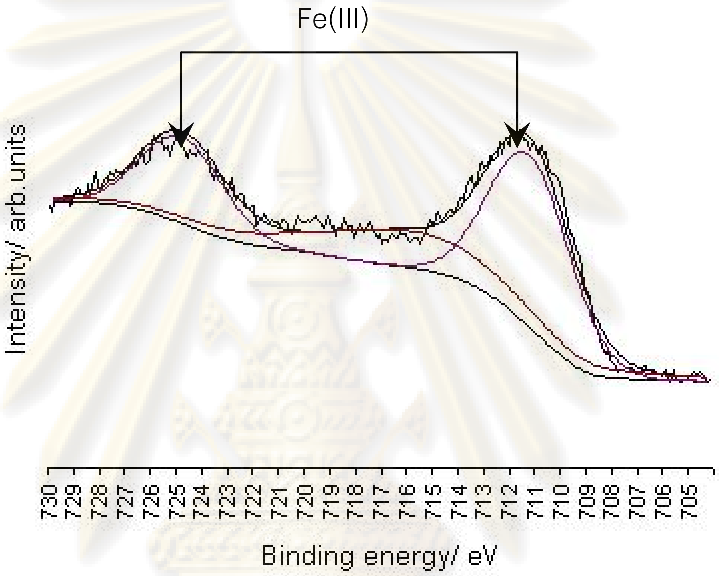


Figure 5.13 Fe2p XPS spectra for coprecipitates from CPU microprocessor.

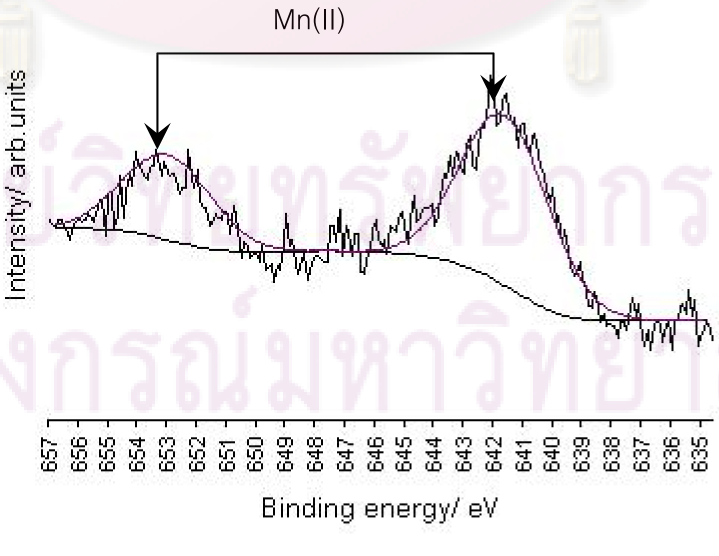


Figure 5.14 Mn2p XPS spectra for coprecipitates from CPU microprocessor.

CHAPTER VI

CONCLUSIONS AND RECOMMENDATION

6.1. Conclusions

6.1.1. Coprecipitation of precious metals with $Mn(OH)_2$

Coprecipitation of gold, platinum and palladium with $Mn(OH)_2$ was conducted at pH 9 at ambient temperature. The coprecipitation effectiveness of each precious metal and their changes in chemical states are as summarized in Table 6.1.

Table 6.1 Summarization of results from precious metals coprecipitation with $Mn(OH)_2$

Metals	%Coprecipitated	%Coprecipitated in the presence of Au	Valence states	
			Before coprecipitation	After coprecipitation
Mn	>99%	n/a	Mn(II)	Mn(II), Mn(IV)
Au with Mn	>99%	n/a	Au(III)	Au(0)
Pt with Mn	40%	60%*	Pt(IV)	Pt(II), Pt(IV)
Pd with Mn	>99%	>99%**	Pd(II)	Pd(II), Pd(0)***

Note: * %Coprecipitated of Pt in the presence of Au in which Au:Pt:Mn mole ratio was 6:1:10.

** %Coprecipitated of Pd in the presence of Au in which Au:Pd:Mn mole ratio was 6:1:10.

*** Pd(0) presented only on the coprecipitate from coprecipitation of Pd with $Mn(OH)_2$ in the presence of Au.

Au(III) and Pd(II) complex ions were effectively coprecipitated with $Mn(OH)_2$ as Au(0) and Pd(II), respectively, regardless of their initial concentrations. Pt(IV) complex ions were gradually but not effectively coprecipitated to Pt(IV) and partly Pt(II) upon reaction time. The coprecipitation rates of Pt were regardless of initial concentrations of Pt. However, coprecipitated Pt was enhanced by the presence of Au(III) complexes and could effectively coprecipitated after 24 hours. The optimum Au:Pt:Mn initial mole ratio giving the most effective coprecipitated percentage for both Au and Pt recovery was 6:1:10. It is noted that the maximum Au:Mn atomic ratio in which Au(III) will be completely coprecipitated as Au(0) is 0.6:1 (Yamashita et al., 2008).

Au(III) was reduced to nano-sized metallic Au (Au(0)), which was considered to be caused by electron transfer through Au-O-Mn bonding. Pt(IV) and Pd(II) was coprecipitated with $Mn(OH)_2$ by mechanical entrapment or incorporation into Mn oxides structures.

6.1.2. Selective separation of coprecipitated precious metals by HCl dissolution and confirmation of presence of Au nanoparticles

After coprecipitation, Au and Pd could be successfully separated from Pt by dissolving with 0.1 mol dm^{-3} HCl. This is because Au nanoparticles and coprecipitated Pd are soluble in HCl and Pt is incorporated in structure of MnO_2. The presence of Au nanoparticles coprecipitated with $Mn(OH)_2$ was confirmed by TEM and the dissolution of gold by HCl was confirmed by UV-Visible spectrometry.

6.1.3. Advantage of gold nanoparticles coprecipitated with $Mn(OH)_2$

Not only being soluble in such acid as HCl, Au nanoparticles could show catalytic ability for CO oxidation. The half conversion temperature given by coprecipitated Au nanoparticles $Mn(OH)_2$ catalyst was 80°C.

6.1.4. Metals distribution and composition on computer CPU microprocessor samples

Computer CPU microprocessor samples were characterized by SEM-EDX, XGT, AAS and ICP-AES. The microprocessor has three parts: body; pins; and; chip. Pins and bonding wires are the most abundant source of gold. The pins are made of Fe, Ni, Co and Cu composite; and coated by very thin Au layer.

The major precious metals contained in the microprocessor are Au, Ag and Pd; and the major base metals are Fe, Cu and Ni. The types of metal composed in each sample are quite similar; however, the amounts of metals are substantially varied.

6.1.5. The fundamental recovery processes of gold from computer CPU microprocessor scrap

Two new processes for recovery of gold from computer microprocessor scrap were introduced according to effect of pH on coprecipitation of metals in the aqua regia leachate from microprocessor and results from model experiments of precious metals coprecipitation with $Mn(OH)_2$. One process is a gold recovery using coprecipitation with metal hydroxides (Page 88). Another process is a gold recovery process using coprecipitation with $Mn(OH)_2$ (Page 95). Only the latter process was demonstrated in this study. The total gold recovery percentage of the new latter method was 78%.

6.2. Implication to recovery of precious metals from electronic wastes

Gold can be selectively concentrated as nanoparticles by coprecipitation with $Mn(OH)_2$, and can be easily dissolved with diluted HCl and converted to $[AuCl_4]^-$. Palladium was also effectively coprecipitated with $Mn(OH)_2$. Meanwhile, platinum, although generally is inert to chemical reactions, could be effectively simultaneously coprecipitated with gold and $Mn(OH)_2$ with the Au:Pt:Mn mole ratio of 6:1:10. According to results in this research, gold, platinum and palladium can be first leached out from electronic wastes by aqua regia, simultaneously coprecipitated with $Mn(OH)_2$, selectively separated by diluted HCl (0.1 mol dm^{-3}). The implication of precious metals recovery procedures from electronic wastes can be described as shown in Figure 6.1. This study also demonstrated that gold, platinum and palladium in solution can be simply and precisely determined in mg dm^{-3} level, which is suitable for recovery of precious metals from low concentrated sources such as electronic wastes. In addition, although the process uses chemical reagents, those of reagents could be simply stabilized or neutralized. Thus, the introduced precious metal recovery methods in this study do not emit hazardous substances to environment; therefore, they are considered to be environmental friendly.

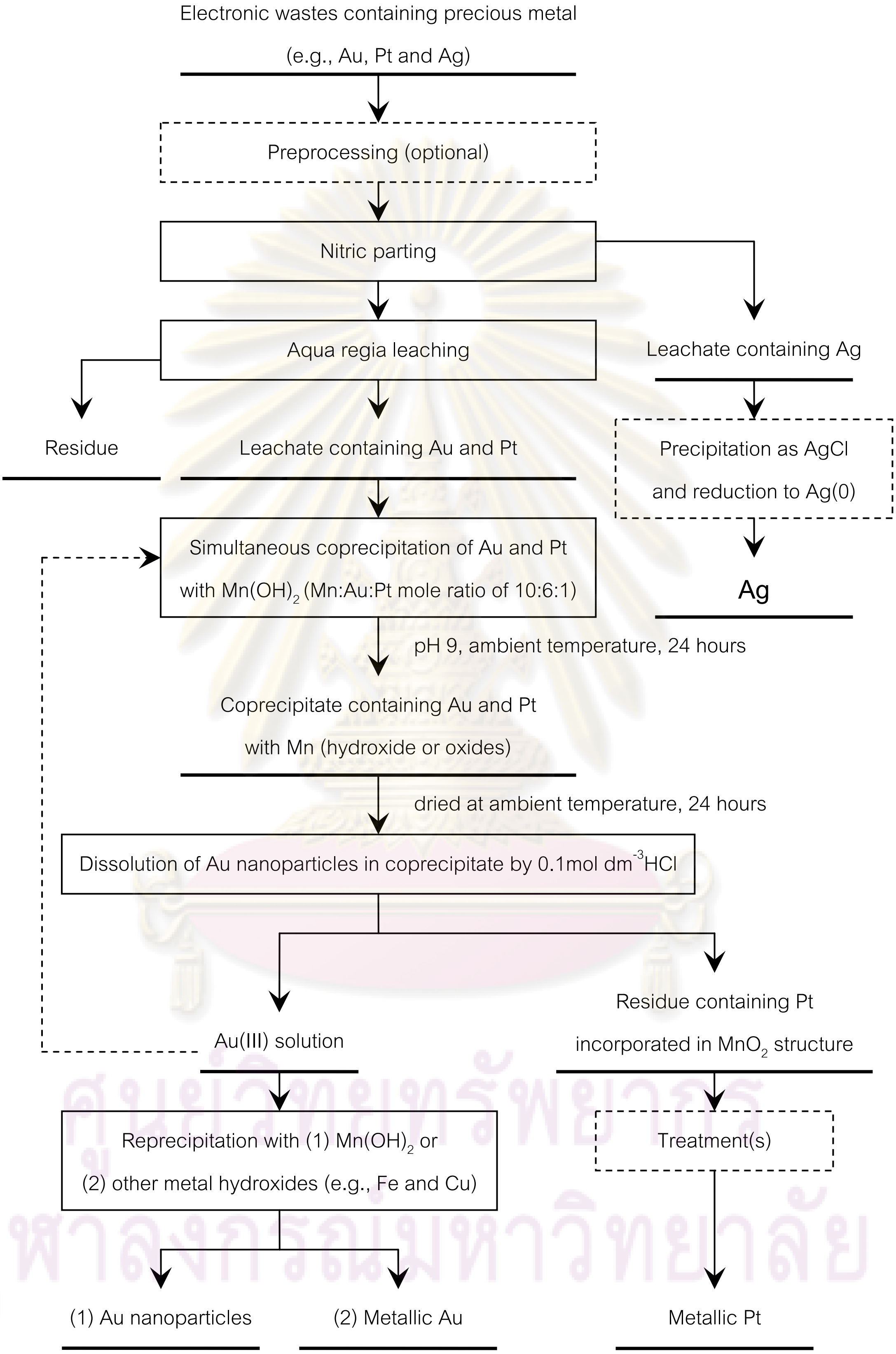


Figure 6.1 The generic process for precious metals recovery from electronic wastes.

6.3. Recommendation

According to this research, some relevant studies or investigations are necessary in order to develop the effective precious metals recovery process from electronic wastes. The recommended studies are as follow:

First of all, although the dissolution behaviors by HCl of coprecipitated palladium and platinum suggested the possibility of their selective separation, coprecipitation of coexisting palladium and platinum with $Mn(OH)_2$ should be investigated to confirm that they can be simultaneous coprecipitated with $Mn(OH)_2$ and subsequently selectively separation by HCl dissolution.

Second, to demonstrate recovery of platinum group elements by coprecipitation with $Mn(OH)_2$, other platinum group elements (e.g., rhodium (Rh)) should be studied in order to conduct general implication precious metals recovery by by coprecipitation with $Mn(OH)_2$ technique.

Third, to obtain metallic palladium and platinum, treatment of coprecipitated incorporated palladium and platinum into MnO_2 structure should be study in, either hydrometallurgical method or pyrometallurgical method.

Fourth, as well as palladium and platinum, study on treatment of coprecipitated gold to obtain bulk gold to complete gold recycling system is necessary. Optionally, to recycle gold as gold supported in metal oxides, the coprecipitated gold supported on metal oxides should be tested for their catalytic performances. Gold supported on Fe and Mn oxides from CPU microprocessor, for example, should be tested to confirm its catalytic ability for CO oxidation, too.

Finally, as noticed in recovery of precious metals in this research, there are several metals composed in CPU microprocessor scrap. Therefore, pre-processing such as acid parting to remove metals (e.g., silver, iron and copper) should be studied in order to concentrate target precious metals.

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APPENDIX

Appendix A

X-ray photoelectron spectroscopy and X-ray analytical microscopy

X-ray photoelectron spectroscopy

Introduction

X-ray photoelectron spectroscopy (XPS) or electron spectroscopy for chemical analysis (ESCA) is the analysis to determine the chemical or valance states of an atom. It works by detecting the energy from the target surface excited by X-ray, ultraviolet or electron. X-ray photoelectron spectroscopy is one of the most popular analyses among electron spectroscopy to measure photoelectron excited and released by X-ray.

Since the electron energy usually ranges from 30 to 3,000 eV in XPS analysis, electron has a strong interaction with the surface of the analyzed material. Therefore, the observed energy released within several nanometers at depth from the surface of the material without losing energy. This attributes the analytical tool for the surface analysis.

General characteristics of XPS are summarized as follow. Most elements can be a target element (except for H and He). Lower detection limit is about 0.1% weight of element. Surface analysis can be attained within several nanometers scale from the surface. Vertical profile can be attained by combination with ion spattering.

XPS has several advantages compared with other electron spectroscopy. The little charge up, for instance, enables us to analyze insulator. Moreover, there are no or little damage on the surface by X-ray irradiation. In addition, it is suitable for the analysis for chemical state. However, a spot diameter for analysis reached up to several ten micrometers, which is quite large for micro region analysis.

In this study, the XPS analysis was performed using Shimadzu Kratos AXIS 165 X-ray photoelectron spectrometer (Figure a.1) at the Center of Advanced Instrumental Analysis, Kyushu University, Japan.

Figure a.1 Shimadzu Kratos AXIS 165 X-ray photoelectron spectrometer.

Principle

Electron is released from atom by irradiation of monochromatic light due to photoelectric effect. The electron is called photoelectron and photoelectron spectroscopy use the energy of the electron. X-ray photoelectron spectroscopy uses X-ray as a probe. In general, following equation can explain the photoelectric effect.

$$E_{k,in} = h\nu - E_b$$

Ekin, hν and Eb represents kinetic energy, energy of incident X-ray and bonding energy, respectively. If monochromatic light is used, hν is constant. Then, Eb can be calculated by measurement of Ek,in instead of direct measurement of Eb. Bonding energy depends on elements and their orbital, therefore it is easy to identify element. In addition, since even same element and orbital can be affected by the surrounding chemical circumstances or state, the calculated bonding energy slightly varied. It is called chemical shift, and it enables us to identify the chemical state of target element such as metallic state or compounds.

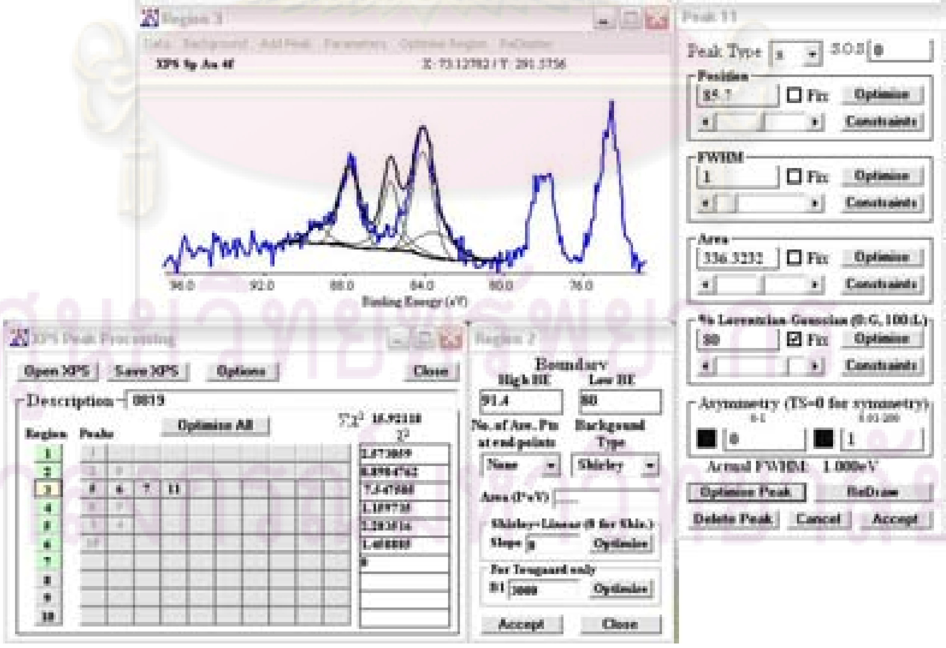
XPS is widely used for surface analysis due to its characteristics. Surface analysis always detects the signal from only the surface. It does not always require that generation area for signal (photoelectron) should be limited from the surface, but detected signal should be resulted in the surface area or separated from the signal derived from inner part. Photoelectron by X-ray irradiation is actually formed even inner part of the sample. However, the photoelectron from inner part easily loses its energy due to scattering, changes direction or is absorbed by the sample itself. Therefore, most of detected photoelectron is derived from the very surface and XPS allows us to observe the surface of the sample.

Application

XPS instruments are basically composed by detector, spectroscope, X-ray source, vacuum and sample chamber. XPS require ultra-vacuum environment (less than 10^{-6} Pa). Theoretically, sample can be solid, liquid or even air; however, solid materials including metal, semiconductor, organic matter and ceramics are usual target materials due to ultra-vacuum environment.

The sample is mounted on the holder and introduced to sample chamber. Usually, there are two sample chambers to achieve moderate vacuum in order to avoid flying sample or large quantity of gas release. The sample is easily contaminated by fine particle or adsorbing air. Therefore, ion etching using ion gun is usually conducted prior to analysis in order to clean the surface up. After introduced into the sample chamber, monochromatic light is irradiated on the surface. Unlike X-ray diffraction or X-ray fluorescent, XPS requires relatively lower energy up to several KeV due to surface analysis. Usually, Al Kα or Mg Kα is used for the X-ray source. Since those lines have small half bandwidth, high resolution analysis can be conducted. The photoelectron released from sample by X-ray irradiation is measured by concentric hemispherical analyzer with high resolution, and then separated energy by spectroscope is converted to electric signal by detector (e.g., multi channels plate). The raw result shows diagram of intensity (count per second) detected at various values of kinetic energy. However conventionally, bonding energy is automatically calculated from kinetic energy; therefore, diagram of intensity at various values of binding energy is prepared.

The obtained diagram is usually fitted by software (e.g., XPSPEAK) (Figure a.2) in order to correct the standard point, evaluate proper background and identify the peak or investigate the chemical shift. As previously mentioned, since each element or orbit has specific energy, the peak position is important to identify. In addition, measurement of reference materials is also necessary for evaluating chemical shift.



Description 0819

FWHM 1

Area 336.3232

% Lorentzian-Gaussian (0:G, 100:L) 80 ☑ Fix

High BE 91.4

Low BE 80

Background Type Shirley

Actual FWHM 1.000eV

Figure a.2 An example of XPS curve fitting (Au4f region) by XPSPEAK 4.1

X-ray analytical microscopy

Introduction

X-ray analytical microscope aims to practically analyze chemical composition and observe structures of a sample in micro region without preprocessing and destruction. SEM-EDX and XRF are also operated to analyze chemical composition with the similar purpose. However, SEM-EDX requires preprocessing (e.g., coating) or vacuum condition with destruction. XRF does not allow us to analyze the sample in micro region. In order to solve those of problems, X-ray analytical microscope is developed by the X-ray guide tube (XGT) techniques and has been used for easy analysis of chemical composition.

In this study, the XGT analysis was performed using Horiba XGT-5000 X-ray analytical microscope (Figure a.3) at the Center of Advanced Instrumental Analysis, Kyushu University, Japan.

Figure a.3 Horiba XGT-5000 X-ray analytical microscope.

Principles

For chemical analysis, X-ray fluorescence is widely used. When X-ray is irradiated on the sample, photoelectron is released from inner shell and the electron present in outer shell fall down to the inner shell to be stable. It is this timing that fluorescence X-ray is generated and the energy is equal to the energy gap of each shell. Since fluorescence X-ray is generated from many elements in the sample, it is important for fluorescence X-ray analysis to separate energy (wavelength) precisely. For this purpose, there are two major spectroscope, those are wavelength dispersive X-ray (WDX) and energy dispersive X-ray (EDX). Here, EDX is explained because X-ray analytical microscope adopts EDX.

In EDX, fluorescence X-ray is directly detected by solid state detector without any dispersive crystals from sample. EDX can catch wide range of energy and multi elemental analysis at the same time. However, the resolution is worse than WDX, thus, overlapping spectrum is often seen and is very difficult to separate. Generated fluorescence X-ray is counted as pulse with respect to energy, and intensity is used for quantitative analysis. Therefore, it is essential for quantitative analysis by EDX to measure intensity precisely. Generated fluorescence X-ray is affected by matrix of sample, coexisting elements, spectroscope, X-ray source and solid state detector. In fact, correction of the spectrum is also important such as using standard material for calibration or ZAF method.

Fluorescence X-ray analysis has many advantages such as quick analysis for several target elements (heavier than Be) at the same time, and nondestructive analysis without preprocessing.

Application

X-ray analytical microscope mainly includes X-ray source, X-ray guide tube and fluorescent X-ray detector. The key of X-ray analytical microscope is X-ray guide tube which allows X-ray to form high brightness and fine beam (around 10 micro meters). X-ray guide tube is a device which extremely smoothly irradiates X-ray with low angle, less than critical angle. The irradiated X-ray is all reflected without loss of any energy keeping strong X-ray as initially irradiated. X-ray is introduced to guide tube to form high brightness and fine beam, and then irradiated on the surface to observe fluorescent X-ray for chemical analysis and transmitted X-ray for the observation of sample. The examples of images captured from XGT analysis are as shown in Figure a.4.

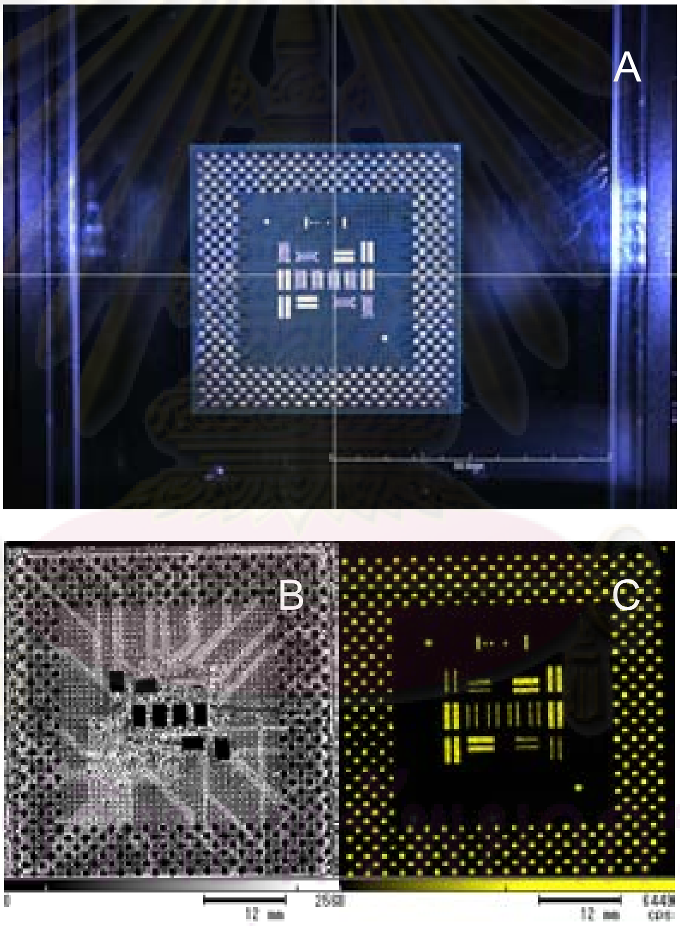


Figure a.4 (A) an image of CPU microprocessor sample placed inside the XGT sample chamber; (B) transmitted X-ray image and (C) characteristic X-ray image of Ni-K for the microprocessor sample.

BIOGRAPHY

Miss Chompunoot Wiraseranee was born on April 20, 1985 in Bangkok, Thailand. She entered Chulalongkorn University in May 2003 and received a Bachelor's degree of Engineering (Georesources Engineering) from the university in May 2007. Then, she directly continued her study in Master's degree at the same department with the study interests of precious metals recovery and recycling.

During Master's course, Miss Chompunoot Wiraseranee received a research scholarship, "Friendship Scholarship", from Kyushu University, Japan, to study and research in Department of Earth Resources Engineering, Faculty of Engineering, Kyushu University from October 2007 to September 2008.

From April 2008 to April 2009, she has four publications published, three as conference proceedings and one as a report of the Center of Advanced Instrumental Analysis of Kyushu University published in Japanese. She made two oral presentations in the 2nd International Workshop and Conference on Earth Resources Technology (Bangkok, Thailand in April 2008) and in the Society of Resource Geology (Tokyo, Japan in June 2008). In addition, she has been accepted for two oral presentations: in the 3rd International Conference on Processing Materials for Properties (PMP-III) (the conference was cancelled due to political situations in Thailand), and in the 3rd International Workshop and Conference on Earth Resources Technology (Sapporo, Japan); and one poster presentation which will be presented in GOLD 2009, Heidelberg, Germany in July 2009.