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วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต


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ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

RECOVERY OF PLATINUM GROUP METALS
FROM AUTOMOBILE CATALYTIC CONVERTERS



Miss Pornthip Parinayok

สถาบันวิทยบริการ
A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering Program in Geo-resources Engineering

Department of Mining and Petroleum Engineering

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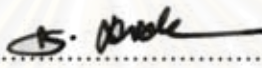
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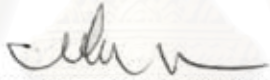
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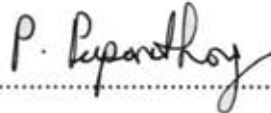
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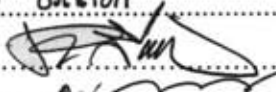


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พรทิพย์ ปริณายก : การเก็บกลับคืนโลหะกลุ่มแพลทินัมจากแคทาลิติกคอนเวอร์เตอร์ของรถยนต์ (RECOVERY OF PLATINUM GROUP METALS FROM AUTOMOBILE CATALYTIC CONVERTERS) อ. ที่ปรึกษา: รศ.ดร. ขวัญชัย ลิเผ่าพันธุ์, อ.ที่ปรึกษาร่วม: รศ.ดร. ดาวัลย์ วิวรรณนะเดช , 95 หน้า.

แพลทินัมเป็นโลหะมีค่าที่มีความสำคัญต่อมนุษย์ เนื่องจากคุณสมบัติทางฟิสิกส์และเคมีที่โดดเด่นของแพลทินัม จึงมีปริมาณความต้องการเพิ่มขึ้นเรื่อยๆ โดยเฉพาะการใช้ในแคทาลิติกคอนเวอร์เตอร์ของรถยนต์ ขณะที่ปริมาณแหล่งแร่แพลทินัมตามธรรมชาติมีอยู่อย่างจำกัด การคิดค้นและพัฒนาระบบการเก็บกลับคืนโลหะแพลทินัมจากแคทาลิติกคอนเวอร์เตอร์ที่ใช้แล้วของรถยนต์ ซึ่งจัดเป็นแหล่งทรัพยากรที่สำคัญของแพลทินัม จึงมีความสำคัญยิ่ง

กระบวนการเก็บกลับคืนโลหะแพลทินัมในการศึกษานี้ ประกอบด้วย 2 ขั้นตอน คือ การแยกสกัดแพลทินัมด้วยกรดกัดทองเข้มข้น และการคัดแยกโลหะแพลทินัมออกจากสารละลายด้วยเทคนิคการตกตะกอนร่วม สำหรับการแยกสกัดแพลทินัมออกจากแคทาลิติกคอนเวอร์เตอร์ โดยใช้กรดกัดทองเข้มข้นนั้น ได้ทำการศึกษาปัจจัยที่ส่งผลกระทบต่อ การละลาย ซึ่งได้แก่ อุณหภูมิและเวลาการแยกสกัด ผลการศึกษาพบว่าปริมาณแพลทินัมสามารถละลายออกมาได้มากที่สุด เมื่อทำการละลายอุณหภูมิ 90 องศาเซลเซียสเป็นเวลา 6 ชั่วโมง อย่างไรก็ตามที่อุณหภูมิและเวลาดังกล่าว อะลูมิเนียมในแคทาลิติกคอนเวอร์เตอร์ก็จะละลายออกมาในปริมาณมากด้วยเช่นกัน ซึ่งปริมาณอะลูมิเนียมจำนวนมากนี้จะไปยับยั้งการตกตะกอนร่วมของแพลทินัมกับเหล็กไฮดรอกไซด์ ส่งผลให้การตกตะกอนของแพลทินัมลดลง ดังนั้นอุณหภูมิและเวลาในการแยกสกัดแพลทินัมที่เหมาะสมที่สุดในการศึกษานี้ คือ ทำการละลายที่อุณหภูมิ 90 องศาเซลเซียสเป็นเวลา 1 ชั่วโมง ส่วนในขั้นตอนการคัดแยกโลหะแพลทินัมออกจากสารละลาย ได้ประยุกต์ใช้เทคนิคการตกตะกอนร่วมของแพลทินัมกับโลหะไฮดรอกไซด์หลายชนิด เช่น อะลูมิเนียม เหล็ก และแมกนีเซียม เนื่องจากโลหะทั้งสามชนิดเป็นองค์ประกอบสำคัญในแคทาลิติกคอนเวอร์เตอร์ และละลายอยู่ในสารละลายหลังจากการแยกสกัดอยู่แล้ว ทั้งนี้ได้ศึกษาปัจจัยที่มีผลต่อการตกตะกอน ซึ่งได้แก่ เวลา และ pH ของสารละลาย ผลการศึกษาพบว่าแพลทินัมสามารถตกตะกอนร่วมกับเหล็กไฮดรอกไซด์ได้เกือบทั้งหมดในเวลา 1 ชั่วโมง ที่ pH ประมาณ 6 นอกจากนี้ยังพบว่าเหล็ก (II) ไฮดรอกไซด์ สามารถรีดิวซ์แพลทินัมให้อยู่ในรูปโลหะแพลทินัมได้

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KEY WORD: AUTOMOBILE CATALYTIC CONVERTER/ PLATINUM RECOVERY/ RECYCLING/
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PORNTHIP PARINAYOK: RECOVERY OF PLATINUM GROUP METALS FROM AUTOMOBILE
CATALYTIC CONVERTERS. THESIS ADVISOR: ASSOC. PROF. QUANCHAI LEEPOWPANTH,
Ph.D., THESIS CO-ADVISOR: ASSOC.PROF. DAWAN WIWATTANADATE, Ph.D., 95 pp.

Platinum has played important roles in human life due to their specific physical and chemical properties. The demand of platinum was reported to be continuously increasing, especially the use in automobile catalytic converters, while natural resources of platinum becomes limited. Therefore, the study of platinum recovery from spent automobile catalytic converter, which is an important secondary resource of platinum, becomes significant.

In this study, platinum recovery process consists of two stages; platinum extraction by leaching with aqua regia and then platinum separation from the solution by co-precipitation. In the platinum extraction process, influences of time and temperature were investigated to identify optimum condition for the leaching process. The result showed that the maximum platinum extraction was obtained when leaching at 90 °C for 6 hours. However, at this condition, aluminum which is the major component in catalytic converter was also highly extracted. The coexistence of aluminum in the leachate will retard the co-precipitation of platinum (IV) with iron hydroxides, which is the second stage of platinum recovery. Hence, the optimum leaching condition here was considered to be leaching at 90°C for 1 hour. In the second stage of platinum recovery, platinum co-precipitation with various metal hydroxides was selected for this study. The metal hydroxides used in this study were hydroxides of Al, Mg, Fe (II) and Fe (III), which are major components in the catalytic converter and also dissolved in the leachate. Influences of pH and precipitation time were investigated. The result showed that almost all platinum (IV) was effectively co-precipitated with iron hydroxides at pH 6 in 1 hours. The chemical state of platinum investigated by XPS showed that co-precipitated platinum was partly reduced to platinum (II) with iron (III) hydroxide and some was further reduced to metallic platinum with iron (II) hydroxide. These facts suggest that iron hydroxide is considered as an effective carrier for co-precipitation of platinum.

Department... Mining and Petroleum Engineering...Student's signature.....^{R.P.P. Rukh.}
Field of study... Geo-resources Engineering.....Advisor's signature.....^{Q. Leepowpanth}
Academic year.....2007.....Co-advisor's signature.....^{Dawan Wiwattanadate}

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The author alone assumes responsibility for the conclusions of this thesis and any errors it may contain.

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CHAPTER I

INTRODUCTION

1.1 General introduction

Platinum has played many important roles in human life due to their specialty in both physical and chemical properties. Platinum has been employed in various applications; e.g. for corrosion resistant materials in chemical industry, for many devices in electrics industry, for ornaments in jewelry industry, for dental alloy in medical industry and for catalysts in the chemical, petroleum refining and automobile industries (Hoke, 1940; Loewen, 1995; Angelidis and Skouraki, 1996).

Since 1985, the automotive industry has emerged as a principal consumer of platinum group metals used for three way catalyst (reduction of NO_x and oxidation of CO and unburned hydrocarbon) to treat exhaust emissions (Benson et al., 2000). Such a three way catalyst forms honeycomb structure and is consisted of monolith substrate, catalyst layer (wash coat) and catalysts. Platinum group metals are deposited on catalytic layer, such as alumina with specific high surface area. As monolith substrate ceramic, such as cordierite $[(\text{Mg,Fe})_2\text{Al}_3(\text{Si}_5,\text{Al})\text{O}_{18}]$ is coated by alumina (Puig and Alvarado, 2006). Catalyst promoters, such as oxides of lanthanum and cerium, are usually used in the form of mixture in order to provide oxygen during catalytic reaction.

Demand for platinum is expected to grow by 2.9% to a record of 6.93 million ounces in 2007. The driving force behind this is the use of platinum in automobile catalysts, particularly those fitted to diesel vehicles. Altogether, the automotive sector will use 4.24 million ounces this year, a rise of 2.3% from 2006. On other hand, the supply for platinum decreased by 2% in 2007 (Johnson Matthey Platinum Interim Review 2007).

In spite of continuously increasing demand for platinum, while the natural resource of platinum is limited, the platinum recovery from spent automobile catalytic converters becomes significantly important.

Table 1.1 Platinum supply and demand in 2006 and 2007
(Johnson Matthey Platinum Interim Review, 2007)

Platinum Supply and Demand '000 oz		
	2006	2007
Supply		
South Africa	5,290	5,220
Russia	890	820
North America	345	340
Others	270	280
Total Supply	6,795	6,660
Demand		
Autocatalyst: gross	4,140	4,235
recovery	(855)	(885)
Jewellery	1,620	1,595
Industrial	1,865	1,905
Investment	(40)	75
Total Demand	6,730	6,925
Movements in Stocks	65	(265)

The recovery process of precious metals from industrial wastes generally consists of two stages. The first stage involves leaching or extraction of precious metals from the wastes by using hydrometallurgical and/or pyrometallurgical process. The second stage involves separation, concentration and/or purification of precious metals by using an appropriate technique such as precipitation, cementation, solvent extraction or ion exchange. Recently, successful recovery of gold from waste electronic products such as mobile phone by co-precipitation with Fe(III) hydroxide was reported as a new technique with an effective, practical and environmental friendly recovery system of gold (Kitamoto et al. 2007).

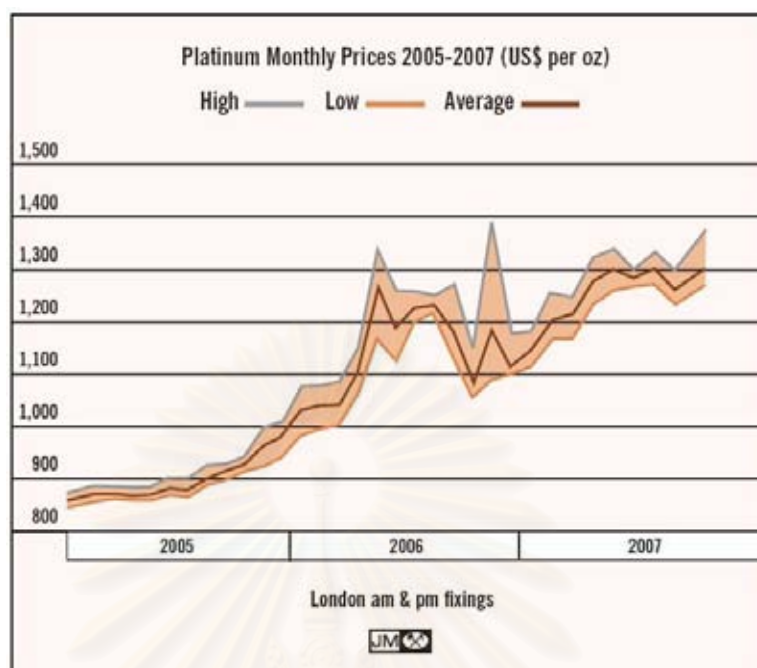


Figure 1.1 Platinum monthly prices in 2005-2007 (US\$ per oz)

(Johnson Matthey Platinum Interim Review, 2007)

In the present study, an aqua regia leaching experiment to extract platinum from spent automobile catalytic converters was applied as a function of temperature and time. Then, separation and concentration behavior platinum by co-precipitation with aluminum, magnesium and iron hydroxides were investigated as a function of pH and time by using synthetic leachate of aqua regia leaching.

1.2 Objective of this study

Objective of the present study is to establish an environmental friendly and systematic platinum recovery process from spent automobile catalytic converters. The recovery process consists of two stages; platinum extraction and platinum purification. On the first stage, platinum was extracted by aqua regia leaching method. On the second stage, platinum in a model leachate was separated and concentrated by co-precipitation with aluminum, magnesium and iron in the view of green and sustainable chemistry.

1.3 Outline of the study

The Schematic flowchart of platinum recovery process from spent automobile catalytic converters is shown in Figure 1.2.

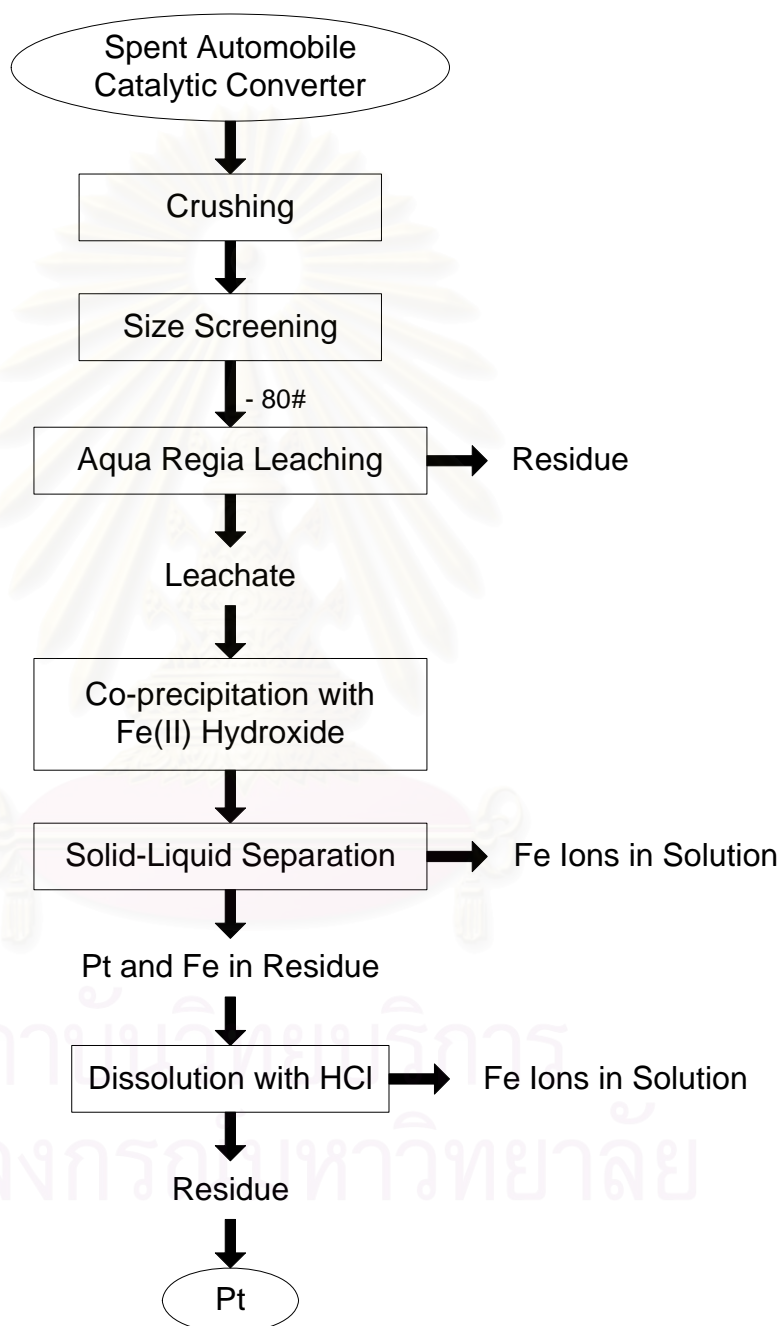


Figure 1.2 Schematic flowchart of the present study

1.4 Expected benefits

The benefits of this study is to obtain a new, practical, environmental friendly and effective platinum recovery process, which can be applied for platinum recycling industry.

1.5 Order of presentation

In order to present this research and make it easy to understand for readers, the author has divided this research into these 6 chapters;

Chapter 1 Introduction : General introduction, objectives of the study, outlines of the study and expected benefits.

Chapter 2 Backgrounds and literature reviews : The importance of catalytic converter, description of a catalytic converter, spent automobile catalytic converter in recycling industry and literature reviews.

Chapter 3 Characterization of spent automobile catalytic converter : Introduction, experimental, results and discussion, conclusion.

Chapter 4 Platinum extraction by aqua regia leaching : Introduction, experimental, results and discussion, conclusion.

Chapter 5 Platinum separation and concentration by co-precipitation with metals hydroxides : Introduction, experimental, results and discussion, conclusion.

Chapter 6 Conclusion : Conclusion, recommendation and suggestion.

CHAPTER II

BACKGROUNDS AND LITERATURE REVIEWS

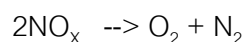
2.1 The importance of automobile catalytic converter

Air contamination by emissions from the operation of car engines has been of concern in many countries for over 30 years. Massive automobile traffic in highly populated areas leads to the release of vast amounts of carbon monoxide, nitrogen oxides and uncombusted hydrocarbons into the atmosphere (Fifield and Haines, 1995).

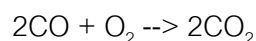
Car manufacturers claim that emissions of these contaminants can be reduced to almost negligible levels by improvement in the combustion engineering of the fuel-air mixture. However, it is also recognized that some time is still needed for the technology to mature and to comply with the current emission legislation without significantly penalizing the fuel consumption and the drive-ability of the vehicle. In the interim, the best known remedial action is to fit the cars with catalytic converters. These devices are capable of catalyzing the transformation of these compounds into less harmful chemicals such as carbon dioxide, nitrogen and water. The active components in charge of the catalytic action belong to the platinum group metals (PGMs), namely platinum, palladium and rhodium, which under optimal engine and catalyst operation, are capable of removing more than 90% of the pollutants from the exhaust gases (Lucena and Laserna, 2001). Catalytic converters are also used on generator sets, forklift, mining equipment, trucks, buses, trains, and other engine-equipped machine. The use of such converters has become one of the most important applications of heterogeneous catalysis (Emission control catalysts, 1975).

Catalytic converter fitted inside the exhaust pipe between combustion chamber and muffler, convert over 90% of hydrocarbons (HC), carbon monoxide (CO) and nitrogen oxide (NO_x) from the engine into less harmful carbon dioxide (CO_2), nitrogen (N_2) and water vapor as these following equations (Cooper et al., 1987):

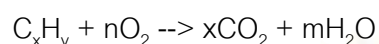
1. Reduction of nitrogen oxide to nitrogen and oxygen :



2. Oxidation of carbon monoxide to carbon dioxide :



3. Oxidation of unburned non-methane hydrocarbons :



2.2 Description of a catalytic converter

The main parts of a catalytic converter are as follow (Kuczka et al., 1991):

Monolith substrate or the core or the structured catalyst supports: Structured catalyst supports are widely used in automotive exhaust gas converters. Small sized channels are contained in monoliths to provide large surface area (Stary et al., 2006). Typically, both metal and ceramic are used in modern catalytic converters (Cybulski and Moujin, 1998).

Ceramic monoliths made from cordierite $[(\text{Mg,Fe})_2\text{Al}_3(\text{Si}_5,\text{Al})\text{O}_{18}]$ with square channels are employed quite extensively because of relatively low production costs (Heck and Farrauto, 2002).

The wash-coat layer: In an effort to make converters more efficient, a wash-coat layer is utilized. The most commonly used wash-coat material is $\gamma\text{-Al}_2\text{O}_3$ with a surface area of 100-200 m^2/g (Stary et al., 2006). The wash-coat layer, when added to the substrate, forms a rough-irregular surface which has a far greater surface area than the flat core surface, which is desirable to give the converter a larger surface area, and therefore more places for active precious metal sites (Kuczka et al., 1991). The excess of the deposited material (wash-coat) is then brown out with hot air and monolith is calcined to obtain the catalyst.

The catalysts: The main function of catalysts is to convert toxic gas into non-toxic one. Platinum is the most active catalyst, and is widely used. Palladium and rhodium are other two precious metals that are used in three-way catalytic converter to perform the three simultaneous tasks (one reduction and two oxidations as mentioned above). There

are some other metals (iron, nickel and copper) and oxides of rare earth elements (lanthanum and cerium), used as the catalyst promoters in the catalytic reaction (Kuczka et al., 1991).

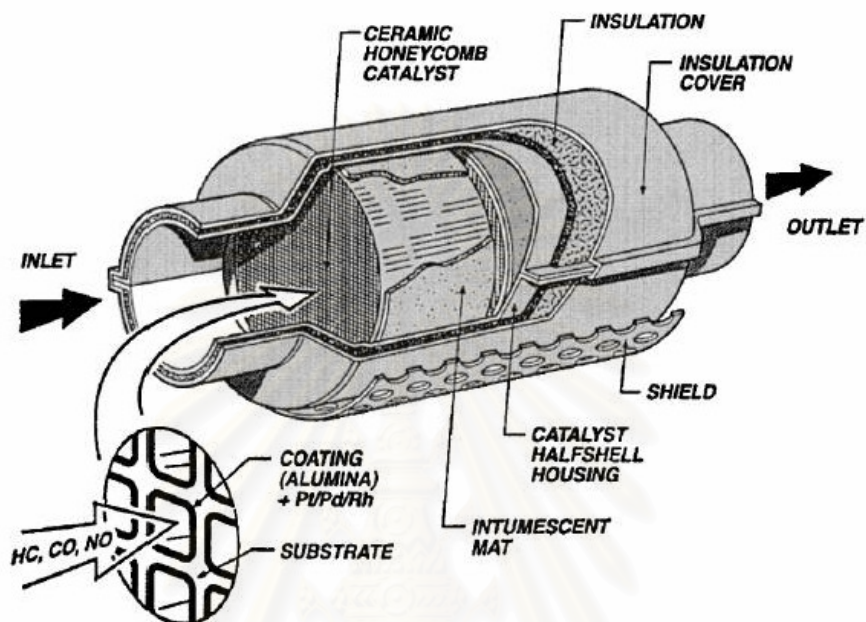


Figure 2.1 Automotive catalyst structural design including honeycomb support and mounting can(Heck and Ferrauto, 2001)



Figure 2.2 Spent automobile catalytic converter used in this present study



Figure 2.3 Cross section of spent automobile catalytic converter used in this present study

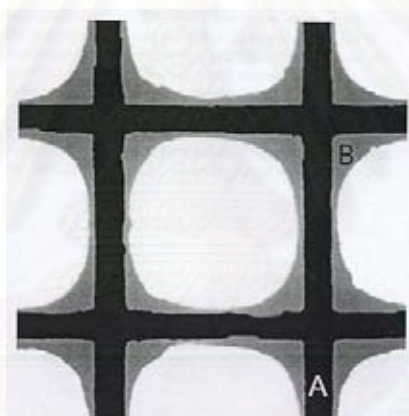


Figure 2.4 Cross section model of the honeycomb structure of a catalytic converter; (A) monolith substrate and (B) catalyst layer (Stary et al., 2006)

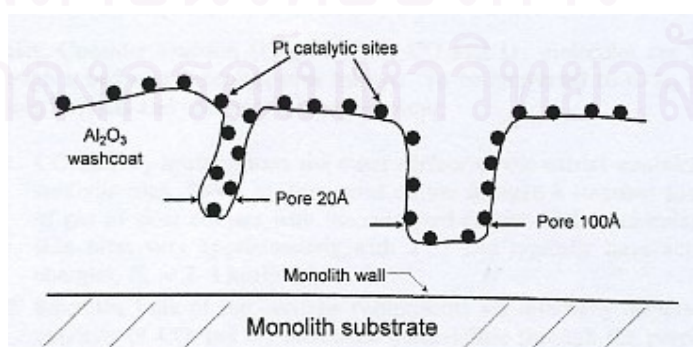


Figure 2.5 Conceptual model for catalytic converter sites dispersed on a high-surface-area Al_2O_3 carrier bonded to a monolith (Heck and Ferrauto, 2002).

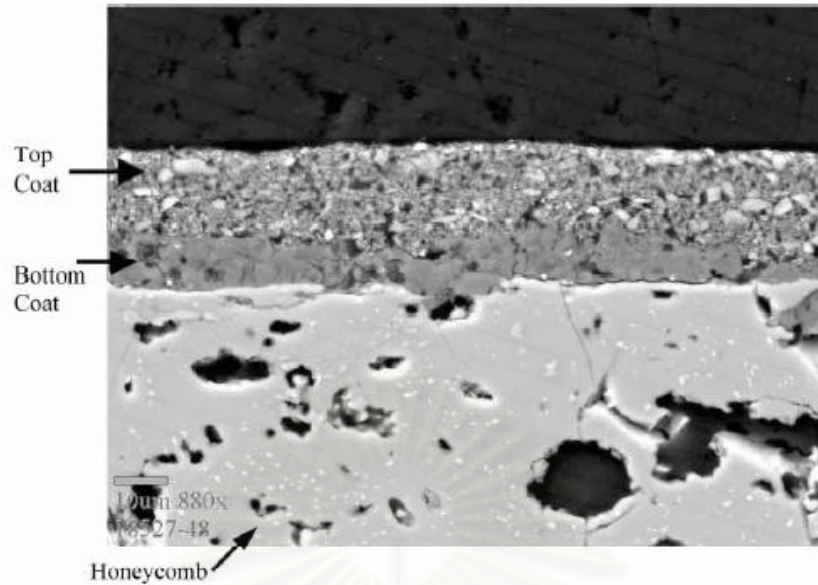


Figure 2.6 SEM image of different surface structures of wash-coat on automotive catalyst (Heck and Farrauto, 2001)

Figure 2.5 shows 20- and 100- Å pores into which Pt has been deposited by solution impregnation. The Pt particles or crystallites are represented as dots. When Al_2O_3 is bonded to a monolith honeycomb support, it is called wash-coat layer. The tiny Pt-containing particles shown in Figure 2.5 are dispersed through out the porous Al_2O_3 carrier network and generate a high-Pt surface area, in order to maximize the catalytic areas (Heck and Ferrauto, 2002).

The size and shape of converters, along with their platinum group metals catalyst loading, may vary according to the size of the vehicle's engine. An average catalytic converter contains 1.8 g of active constituent, consisting of 1.5 g platinum and 0.3 g rhodium. The weight percentage content of the ceramic substrate is 0.14-0.28% platinum and 0.03-0.05% rhodium. The weight of a ceramic catalytic converter depends on the vehicle type and ranges from 600-4,500 g (average weight 900 g), whereas its density is 500-600 g per 1 ceramic substrate (Mouza et al., 1995).

2.3 Recovery and recycling of the spent automobile catalytic converters

Recovery and recycling system for spent automobile catalytic converter generally consists of 6 stages shown below (Umicore: autocatalyst recycling process):

- 1) Collection
- 2) Decanning of ceramic converters
- 3) Shredding of metallic converters
- 4) Weighing and sampling
- 5) Assaying
- 6) Smelting and refining

1) Collection

The point of origin of a used or end-of-life catalytic converter is a service garage, a muffler shop, a car dismantling yard, a junkyard, a shredder of ferrous and non-ferrous scrap, a scrap collector. Collectors (whether specialize in spent catalytic converters, automotive spare parts or scrap in general) take it upon themselves to go to all these points, collect smaller individual quantities and bring it to their own yard or warehouse in order to accumulate larger quantities.

In a later step, these collectors will possibly sell to wholesale collectors, alternatively ship directly to a platinum group metal refiner for direct sale or toll-refining.

2) Decanning of ceramic converters

The decanning of (ceramic) catalytic converters, containing ceramic honeycomb bricks, implies opening the converter in order to separate the ceramic brick (or broken brick) from the steel can. This type of operation is mostly done by some forms of hydraulic shear (commonly called "guillotines" in North America; in Europe, the most common process is best described as a modified alligator shear). Alternative processes include a plasma burner or a disc saw, but the latter two processes are usually limited to small quantities.

3) Shredding of metallic converter

The shredding of (metallic) catalytic converters, containing a metallic substrate (rolled up corrugated foil), itself coated with a thin layer of metal oxides (wash-coat), is achieved by passing it through one or more different types of shredders, zerdirators, hammer mills, and the like, followed by separation of various fraction of steel scrap (such as can-fraction, foil-fraction) from the precious metal containing fraction (wash-coat).

4) Weighing and sampling of ceramic honeycomb or wash-coat

Making sure that material is accurately weighed and sampled (hence generates correct weights, moisture content and representative samples for assaying) is one of the most important steps in an assay-based transaction.

5) Assaying

Representative samples are assayed by the refinery's lab as well as, when desired, by alternatively an external lab. Assay of both labs can then be exchanged and compared, leading to settlement by splitting or, if the differences are too large, reliance on assays by a third party. Assaying can be done by a variety of different techniques, possibly leading to similar results.

6) Smelting and refining

Smelting and refining process can be divided into 2 operations:

- Precious metals operations

The main processing steps of the precious metals operations are the smelter, the Cu-leaching & electro winning plant, and the precious metals refinery. The operations are designed in such a way that raw materials can enter the flow chart at the most optimal process step, determined by their physical aspect, their analytical fingerprint and their (precious metals) value.

The smelter separates precious metals in a copper bullion, from mostly all other metals, concentrated in a lead slag, further treated at the Base Metals Operations. After

leaching out the copper in the leaching and Cu- electro winning plant, the precious metals are collected in a residue that is further refined at the precious metals refinery.

- **Base metals operations**

Main processing steps of the base metals operations are the lead blast furnace, lead refinery and the special metals plant. The lead blast furnace reduces the oxidized lead slag from the smelter together with high lead containing third party raw materials and transforms them into impure lead bullion, nickel speiss, copper matte and depleted slag.

The impure lead bullion, collecting most of the non-precious metals, is further treated in the lead refinery. Besides pure lead the process generates special metals residues. These are, together with the main side-streams of the precious metals operations, further refined into pure metals and metals salts in our special metals refinery to produce high quality indium, selenium, tellurium and antimonite. Some intermediates are tolled out to dedicated companies to produce tin and bismuth.

After leaching the nickel out of the nickel speiss (Ni-As-S alloy) and turning it into nickel sulfate, the remaining precious metals residue is treated at the precious metals refinery. The copper matte is returned to the smelter. The depleted blast furnace slag is physically calibrated for use in the concrete industry or used as dyke fortification substance.

Smelting and refining process of platinum mentioned above is used in the recycling industry. However, this method is not easy to operate or control and it also cause hazardous waste and pollution. This study, with the aim of developing a practical, environmental friendly and effective platinum recovery system, platinum recovery by co-precipitation method is focused in the point of view of green and sustainable chemistry.

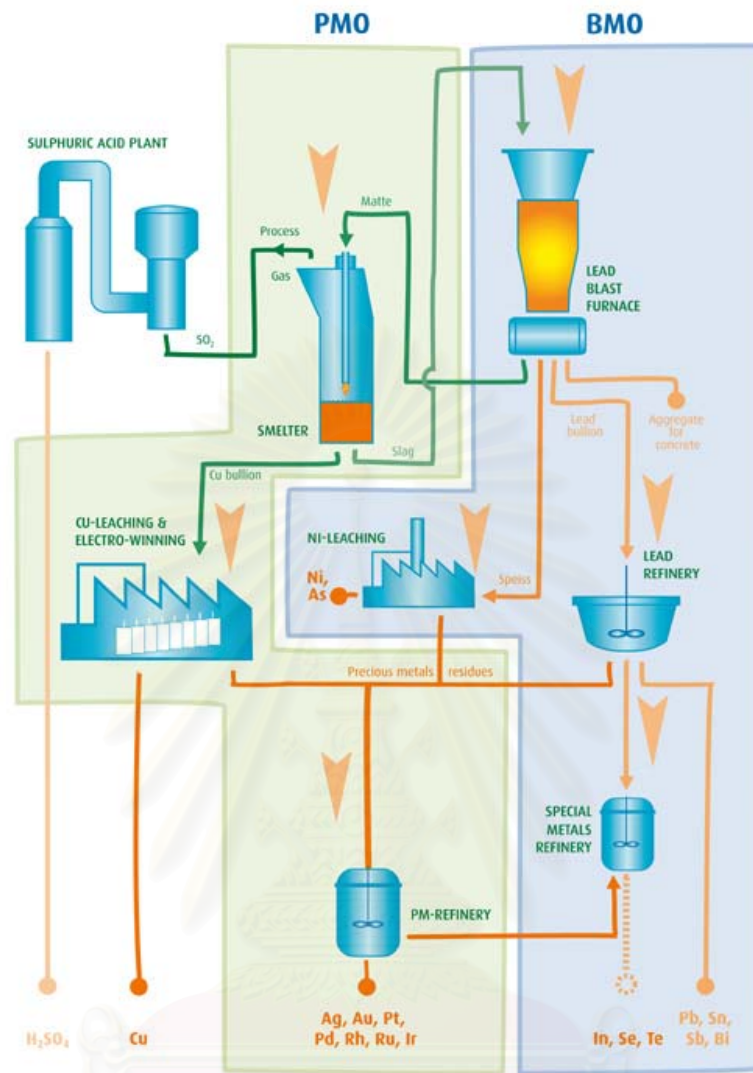


Figure 2.7 Schematic flow chart of precious metals operations (PMO) and base metals operations (BMO) (Umicore : autocatalyst recycling process)

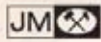
According to Johnson Matthey Platinum Interim Review 2007, it is forecasted that 88,500 oz of platinum will be reclaimed from spent automobile catalysts in 2007, 3.5% higher than the figure in 2006. Recovery rates continue to grow as a higher percentage of scrapped catalysts are recycled.

High commodity prices provide an incentive for the recycling industry to maximize collection and processing of spent catalysts in all regions. Most metal will be recovered in North America. However, the amount of platinum refined from end-of-life catalysts in Europe should increase more quickly, reflecting the rise in platinum loadings

on European diesel vehicles sold at the end of the last millennium, which are now being scrapped in significant numbers (Johnson Matthey Platinum Interim Review 2007).

Table 2.1 Platinum demand for autocatalyst recovery.
(Johnson Matthey Platinum Interim Review 2007)

Platinum Demand: Autocatalyst Recovery		
'000 oz		
	2006	2007
Europe	(185)	(215)
Japan	(35)	(35)
North America	(575)	(575)
Rest of the World	(60)	(60)
Total	(855)	(885)



The amount of spent automobile catalytic converters for the recycling industry in Thailand is estimated by the number of cars registered by the Department of Land Transport, Ministry of Transport. The use-of-life of an automobile catalytic converter is generally 5-7 years. Therefore, the number of spent automobile catalytic converters can be forecasted by estimating 50% of number of cars 7 years prior to now. For example, the number of spent automobile catalytic converters in 2007 is approximately 450,000 (50% of 900,000 - the number of cars registered in 2000). An average spent automobile catalytic converter contains 1.8 g. of catalyst (Mouza et al., 1995). The amount of spent autocatalyst in 2007 can be estimated by calculating the number of spent automobile catalytic converters and the average amount of autocatalyst in each automobile catalytic converter. Therefore, the amount of spent autocatalyst in 2007 is 25,000 oz.

It is obvious that the number of cars each year in Thailand has a tremendous impact on the amount of spent autocatalyst. Figure 2.8 shows the number of new cars registered each year in Thailand. The number of new cars has tendency to increase,

while the amount of spent autocatalyst will also increase. Therefore, the effective and environmental-friendly platinum recovery process is significantly required.

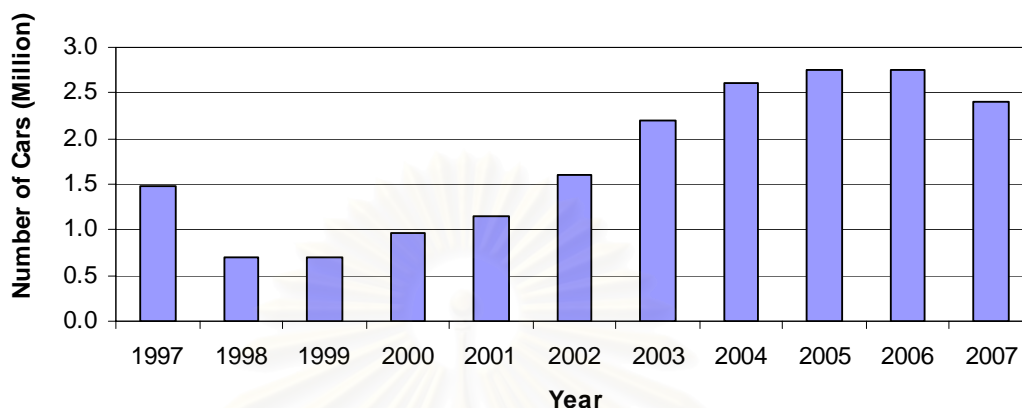


Figure 2.8 The number of new cars registered in Thailand
(Department of Land Transport, Ministry of Transport, Thailand)

2.4 Literature reviews

Desmond et al., 1991 studied about the leaching of automobile catalysts with NaCN solutions at high temperature to recover platinum group metals. The catalyst samples were crushed to minus 12 Mesh. Twenty-gram samples of catalysts were leached with 100 ml of 5% NaCN solution both with and without agitation for 1 hr at different temperatures. Best leaching results obtained at 160 °C with agitation were 97% of platinum and palladium and 90% of rhodium. Liquid-solid ratios were kept at 5. Thermal decomposition of all cyanide complex method was used to recover platinum group metal. PGM recovery reached 99.8% as a precipitate by treating the solutions at 250 °C for 1 hr, while the total cyanide concentration decreased to be less than 0.2 ppm.

Xueyi et al., 1999 studied a new process to recover platinum group metals from spent automobile catalytic converter. Sulphation roasting was employed followed by leaching with water, consequently the γ -Al₂O₃ in catalysts entered into solution and finally Al₂(SO₄)₃·nH₂O were produced as a by-product, whereas most of platinum group metals were enriched in residue; Then the dissolved platinum group metals were recovered by cementation with Al powder at 70 °C for 1 hr. By this process the total

recovery of platinum, palladium and rhodium reached 97-99%, 99% and 96% respectively. Assessment from technical and economic aspect showed that this process was suitable routine for such kind of waste treatment.

Barakat et al., 2004 studied about recovery of platinum from catalytic platinum gauze. There is usually a slow loss of this fine dust during the manufacture of nitric acid from ammonia. The catalytic platinum gauze contains 13.7% Pt, 1.3% Rh and other impurities such as iron oxide and silica, is deposited on the internal reactor walls and cooling coils. The dust was refluxed by aqua regia at a liquid-solid ratio of 7.5 for 1.5 hr to solubilise platinum for subsequent recovery. Platinum was separated from the leached liquor by direct precipitation and by solvent extraction using trioctylamine in kerosine. In both cases platinum was recovered as diammonium hexachloroplatinate by precipitation using ammonium chloride. The precipitate was decomposed by ignition to produce platinum powder with the purity of 97.9% and 99.9% for direct and SX routes, respectively. Platinum recovery of 97.5% was achieved by both routes.

Cao et al., 2005 suggested a new method for leaching platinum group metals from spent automobile catalytic converter by using HCl-NaClO-H₂O₂ solution. The spent catalysts were crushed to minus 30 Mesh (500 μm), in order to make the powder homogenous and easy to agitate during the leaching. The leaching process was based on the formation of their chloro-complexes by a mild solution mixture of NaClO-HCl and H₂O₂. The addition of NaClO exhibits a promotion effect on the leaching of palladium and rhodium, where the leaching rate has been increased with 4-8 percentages, but the effect on platinum leaching was found to be limited under identical leaching condition. The optimum condition to dissolve platinum, palladium and rhodium was achieved by using a mixture of 3% NaClO and 5 M HCl with addition of 1% H₂O₂. The recovery of platinum, palladium and rhodium after the 3 hr on stream of 65 °C leaching reached 88%, 99% and 77%, respectively.

Chairaksa et al., 2005 proposed a recovery process of gold and silver in secondary slag from gold refining process by co-precipitation with metal hydroxide.

Physical and chemical separations were used in this study. Precious metals were effectively concentrated from jewelry secondary slag by physical separation – crushing and gravity concentration. Next, the two-stage leaching by nitric acid and aqua regia is applied to remove based metals including copper, iron and silver, and to dissolve gold, respectively. More than 90% of gold were dissolved in aqua regia leaching within 1 hour. The dissolved solution containing gold ions were co-precipitated with metal (Fe, Cu) hydroxides at pH 6. The chlorohydroxy Au(III) complexes adsorbed on metal hydroxides are reduced to elemental gold without specific reducing agent and could be seen as gold particle. The purification of gold by dissolving with nitric acid was operated after co-precipitation.

Yamashita et al., 2008 studied about the co-precipitation of gold(III) complex ions with manganese(II) hydroxide and the stoichiometric reduction to atomic gold (Au(0)). The co-precipitation behavior of $[\text{AuCl}_{4-n}(\text{OH})_n]^-$ ($n=4$) (Au(III)) complex ions with manganese(II) hydroxide ($\text{Mn}(\text{OH})_2$) and the change in chemical state were examined, in order to elucidate the formation process of precursor of gold-supported manganese dioxide (MnO_2). The Au(III) complex ions were rapidly and effectively co-precipitated with $\text{Mn}(\text{OH})_2$ at pH 9. According to the Moessbauer spectra for Au co-precipitated with $\text{Mn}(\text{OH})_2$, below an Au content of 60 wt% in the co-precipitates, all of the co-precipitated Au existed in the atomic state (Au(0)), while, above an Au content of 65 wt%, part of gold existed in Au(III) state, and the proportion increased with increasing co-precipitated Au content. Based on the results of X-ray photoelectron spectroscopy, Mn(II) in $\text{Mn}(\text{OH})_2$ converted to Mn(IV) in conjunction with co-precipitation of Au(III) complex ions. These results indicate that the rapid stoichiometric reduction of Au(III) to Au(0) is caused by electron transfer from Mn(II) in $\text{Mn}(\text{OH})_2$ to the Au(III) complex ion through an Mn-O-Au bond.

CHAPTER III

CHARACTERIZATION OF SPENT AUTOMOBILE

CATALYTIC CONVERTER

3.1 Introduction

In this chapter, as a part of establishment of platinum recovery system, characterization of the spent automobile catalytic converter was investigated. The spent automobile catalytic converter used in this study was supplied from Toyota Motor Thailand Company.

Quantitative solid sample analysis of spent catalytic converter was done by X-ray diffraction (XRD) analysis and X-ray fluorescence spectrometer (XRF) analysis. However; for an accurate and precise analytical method for the determination of platinum, Scaccia and Goszczynska, 2004 suggested the analytical method of flame atomic absorption spectrometry (FAAS) and graphite furnace atomic absorption spectrometry (GFAAS). Digestion and decomposition method for the determination of platinum is also suggested by Bencs et al., 2003. The most common decomposition method is the acidic dissolution, based on the application of aqua regia and hydrofluoric acid, the latter used only in the presence of silica matrix constituents. Sulphation roasting of catalytic converter with sulfuric acid is suggested by Xueyi et al., 1999, in order to eliminate aluminum matrix constituents in platinum recovery process.

With the limitation of some analytical equipment, the decomposition method with the concept of eliminating silica and aluminum matrix constituents was used in this study, in order to determine the concentration of trace platinum in spent automobile catalytic converter accurately and precisely. The surface analysis of spent catalytic

converter was done by scanning electron microscopy with energy dispersive x-ray (SEM-EDX), in order to identify its structure and surface characteristics.

3.2 Experimental

Firstly, the spent automobile catalytic converter was disassembled the outside stainless steel case. The honeycomb cordierite (see figure 2.2 and 2.3), which is inside the stainless steel case, was primarily crushed with hammer in a large sheet of paper. Secondary crushing was done by hand crushing with agate mortar. Cao et al., 2005 suggested the size of catalyst powder less than 500 μm for platinum metal groups extraction by HCl-NaClO-H₂O₂ solution. The size of the crushed sample was less than 80# (approximately 200 μm) after sieving. The sample was kept in desiccators to avoid contamination.

XRD analysis of the catalytic converter was carried out by a Rigaku RINT 2100 X-ray diffractometer at Department Earth Resources Engineering, Kyushu University, Japan. Bulk chemical composition of spent automobile catalytic converter was determined by a Rigaku RIX 3100 X-ray fluorescence spectrometer (XRF) at Department Earth Resources Engineering, Kyushu University, Japan. The pieces of spent automobile catalytic converter were examined by Shimadzu SS-550 scanning electron microscopy (SEM) at the Center of Advanced Instrumental Analysis, Kyushu University, Japan in order to identify microstructure and characteristics of the catalysts.

In order to determine the trace amount of platinum, the decomposition of the catalytic converter was demonstrated. All chemicals were analytical reagent grade supplied from Wako chemical and all the solution was prepared with ultra pure water. The decomposition was attempted by four different systems (see also figure 3.1). A sample of 1 gram was weighed and placed into PFA (polymer of tetrafluoroethylene and perfluorovinylether) jar.

As a first step, 5 ml of either HNO₃ or H₂SO₄ (in order to eliminate aluminum and magnesium), 5 ml of HClO₄ (in order to enhance the efficiency of HF) and 20 ml of HF

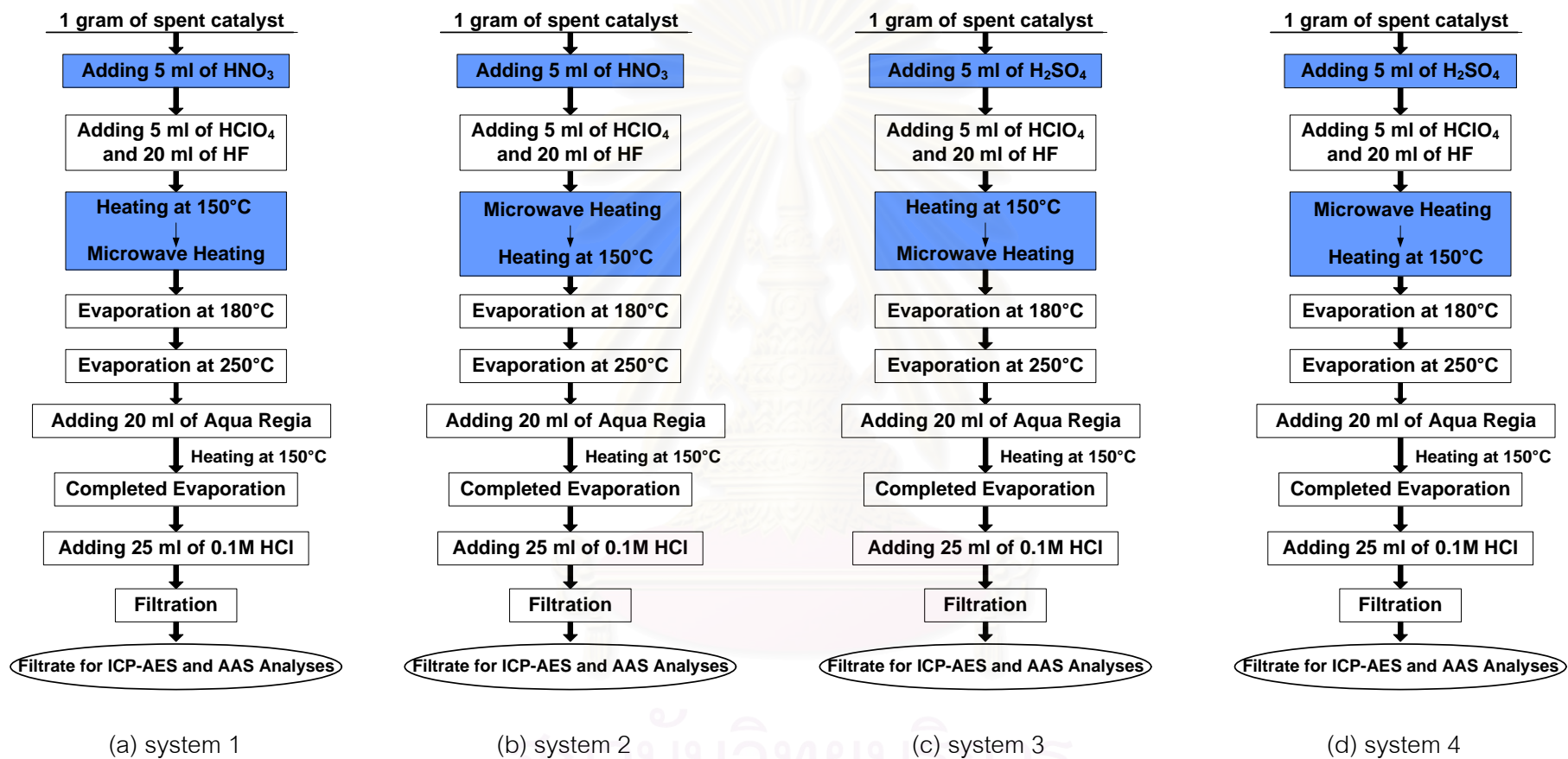


Figure 3.1 (a), (b), (c) and (d) Decomposition flow charts of 4 systems

(in order to eliminate silica) were added into the PFA jar. The sample was placed on the hot plate at 150 °C for four days, and followed with 0-8 times microwave heating for 40 seconds. Reverse process of the both steps was also attempted (see Figure 3.1). Both microwave and hot plate heating were used in this decomposition experiment, in order to see the maximum dissolution rate of matrix constituents (cordierite). Next, the sample solution was evaporated on the hot plate at 180 °C for one night, and then evaporated at 250 °C to form HClO_4 salt. After that, 20 ml of aqua regia was added into the PFA jar to dissolve residue and heated again at 150 °C for one night, and then evaporated completely. Finally, 25 ml of 0.1 M HCl was added into the PFA jar to recover platinum. The sample solution was filtered with 0.45 μm membrane filter. Concentrations of platinum and major metals (aluminum, magnesium and iron) in the filtrate were determined by ICP-AES and AAS.

3.3 Results and Discussion

Figure 3.2 shows that cordierite is the major component while peprossiite and chalcopyrite are the minor ones and platinum and palladium are the trace constituent.

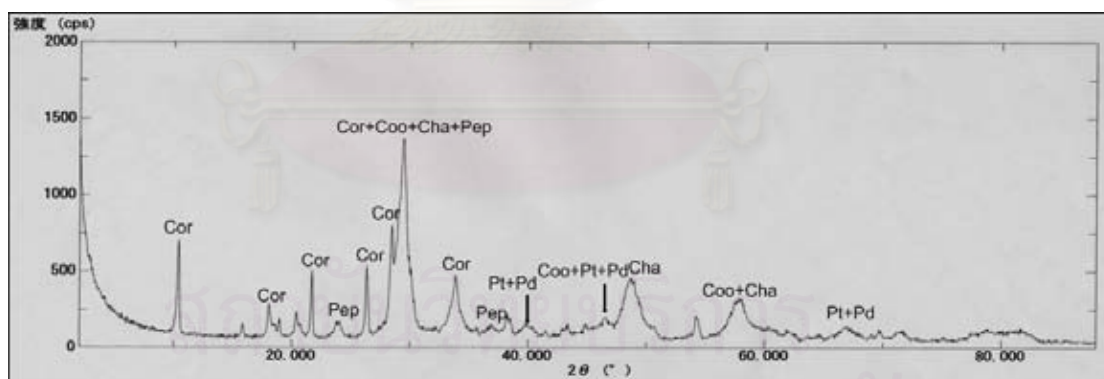


Figure 3.2 XRD pattern of the spent automobile catalytic converter.

Cor = Cordierite $((\text{Mg,Fe})_2\text{Al}_3(\text{Si}_5,\text{Al})\text{O}_{18})$, Pep = Peprossiite $((\text{Ce,Lu})(\text{Al}_3\text{O})_{2/3}\text{B}_4\text{O}_{10})$,

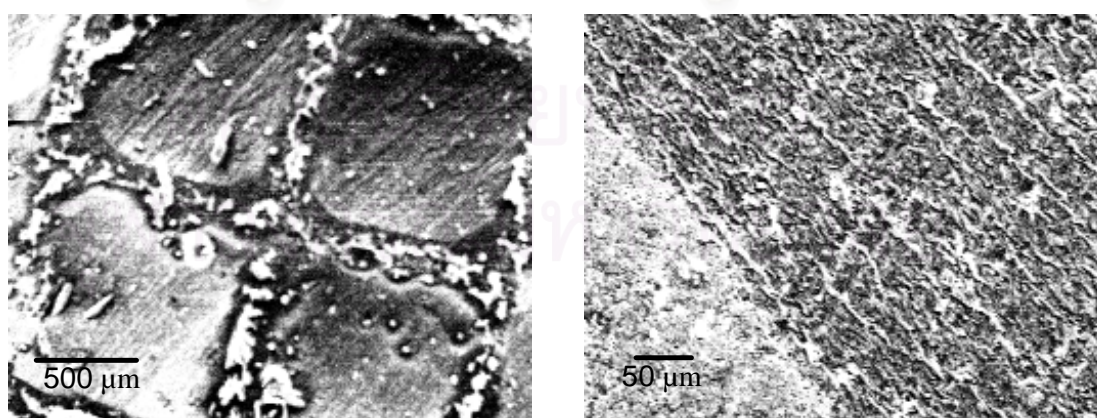
Coo = Cooperite $((\text{Pt,Pd,Ni})\text{S})$, Cha = Chalcopyrite (CuFeS_2) , Pt = Platinum

and Pd = Palladium

Table 3.1 Semi-quantitative analysis data of major components
of spent automobile catalysts by XRF

<i>Element</i>	<i>Si</i>	<i>Al</i>	<i>Fe</i>	<i>Mg</i>	<i>S</i>	<i>Ca</i>	<i>Ni</i>	<i>Zn</i>
						(%)		(ppm)
<i>Content</i>	34.28	33.34	0.43	3.32	7.61	0.14	220	225

The pieces of spent automobile catalytic converter were observed by SEM-EDX. Figure 3.3 (a) and (b) show the honeycomb structure of catalytic converter, which is perpendicular and parallel with the exhaust gas flow channel respectively. Two different surfaces corresponding to cordierite (dark layer) and alumina (bright layer) could be distinguished in figure 3.3 (b), while no difference was recognized in figure 3.3 (a). According to the EDX analysis, platinum existed on alumina wash-coat (figure 3.4 (a)), but not on cordierite. Moreover, rear earth elements, such as cerium and lanthanum, were also found on alumina wash-coat. Kaspar et al., 2003 reported that oxides of some rare earth elements provide many promotional effects in catalytic converter, such as the ability to promote the noble metal dispersion, increase the thermal stability of the Al_2O_3 support, favor the catalytic activity at the interfacial metal-support site, promote CO removal through oxidation employing a lattice oxygen, and the most important task – to store and release oxygen under the lean and rich condition.

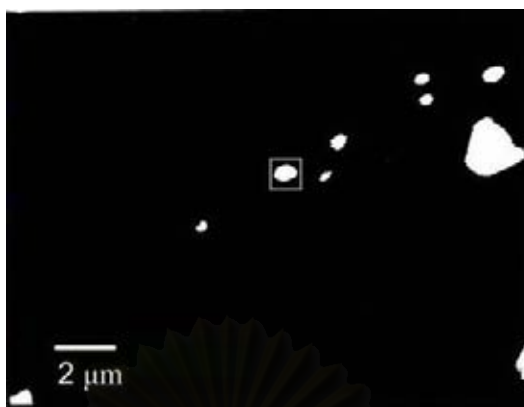


(a)

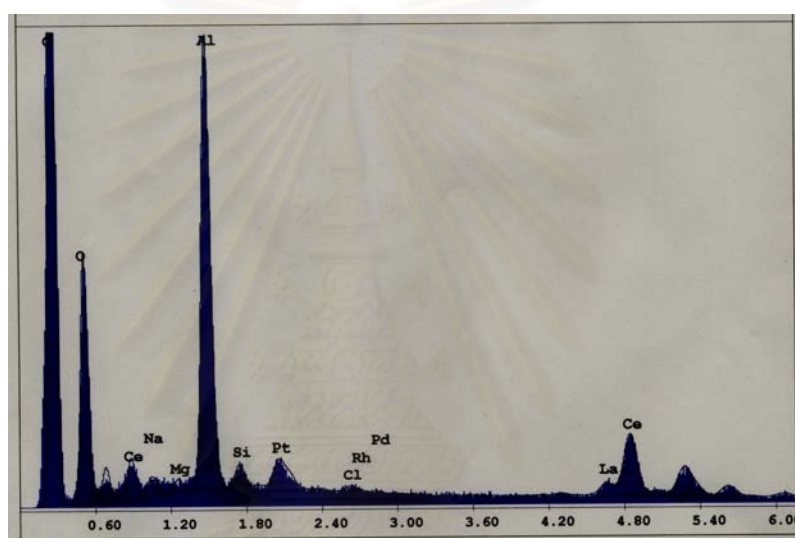
(b)

Figure 3.3 Secondary electron images for cross section of the catalytic converter

(a): across with the channel and (b): along with the channel.



(a)



(b)

Figure 3.4 (a) Backscattered electron image and
(b) EDX spectrum for the alumina wash-coat.

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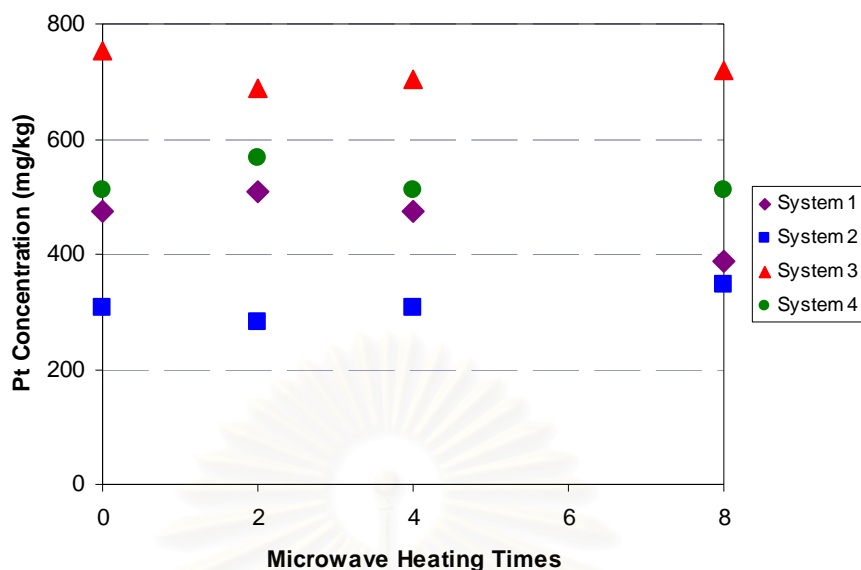


Figure 3.5 Percentage of platinum concentration with respect to microwave heating times in four different decomposition systems.

Table 3.2 Percentage of platinum concentration with respect to microwave heating times in four different decomposition systems.

Microwave heating time	Platinum concentration (mg/kg) ± S.D.			
	System 1	System 2	System 3	System 4
0	475.56±16.23	306.87±7.15	754.12±18.93	511.03±16.51
2	509.67±13.51	283.05±10.78	688.15±16.10	567.81±19.65
4	475.80±10.13	308.46±11.84	702.49±17.35	511.45±17.59
8	388.98±10.74	346.57±12.30	719.98±19.87	511.03±11.86

In four different systems of decompositions, the efficiency of nitric acid or sulfuric acid in order to eliminate the major elements of cordierite (structure of catalytic converter) and the effect of the order of microwave heating and 150°C hot plate heating on Pt decomposition are investigated.

In order to eliminate the major elements of cordierite (especially Al), the efficiency of nitric acid (HNO₃) was investigated in system 1 and system 2, and the efficiency of sulfuric acid (H₂SO₄) was investigated in system 3 and 4.

The effect of the order of microwave heating and 150°C hot plate heating on Pt decomposition can be seen between system 1 and 2 (with HNO₃ as a reagent to decompose cordierite's major elements) and between system 3 and 4 (with H₂SO₄ as a reagent to decompose cordierite's major elements). The effect of microwave heating time is also investigated in all systems.

The effect of microwave heating times on the percentage of platinum concentration in four different decomposition systems was shown in figure 3.5. The maximum concentration of platinum was determined as 754.12±18.93 mg/kg in system 3, without microwave heating. This value was defined as the initial concentration of platinum in this present study. In system 3 and 4, platinum concentration was relatively higher than in system 1 and 2. It can be explained that in system 3 and 4, aluminum was effectively dissolved with H₂SO₄ as a form of Al₂(SO₄)₃ and platinum liberation was relatively enhanced. Hence, it helps platinum to be dissolved effectively in aqua regia. Matjie et al.,2005 also reported the similar result that H₂SO₄ had more extraction efficiency than HNO₃ in selectively dissolved aluminum from spent catalysts contained aluminum, silica, zirconium, cobalt and platinum. However; the effect of microwave heating is not clearly seen in system 3. The maximum platinum concentration is without microwave heating and platinum concentration dropped to the lowest with 2 times-microwave heating, but it increased with higher microwave heating time. This may be due to the interference of secondary mineralization of Al-bearing minerals in the decomposition during repetition of microwave heating. While the maximum platinum concentration in system 3 was obtained without any microwave heating, system 1 and 4 had the same tendency in microwave heating. Maximum platinum concentration in system 1 and 4 were obtained with 2 times-microwave heating, while in system 2 platinum concentration reached its maximum at 8 times-microwave heating.

The effect of the order of microwave heating and 150°C hot plate heating can be seen in figure 3.5. It is obvious that platinum concentration in the system with 150°C heating on hot plate before microwave heating (system 1 and 3) was relatively higher than in one in the system with microwave heating before 150°C hot plate heating

(system 2 and 4). However; decomposing reagent (HNO_3 and H_2SO_4) give the bigger effect in eliminating cordierite's major element (aluminum and magnesium) than the order of microwave heating and 150°C hot plate heating and microwave heating time. The system with the maximum platinum concentration and the most efficiency in eliminating cordierite's major elements is system 3, system 4, system 1 and system 2.

3.4 Conclusion

X-ray diffraction (XRD) analysis and X-ray fluorescence spectrometer (XRF) analysis showed that the catalytic converter is mainly consisted of cordierite $[(\text{Mg,Fe})_2\text{Al}_3(\text{Si}_5,\text{Al})\text{O}_{18}]$ and alumina (Al_2O_3). Copper, nickel and zinc were also found as minor elements, while platinum and palladium were detected as trace constituents. Oxides of some rare earth elements, such as lanthanum and cerium were contained in catalytic converter with some promotional effects, especially storing and providing oxygen during catalytic reaction.

The honeycomb catalytic converter structures were observed by scanning electron microscopy with energy dispersive x-ray (SEM-EDX). Platinum as well as lanthanum and cerium were observed only on the surface of alumina not cordierite.

The accurate and precise determination of platinum in this spent automobile catalytic converter is done by four different decomposition methods with the aim of eliminating cordierite's major elements and as a result, the highest concentration of platinum in the solution after the decomposition. Four different decomposition systems were investigated in order to see the effect of decomposing reagent (HNO_3 and H_2SO_4), the order of microwave heating and 150°C hot plate heating and the microwave heating time. Decomposing reagent played the most important role in eliminating cordierite's major elements (aluminum and magnesium) as maximum platinum concentration is found 754.12 ± 18.93 mg/kg in system 3, while the effect of microwave heating was not clearly seen. Without microwave heating, platinum concentration in system 3 reached the maximum value. The effect of the order of microwave heating and 150°C heating on hot plate can be seen between system 1 and 2 (using HNO_3 as a decomposing

reagent) and between system 3 and 4 (using H_2SO_4 as a decomposing reagent). Heating at 150°C on hot plate before microwave heating is the method for higher concentration of platinum in the solution after decomposition as seen in system 1 and 3.



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CHAPTER IV

PLATINUM EXTRACTION WITH AQUA REGIA LEACHING

4.1 Introduction

Platinum is separated from the catalyst substrate with a variety of techniques, which may be classified into two major groups: hydrometallurgical and pyrometallurgical. Hydrometallurgical processes are classified in (Angelidis et al., 1996):

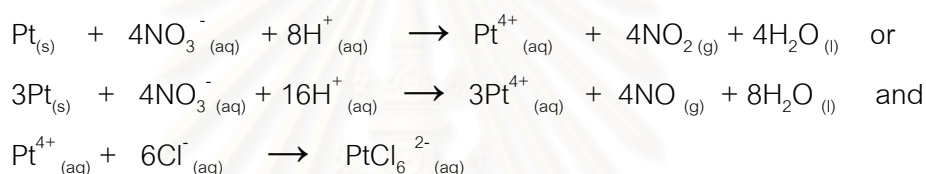
1. Substrate dissolution. The substrate is dissolved with non-oxidizing acid or base. The noble metals are not dissolved, but remaining as insoluble sludge.

2. Solution extraction. The noble metals are extracted from the substrate with an acid solution of an oxidant, leaving the bulk of the substrate unaffected.

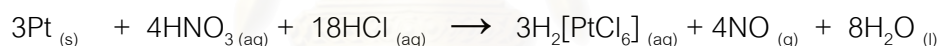
Matjie et al., 2005 studied the selective dissolution of alumina, cobalt and platinum from a calcined spent catalyst using different lixivants, such as NaOH and aqua regia. Approximately 89% of aluminum was selectively dissolved in NaOH with 9 bar elevated pressure and at 190 °C during two consecutive leaching steps, while platinum is insoluble residue. As a next step, aqua regia is used to dissolve platinum. Almost all of platinum was dissolved in aqua regia at 80 °C for 4 hours to form a solution of chloroplatinic acid ($\text{H}_2[\text{PtCl}_6]$).

It is reported that platinum leaching with aqua regia is temperature-dependant. Approximately 98% of platinum was leached by aqua regia after 1.5 hour at 109 °C with a liquid/solid ratio of 10 (Barakat and Mahmoud, 2004). Ultra fast microwave-assisted leaching for recovery of platinum from spent catalyst was investigated by Jafarifar et al., 2005. Platinum recovery by aqua regia leaching with 150 watt microwave power was very rapid reaching the maximum recovery of 98.3% after 5 minutes at a liquid/solid ratio of 2.

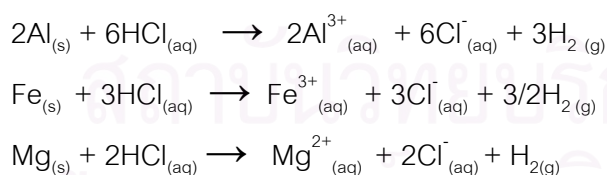
In this study, hydrometallurgical process of solution extraction is applied. Aqua regia is used as the leaching reagent with the point of view of sustainable and green chemistry. Aqua regia is a mixture of three parts of hydrochloric acid and one part of nitric acid. Aqua regia dissolves platinum, even though neither constituent acid will do so alone, because, in combination, each acid performs a different task. Nitric acid is a powerful oxidizer, which will actually dissolve a virtually undetectable amount of platinum, forming platinum ions (Pt^{4+}). The hydrochloric acid provides a ready supply of chloride ions (Cl^-), which react with platinum to produce chloroplatinate ions. The following equations show the different tasks performed by nitric acid and hydrochloric acid.



The simplified chemical reaction is the following:



The major elements in catalytic converter such as aluminum, iron and magnesium are also dissolved in aqua regia with chloride ions from hydrochloric acid as in these following equations:



Aqua regia leaching in this study is considered as a heterogeneous reaction, due to the fact that the reaction consists of solid substrate (spent automobile catalytic converter) and concentrated acid solution (aqua regia). The kinetic of this heterogeneous reaction can be explained by breaking down the overall reaction process into the following steps: (i) transport of reactants in solution to the solid-liquid interface; (ii) adsorption of reactants to the surface; (iii) reaction at the surface; (iv)

desorption of the soluble products of the reaction; (v) transport of soluble products away from the solid-liquid interface. Stages (i) and (v) are controlled by the rates of diffusion of the solute species and in a stirred system, by the hydrodynamics of the system. Stages (ii), (iii) and (iv) may be considered as chemically controlled process (Burkin, 1966). Therefore, aqua regia leaching process in this chapter is investigated as a function of time and temperature in stirred system.

4.2 Experimental

4.2.1 Instruments

1. 500 ml Pyrex beaker
2. Magnetic stirrer
3. Water bath boiler
4. Vacuum filter kit
5. Parafilm
6. Glass pipette
7. Thermometer
8. SEIKO / VISTA-MPX inductively coupled plasma atomic emission spectroscopy (ICP-AES)
9. NIPPON Jarrel Ash AA-835 flame atomic absorption spectrometer (AAS)

4.2.2 Chemical reagents

1. HNO_3 analytical grade (Wako chemical)
2. HCl analytical grade (Wako chemical)
3. Ultra pure water

4.2.3 Procedure

Aqua regia was used as the leaching reagent of platinum in spent automobile catalytic converter. All chemicals were analytical reagent grade supplied from Wako chemical and all the solution was prepared with ultra pure water. In order to investigate the leaching effect of time and temperature, the leaching experiments were conducted at 30°C , 60°C and 90°C for six hours. Amount of the sample was 2 g and volume of

aqua regia was 20 ml. The ratio of liquid and solid was kept at 10. All experiments were kept as a close system in water bath boiler and magnetically stirred. After 0.5, 1, 3 and 6 hours, aliquot of the sample solutions were collected and filtered with 0.45 μm membrane filter. All experiments were repeated 3 times, in order to obtain the accurate result and the standard deviation of the results. The concentration of Pt and major metals (Al, Mg and Fe) in filtrate were determined by ICP-AES (SEIKO Instrument / VISTA-MPX) and AAS (Jarrel Ash AA-835) at the department of Earth Resources Engineering, Kyushu University, Japan.

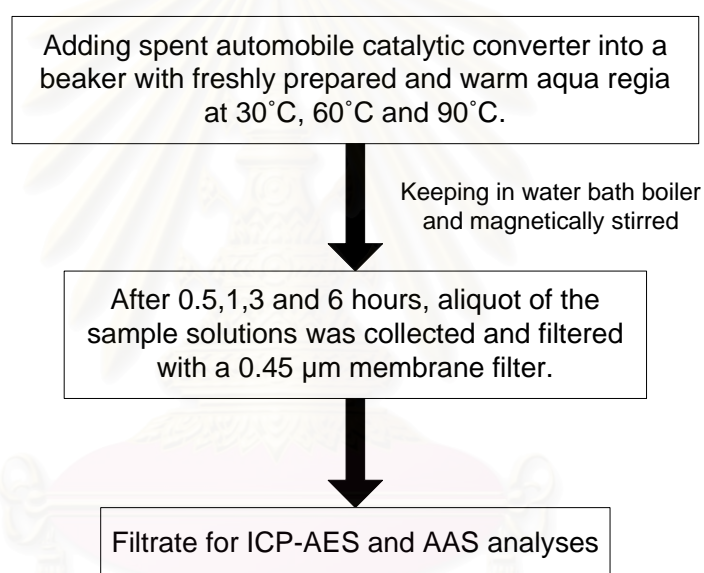


Figure 4.1 Schematic flowchart of aqua regia leaching

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4.3 Results and Discussion

The effect of time and temperature on platinum leaching by aqua regia is shown in figure 4.2. The amount of platinum leached increased with the increasing temperature and time. This temperature dependency on platinum leaching was also reported by Barakat et al., 2004. The ICP-AES solution analysis showed that the highest amount of platinum leached was 65.09 ± 1.65 ppm at 90°C after 6 hours. The amount corresponds to the 86.32% of total platinum composition. However, it is noticeable that the rate of platinum leaching at 30°C , 60°C and 90°C increased remarkably during the first hour and increased slightly after attaining the equilibrium after the first hour. This suggests that the trace amount of platinum on the surface of catalytic converter can be leached by the strong corrosion function of freshly prepared aqua regia. Hence, platinum leaching by aqua regia is a temperature dependent process rather than a time dependent process.

Due to the strong corrosion function of aqua regia, aluminum, iron and magnesium were also dissolved in the leachate. The effect of time and temperature on aluminum, iron and magnesium leaching by aqua regia is shown in figure 4.3, 4.4 and 4.5, respectively. The amount of aluminum, iron and magnesium leached increased with the increasing time and temperature. At 90°C aluminum, iron and magnesium leaching rate showed the similar tendency. The leaching rate increased sharply during the first 30 minutes and reached to higher concentration after 6 hours without any sign of attaining the equilibrium. It can be forecasted that after 6 hours aluminum, iron and magnesium would be still dissolved more in aqua regia. While at 30°C and 60°C , aluminum, iron and magnesium leaching rate also showed similar tendency. However, the leaching rate increased sharply only within first 30 minutes and after one hour the leaching rate remained constant and reached the equilibrium. The highest amounts of aluminum, iron and magnesium leached were $7,513 \pm 68$, 74.91 ± 2.74 and 211.73 ± 5.10 ppm at 90°C after 6 hours.

Hence, leaching of aluminum, iron and magnesium with aqua regia is also temperature dependent process. Moreover, at 90 °C the leaching also showed that it is time dependent process.

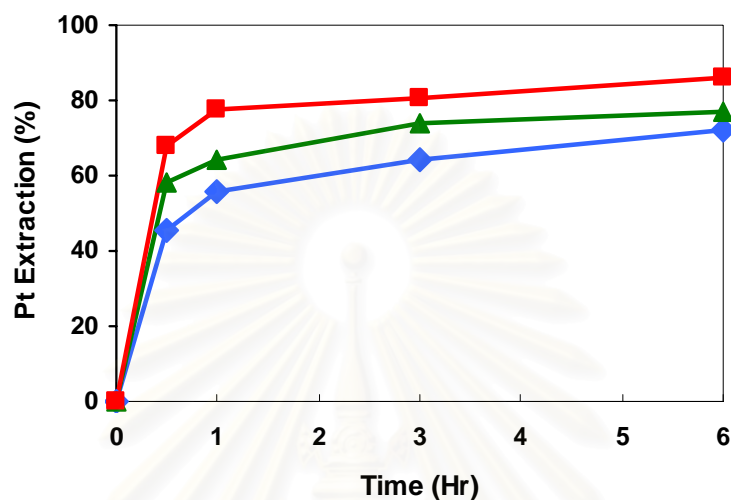


Figure 4.2 Effect of time and temperature on platinum leaching by aqua regia at 30 °C (♦), 60 °C (▲) and 90 °C (■)

Table 4.1 Effect of time and temperature on platinum leaching by aqua regia at 30 °C, 60 °C and 90 °C

Time	Pt leached ± S.D. in mg/l (%)		
	30 °C	60 °C	90 °C
30 min	34.25±0.09 (45.43%)	43.86±1.41 (58.17%)	50.95±1.17 (67.58%)
1 hour	42.22±1.32 (56.00%)	48.41±1.05 (64.20%)	58.41±1.41 (77.46%)
3 hours	48.63±1.59 (64.49%)	55.97±1.47 (74.22%)	60.65±2.07 (80.43%)
6 hours	54.41±1.56 (72.16%)	58.04±1.92 (76.98%)	65.09±1.65 (86.32%)

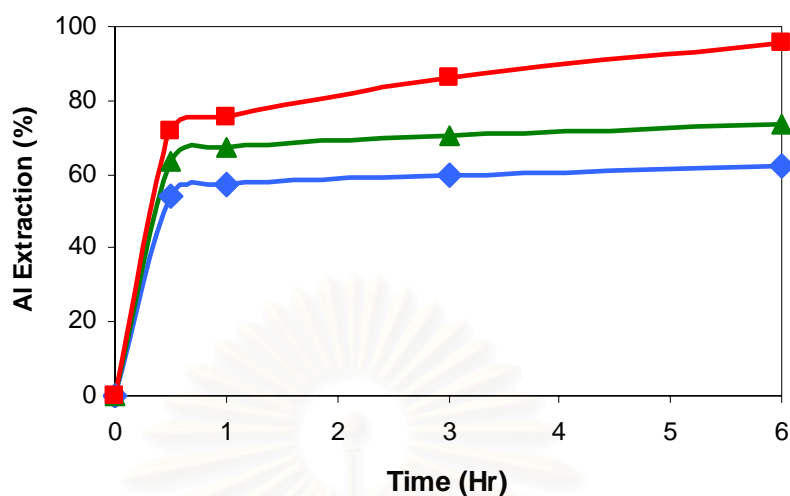


Figure 4.3 Effect of time and temperature on aluminum leaching by aqua regia at 30 °C (♦), 60 °C (▲) and 90 °C (■)

Table 4.2 Effect of time and temperature on aluminum leaching by aqua regia at 30 °C, 60 °C and 90 °C

Time	Al leached ± S.D. in mg/l (%)		
	30 °C	60 °C	90 °C
30 min	1,938±84 (54.29%)	2,328±126 (63.52%)	2,685±135 (71.84%)
1 hour	2,052±87 (57.44%)	2,457±123 (67.30%)	3,060±156 (75.69%)
3 hours	2,124±93 (59.99%)	2,655±111 (70.79%)	5,142±183 (86.40%)
6 hours	2,229±75 (62.41%)	2,988±141 (73.16%)	7,513±68 (95.84%)

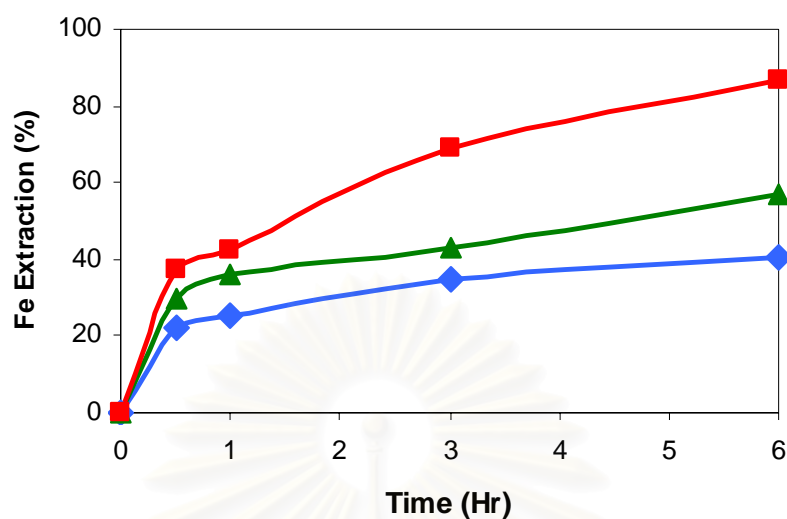


Figure 4.4 Effect of time and temperature on iron leaching by aqua regia at 30 °C (♦), 60 °C (▲) and 90 °C (■)

Table 4.3 Effect of time and temperature on iron leaching by aqua regia at 30 °C, 60 °C and 90 °C

Time	Fe leached ± S.D. in mg/l (%)		
	30 °C	60 °C	90 °C
30 min	7.30±0.20 (21.98%)	12.00±0.45 (30.03%)	18.35±0.65 (37.51%)
1 hour	9.20±0.20 (25.52%)	14.45±0.50 (36.09%)	20.18±0.78 (42.25%)
3 hours	13.85±0.45 (34.61%)	17.35±0.65 (43.33%)	50.54±1.48 (69.25%)
6 hours	16.10±0.70 (40.31%)	23.80±1.20 (56.97%)	74.91±2.74 (86.43%)

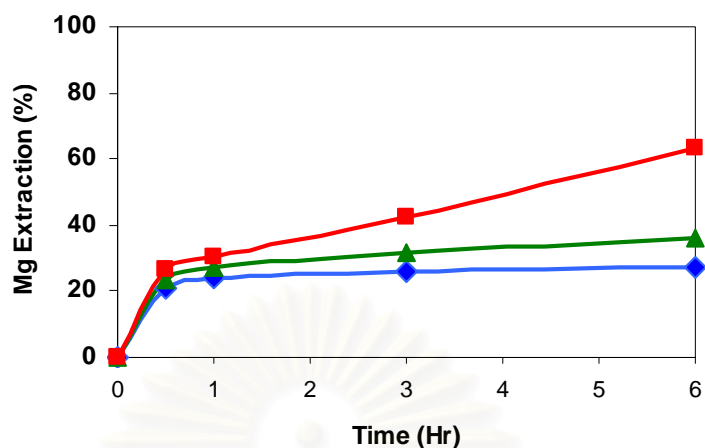


Figure 4.5 Effect of time and temperature on magnesium leaching by aqua regia at 30 °C (♦), 60 °C (▲) and 90 °C (■)

Table 4.4 Effect of time and temperature on magnesium leaching by aqua regia at 30 °C, 60 °C and 90 °C

Time	Mg leached ± S.D. in mg/l (%)		
	30 °C	60 °C	90 °C
30 min	70.53±1.92 (21.16%)	77.74±1.83 (23.65%)	88.23±1.91 (26.65%)
1 hour	80.53±2.04 (24.87%)	90.03±2.12 (27.76%)	102.00±2.67 (30.54%)
3 hours	87.76±1.84 (26.26%)	105.25±2.03 (31.65%)	140.53±3.48 (42.54%)
6 hours	90.14±1.98 (27.13%)	120.31±2.73 (36.87%)	211.73±5.10 (63.07%)

4.4 Conclusion

The leaching results showed that leaching time and temperature had significant effects on the extraction efficiency of platinum by aqua regia. The amount of platinum leached increase with the increasing time and temperature, especially the dramatically rise in the first hour, due to the strong corrosion function of freshly prepared aqua regia. However; temperature had more significant effect and platinum extraction by aqua regia leaching is temperature dependent process. The maximum platinum leached in this experiment is 65.09 ± 1.65 ppm at 90°C after 6 hours which corresponds to 86.32% of total platinum composition.

Aqua regia leaching results of aluminum, iron and magnesium showed that the extraction efficiency was effected by time and temperature. The amount of aluminum, iron and magnesium leached increased with the increasing time and temperature. At 90°C aluminum, iron and magnesium leaching rate increased continuously until 6 hours and had tendency to increase after 6 hours, while at 30°C and 60°C the leaching rate attained the equilibrium after the first hour. This result indicated that temperature had significant effect on metal extraction by aqua regia. The highest amounts of aluminum, iron and magnesium leached were $7,513 \pm 68$, 74.91 ± 2.74 and 211.73 ± 5.10 ppm at 90°C after 6 hours.

Platinum, aluminum, iron and magnesium extraction by aqua regia were effected by time and temperature, while temperature had significant effect. The highest amount of platinum, aluminum, iron and magnesium were leached at 90°C after 6 hours. However, the optimum condition of aqua regia leaching for platinum separation (co-precipitation method) in the next step, will be determined in chapter 5 after the effects of aluminum, iron and magnesium concentration in the leachate on platinum co-precipitation have been investigated.

CHAPTER V

PLATINUM SEPARATION AND CONCENTRATION BY CO-PRECIPIATION WITH METAL HYDROXIDES

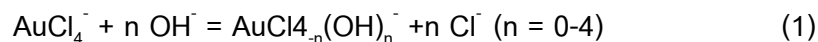
5.1 Introduction

Due to the continuously increasing demand of platinum during the past decade (Johnson Matthey Platinum Interim Review 2007), the low natural abundance of platinum and the hazardous waste from the industrial process of platinum separation and concentration (such as cyanidation method, solvent extraction method, zinc cementation method and ion exchange method), significant development of environmental friendly platinum recovery from spent automobile catalytic converter becomes requirement.

In this chapter, as a part of an establishment of a systematic platinum recovery process, a co-precipitation method is recommended. Many advantages of this method are easy to operate and control, environmental friendly and not costly. Co-precipitation method is quite suitable for these reasons (Uchida et al., 2002). It is reported that gold(III) ions are co-precipitated with iron(III) hydroxide and spontaneously reduced to elemental gold without reducing agent. This method is successfully observed and applied to recover gold from wastes of electronic products (Kitamoto et al., 2007) and to recover gold in jewelry secondary slag from gold refining process (Chairaksa et al., 2005). Also, co-precipitation of gold(III) complex ions with manganese(II) hydroxide and their stoichiometric reduction to elemental gold is reported by Yamashita et al., 2008.

Baes and Mesmer, 1976 reported that AuCl_4^- complex generally hydrolyze to give various chloro-hydroxy forms, $\text{AuCl}_{4-n}(\text{OH})_n^-$, in aqueous solution and the equilibrium among $\text{AuCl}_{4-n}(\text{OH})_n^-$ species attained in one day at ambient temperature even in alkaline solution. AuCl_4^- is the dominant species in acidic and chloride-rich solution, but

as pH increases, this molecule is believed to hydrolyze to form complexes with the general formula $[\text{AuCl}_n(\text{OH})_{4-n}]^-$ as follows:



AuCl_4^- was certainly hydrolyzed to form hydrolysis product species $\text{AuCl}_3(\text{OH})^-$, $\text{AuCl}_2(\text{OH})_2^-$ and $\text{AuCl}(\text{OH})_3^-$ with increasing pH. (figure 5.1)

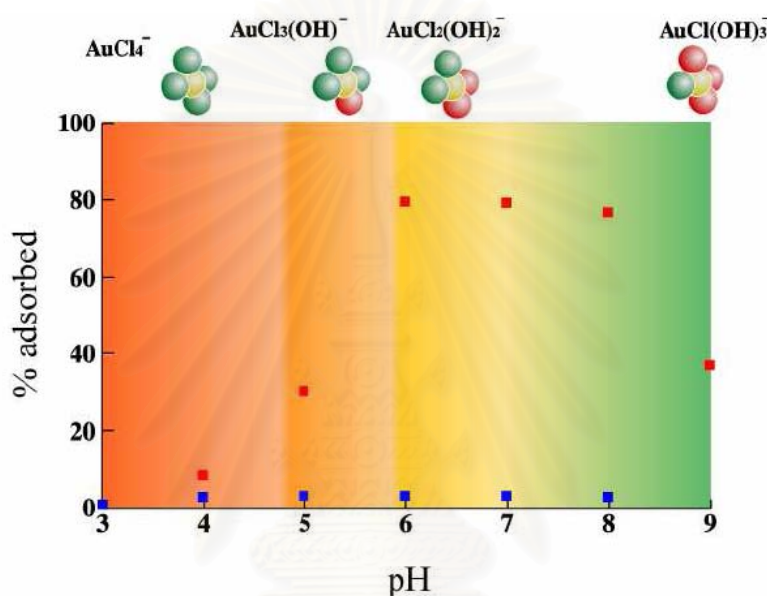
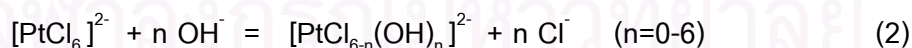


Figure 5.1 The effect of pH on adsorption of gold ions (below) and the pre-dominant gold species in each pH solution.

Similarly to AuCl_4^- complex, $[\text{PtCl}_6]^{2-}$ complex (complex ion of Pt^{4+}) is generally known to hydrolyze to give various chlorohydroxy forms, $[\text{PtCl}_{6-n}(\text{OH})_n]^{2-}$, in aqueous solution with the increasing pH as follows:



After the hydrolysis of $[\text{PtCl}_6]^{2-}$ complex, the electrostatic adsorption of $[\text{PtCl}_{6-n}(\text{OH})_n]^{2-}$ with iron hydroxide occurs spontaneously to form Fe-O-Pt bond. This electrostatic adsorption is controlled by the balance between the degree of hydrolysis of $[\text{PtCl}_6]^{2-}$ complex and the positive charge density on the surface of adsorbent such as iron hydroxide. The mechanism of the hydrolysis of $[\text{PtCl}_6]^{2-}$ complex and the

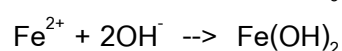
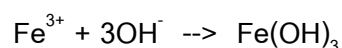
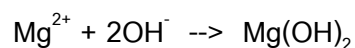
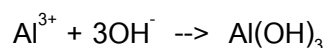
electrostatic adsorption of $[\text{PtCl}_{6-n}(\text{OH})_n]^{2-}$ with iron hydroxide in this study is similar to those of $[\text{AuCl}_4]^-$ complex explained by Uchida et al., 2002.

The reduction of platinum(IV) complex ions ($[\text{PtCl}_6]^{2-}$) to platinum metal (Pt(0)) is caused by the electron transfer from iron(II) ions to $[\text{PtCl}_6]^{2-}$ complex ion through the Fe-O-Pt bond. Platinum(IV) complex ions are reduced to platinum(0) only when iron(II) ions are co-precipitated. The redox reactions and standard redox potentials (E_0 : V vs. SHE) for Pt(IV)/Pt(0) and Fe(II)/Fe(0) are as follows (Andrews et al., 1997):



Generally, redox pairs with more negative E_0 values donate electron more easily. In contrast, redox pairs with more positives E_0 values accept electron more easily. As a result, as the E_0 values in Eq.(4) is relatively negative and the E_0 values in Eq.(3) is relatively positive, iron(II) donates electrons and platinum(IV) accepts electrons. After the consideration of redox potential between platinum(IV) and iron(II), it can be reasonably concluded that the reduction of platinum(IV) to platinum(0) is caused by electron transfer from iron(II) to platinum(IV) complex ions through the Fe-O-Pt bond as described above.

Meanwhile, the metal ions (aluminum, magnesium and iron ions) precipitate to metal hydroxides. The precipitation of these metal is controlled by log metal ion activity and pH as shown in figure 5.2. Ideally aluminum, magnesium and iron ions start to precipitate pH 4, 11 and 4, respectively as follow equations:



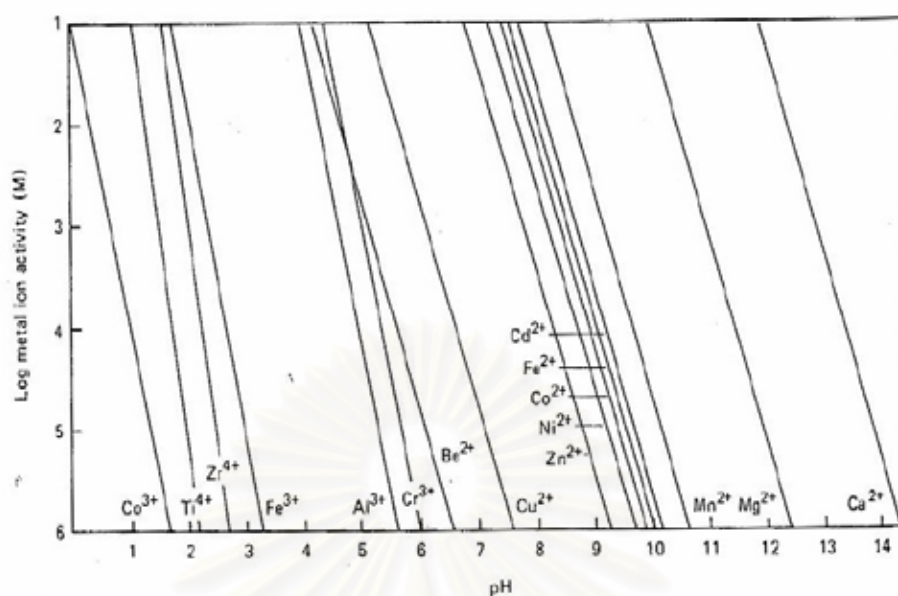


Figure 5.2 Precipitation diagram for metal hydroxides

Two experiments were conducted in this chapter: preliminary co-precipitation experiments of platinum with hydroxides of aluminum, magnesium, iron and co-precipitation experiments of the synthetic leachate from aqua regia leaching.

The co-precipitation behaviors of platinum with hydroxides of aluminum, magnesium, iron were preliminary investigated as a function of pH and time. Aluminum, magnesium and iron hydroxides were investigated because of their major components in the catalytic converter. During the leaching process, these metals were also dissolved in the leachate. The experiment of platinum co-precipitation was investigated separately with each metal hydroxide, in order to see the effect of each metal. From the point of view of easy, economics and green chemistry, it is significant to examine the co-precipitation behaviors of platinum with hydroxides of these metals before establishing the platinum recovery system.

Next, co-precipitation experiment of the synthetic leachate was demonstrated in order to obtain the practical recovery of platinum from spent automobile catalytic converter. The concentration of aluminum, iron, magnesium and platinum in model leachate prepared were based on the result of aqua regia leaching in chapter 4. The details of this model experiment are described later in topic 5.3.

5.2 Preliminary co-precipitation experiments of platinum

5.2.1 Experimental

5.2.1.1 Instruments

1. 1000 ml Pyrex beaker
2. 500 ml Pyrex volumetric flask
3. Magnetic stirrer
4. pH meter (Horiba F-21 Tou pH Series)
5. Vacuum filter kit
6. 0.45 μm membrane filter
7. Glass pipette
8. Parafilm
9. SEIKO / VISTA-MPX inductively coupled plasma atomic emission spectroscopy (ICP-AES)
10. NIPPON Jarrel Ash AA-835 flame atomic absorption spectrometer (AAS)
11. Shimadzu / KRATOS AXIS-165 X-ray photoelectron spectroscopy (XPS)

5.2.1.2 Chemical reagents

1. Platinum standard solution for atomic absorption spectrometry (Wako Chemical)
2. $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ analytical grade (Wako Chemical)
3. $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ analytical grade (Wako Chemical)
4. $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ analytical grade (Wako Chemical)
5. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ analytical grade (Wako Chemical)
6. HCl analytical grade (Wako Chemical)
7. NaOH analytical grade (Wako Chemical)
8. NaCl analytical grade (Wako Chemical)
9. Ultra pure water

5.2.1.3 Sample solution and procedure

Analytical grade reagents were used in this study. All the solutions were prepared with ultra pure water. Aluminum, magnesium, iron(II) and iron(III) stock solution (1 mol dm^{-3}) were prepared by dissolving $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in 0.1 mol dm^{-3} hydrochloric acid. Aluminum, magnesium and iron concentration were analyzed by ICP-AES. Platinum standard solution for atomic absorption spectrometry (AAS) (1000 mg dm^{-3} as Pt, in 1 mol dm^{-3} hydrochloric acid) was used as a stock solution of platinum. Sample solutions (500 cm^3) containing 5 mg dm^{-3} of platinum and 135, 120 and 560 mg dm^{-3} of aluminum, magnesium, iron(II) and iron(III) ions, respectively and were prepared by diluting and mixing the stock solutions. The ionic strength of the sample solutions was adjusted to $7,000 \text{ mg dm}^{-3}$ with NaCl solution, in order to stabilize the pH of the sample solution. All sample solutions were freshly prepared with ultra pure water before conducting each experiment. However, another set of sample solution (500 cm^3) containing 100 mg dm^{-3} of platinum and 560 mg dm^{-3} of each iron(II) and iron(III) hydroxide were prepared in order to conduct the co-precipitation experiment and obtain the solid sample for X-ray photoelectron spectroscopy (XPS) analysis, due to the detection limit of XPS analysis.

In order to investigate the co-precipitation behaviors of platinum with aluminum, magnesium, iron(II) and iron(III) hydroxides, model platinum co-precipitation experiments were conducted separately as a function of reaction time and pH. All experiments were conducted at ambient temperature and magnetically stirred. The pH ranges determined for Pt co-precipitation with aluminum, magnesium, iron(II) and iron(III) ions were from 4 to 9, 11 to 12, 6 to 8 and 4 to 8, respectively. During all of the experiments, the sample solutions were adjusted to the determined pH and the pH was continuously monitored and maintained within ± 0.1 pH with NaOH and HCl solutions. After 0.5, 1, 3 and 6 hours, the aliquots of the sample solutions were collected and filtered with $0.45 \mu\text{m}$ membrane filter. The concentration of platinum and other metals (aluminum, magnesium and iron) in the filtrates were determined by ICP-AES (SEIKO Instrument / VISTA-MPX) and AAS (Jarrel Ash AA-835) at the Department of Earth

Resources Engineering, Kyushu University, Japan. After air dried at room temperature, some of the solid samples on the filter paper were examined by X-ray photoelectron spectroscopy (XPS) (Shimadzu / KRATOS AXIS-165) at the Center of Advanced Instrumental Analysis, Kyushu University, Japan. All spectra were internally corrected by using C1s as 284.6 eV and fitted by XPSPEAK 4.1. Schematic flow chart of preliminary co-precipitation experiments of platinum is shown in figure 5.3.

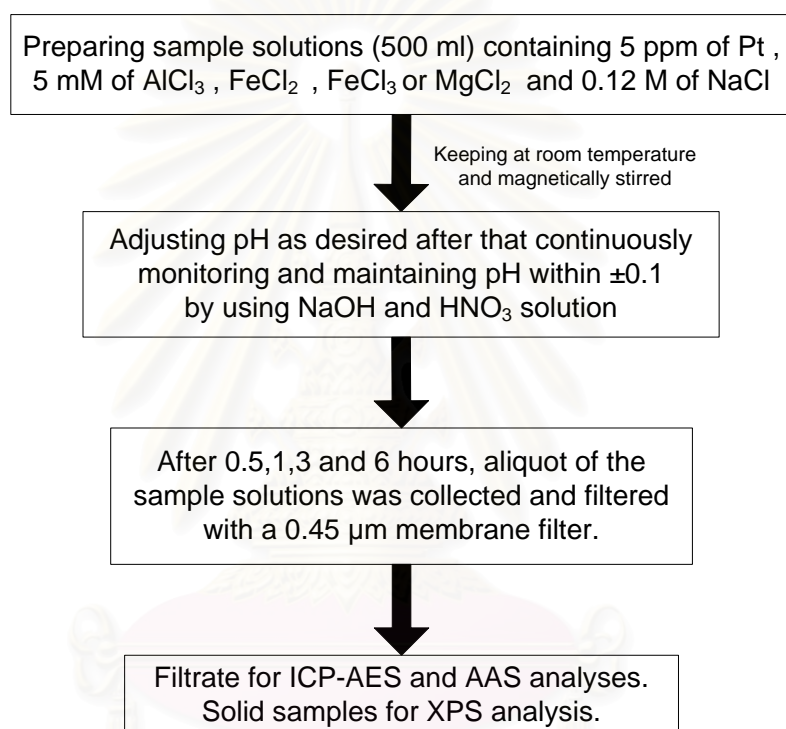


Figure 5.3 Schematic flow chart of preliminary co-precipitation experiments of platinum

5.2.2 Results and discussion

The effect of pH on platinum co-precipitation with aluminum, iron(III), iron(II) and magnesium hydroxides is shown in figure 5.4. The amount of platinum co-precipitated with metal hydroxides was estimated by the decrease in platinum concentration from initial concentration in the solution. Platinum concentration in the solution was determined by ICP-AES analysis. Platinum co-precipitation with aluminum hydroxide decreased with the increasing pH and the highest percentage of co-precipitated

platinum is 48% at pH 5. This fact suggests that the increasing of pH retarded the co-precipitation of platinum with aluminum hydroxide. The percentage of platinum co-precipitation with iron(III) hydroxide is 48% at pH 4, and reached 100 % from pH 5 to 7. However, the percentage of platinum co-precipitation dropped to 50% at pH 8. This result was similar to that of the adsorption of gold(III) ions with iron(III) hydroxide (Uchida et al., 2002). They suggested that the important factor of the adsorption of gold(III) ions by iron(III) hydroxide was the hydrolysis of gold(III) ions as well as the surface charge of iron(III) hydroxides. Therefore, it is considered that the co-precipitation behavior of platinum(IV) ions on iron(III) hydroxides may be caused by the hydrolysis of platinum(IV) complex ions. When platinum(IV) complex ions are in the stock solution, all six ligands are considered to be chloride ions. As increasing pH, the hydrolysis of them proceeds and then chloro-hydroxy platinum(IV) complex ions are formed. The percentage of platinum co-precipitation with iron(II) hydroxide was 100% at pH 6,7 and 8. The co-precipitation of platinum with magnesium hydroxide slightly occurred at pH 11 and 12. The maximum percentage of platinum co-precipitation was only 18% at pH 11. The accuracy of platinum concentration is $\pm 2.5\%$.

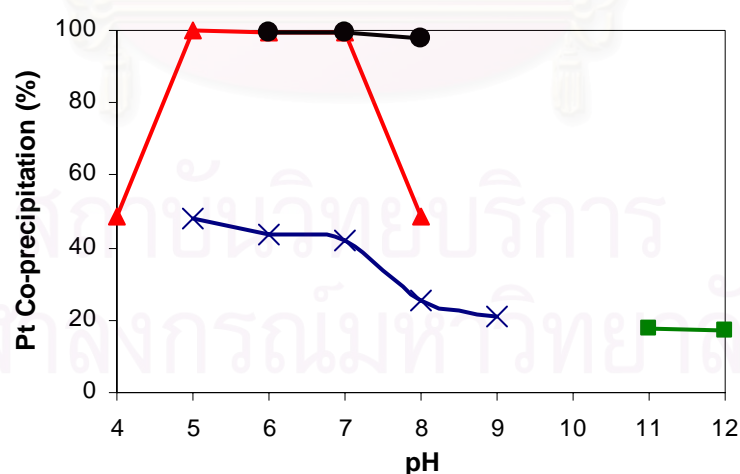


Figure 5.4 The effect of pH on Pt co-precipitation with Al [x], Fe(II) [●], Fe(III) [▲] and Mg [■] hydroxides after 6 hours

Table 5.1 The effect of pH on Pt co-precipitation with Al hydroxide after 6 hours

pH	Platinum concentration (mg/l)		%Pt co-precipitation
	Before Co-precipitation	After Co-precipitation	
4	5.05±0.15	2.53±0.10	50%
5	5.12±0.06	2.92±0.03	43%
6	5.02±0.15	2.91±0.11	42%
7	5.03±0.10	3.77±0.02	25%
8	5.11±0.06	4.04±0.14	21%

Table 5.2 The effect of pH on Pt co-precipitation with Fe(II) hydroxide after 6 hours

pH	Platinum concentration (mg/l)		%Pt co-precipitation
	Before Co-precipitation	After Co-precipitation	
6	5.01±0.04	0.01±0.01	100%
7	5.02±0.10	0.01±0.02	100%
8	5.06±0.08	0.15±0.14	97%

Table 5.3 The effect of pH on Pt co-precipitation with Fe(III) hydroxide after 6 hours

pH	Platinum concentration (mg/l)		%Pt co-precipitation
	Before Co-precipitation	After Co-precipitation	
4	5.05±0.15	2.50±0.15	51%
5	5.12±0.06	0.07±0.03	99%
6	5.03±0.15	0.00±0.01	100%
7	5.07±0.10	0.04±0.01	99%
8	5.03±0.06	2.51±0.14	50%

Table 5.4 The effect of pH on Pt co-precipitation with Mg hydroxide after 6 hours

pH	Platinum concentration (mg/l)		%Pt co-precipitation
	Before Co-precipitation	After Co-precipitation	
11	5.04±0.04	4.13±0.01	18%
12	5.02±0.10	4.12±0.02	18%

Figure 5.5 showed the effect of time on platinum co-precipitation with aluminum hydroxide at pH 5. The amount of platinum co-precipitated with aluminum hydroxide was estimated by the decrease in platinum concentration from initial concentration in the solution which was determined by ICP-AES analysis. The percentage of platinum co-precipitation with aluminum hydroxide increased with the increasing time. Platinum co-precipitation increased rapidly during the first 30 minutes and remained constant until 3 hours. After 3 hours platinum co-precipitation eventually increased up to 50%. However; platinum co-precipitation showed tendency to increase after 6 hours. The result indicated that aluminum hydroxide was not an effective carrier for platinum.

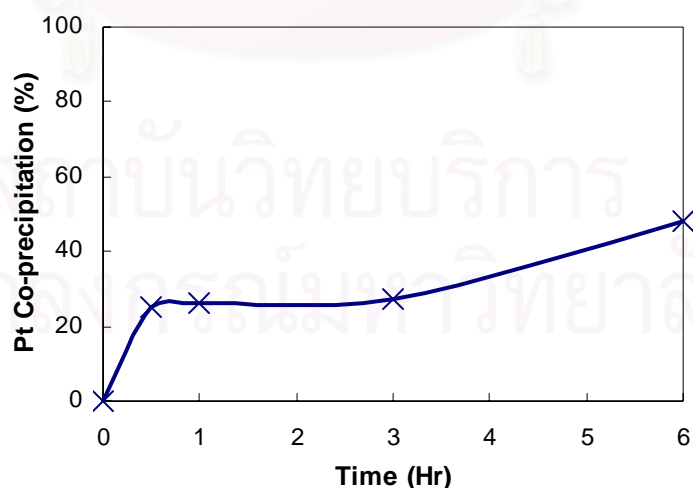


Figure 5.5 The effect of time on Pt co-precipitation with Al hydroxides at pH 5

Table 5.5 The effect of time on Pt co-precipitation with Al hydroxide at pH 5
with initial Al conc. of 135 ppm

Time	Pt co-precipitated with Al hydroxide at pH 5	
	Pt concentration in solution	% Pt co-precipitation
initial	5.02±0.14	0%
30 min	3.75±0.07	25%
1 hour	3.71±0.03	26%
3 hours	3.66±0.04	27%
6 hours	2.51±0.03	50%

Platinum co-precipitation experiment with iron(II) and iron(III) hydroxides were separately conducted; however the effect of time on platinum co-precipitation with iron(II) and iron (III) hydroxides was shown together in figure 5.6 for convenient and easy-to-compare reason. The amount of platinum co-precipitated with iron(II) and iron(III) hydroxides was estimated by the decrease in platinum concentration from initial concentration in the solution which was determined by ICP-AES analysis. The percentage of platinum co-precipitation with iron(II) and iron(III) hydroxides increased with the increasing time. At pH 6, the co-precipitation of platinum with both iron(II) and iron(III) hydroxides occurred rapidly and reached the maximum value of 100% within 1 hour. However, the co-precipitation rate of platinum with iron(II) hydroxide was faster than that with iron(III) hydroxide. This result might be derived from the change in chemical state of platinum on the surface of each iron hydroxide as shown in the next section.

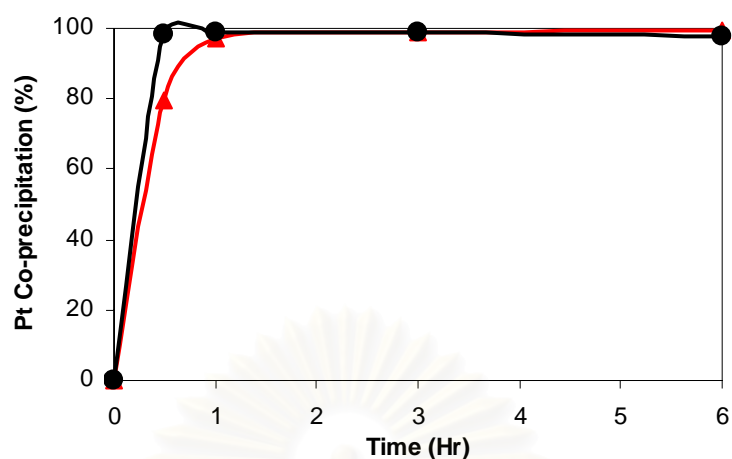


Figure 5.6 The effect of time on Pt co-precipitation separately with Fe(III) [▲] and Fe(II) [●] hydroxides at pH 6

Table 5.6 The effect of time on Pt co-precipitation with Fe(II) hydroxide at pH 6 with initial Fe conc. of 560 ppm

Time	Pt co-precipitated with Fe(II) hydroxide at pH 6	
	Pt concentration in solution	% Pt co-precipitation
initial	5.01±0.04	0%
30 min	0.05±0.01	99%
1 hour	0.01±0.01	100%
3 hours	0.01±0.02	100%
6 hours	0.05±0.02	99%

Table 5.7 The effect of time on Pt co-precipitation with Fe(III) hydroxide at pH 6
with initial Fe conc. of 560 ppm

Time	Pt co-precipitated with Fe(III) hydroxide at pH 6	
	Pt concentration in solution	% Pt co-precipitation
initial	5.02±0.03	0%
30 min	1.00±0.02	80%
1 hour	0.10±0.01	98%
3 hours	0.01±0.02	100%
6 hours	0.00±0.01	100%

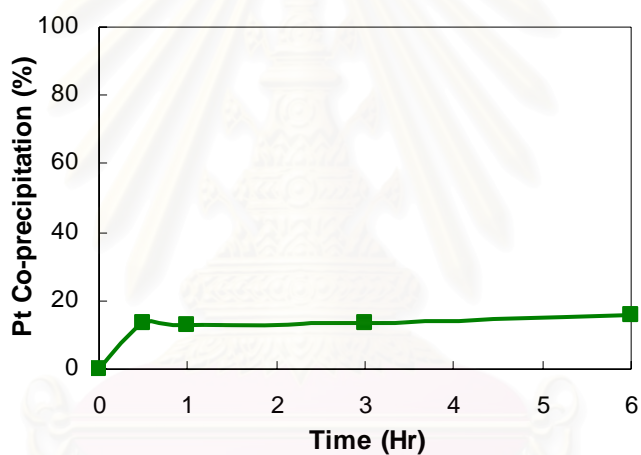


Figure 5.7 The effect of time on Pt co-precipitation with Mg hydroxide at pH 11

Table 5.8 The effect of time on Pt co-precipitation with Mg hydroxide at pH 11
with initial Al conc. of 120 ppm

Time	Pt co-precipitated with Mg hydroxide at pH 11	
	Pt concentration in solution	% Pt co-precipitation
initial	5.01±0.12	0%
30 min	4.15±0.07	17%
1 hour	4.26±0.10	15%
3 hours	4.15±0.04	17%
6 hours	4.11±0.11	18%

Figure 5.7 showed the effect of time on platinum co-precipitation with magnesium hydroxide at pH 11. Magnesium hydroxide normally precipitates at high pH. The amount of platinum co-precipitated with magnesium hydroxide was estimated by the decrease in platinum concentration from initial concentration in the solution which was determined by ICP-AES analysis. The percentage of platinum co-precipitation with magnesium hydroxide increased with the increasing time. Platinum co-precipitation increased rapidly and reached the maximum of 18% during the first 30 minutes and decreased slightly in 1 hour; however platinum co-precipitation attained the equilibrium after 1 hour. The result suggested that magnesium hydroxide was not an efficient carrier of platinum.

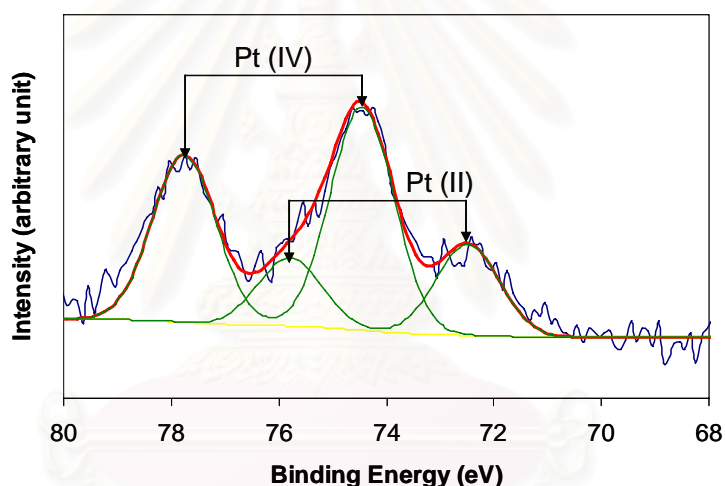


Figure 5.8 Pt4f XPS spectra of platinum co-precipitated with iron (III) hydroxide at pH 6.

As shown in figure 5.4, Fe hydroxide showed the much more co-precipitation capacity for platinum, therefore, the co-precipitation of platinum with iron hydroxide is focused hereafter. The chemical state of platinum co-precipitated with Fe hydroxides was determined by XPS. The Pt4f XPS spectra for platinum co-precipitated with iron (III) hydroxide is shown in figure 5.8. The spectrum can be divided into 2 doublets. According to the handbook of x-ray photoelectron spectroscopy (Moulder et al., 1992), the doublet with lower binding energy (72.5 and 75.7 eV) can be assigned to platinum (II) species. The other one (74.5 and 77.6 eV) is determined as platinum (IV) species.

The existence of platinum (II) species on the iron (III) hydroxide indicates that platinum (IV) ions are reduced to platinum (II) species during the platinum co-precipitation with iron (III) hydroxide. The ratio of platinum (IV) to platinum (II) was estimated as 2 : 1.

Figure 5.9 shows the Pt4f spectra of platinum co-precipitated with iron (II) hydroxide. The spectrum can be divided into 3 doublets, assigned to 3 different platinum species. The assignment of platinum species was referred to the peak position described in Moulder et al., 1992. As a result, the doublets were determined as platinum (0), platinum (II) and platinum (IV) species, respectively as shown in figure 5.9. The slight peak shift was observed about platinum (0), which was moved toward higher binding energies. Roth et al., 2001 reported that the smaller metallic platinum particle is likely to show the higher binding energy than the larger one.

This indicates that the metallic state of platinum is present as fine particles as suggested by Parinayok et al., 2007. It can be reasonably conclude that platinum (IV) species is reduced to platinum (II) or even to platinum (0). Noticeably, the ratio of platinum (0) was relatively intensive and estimated as 65%.

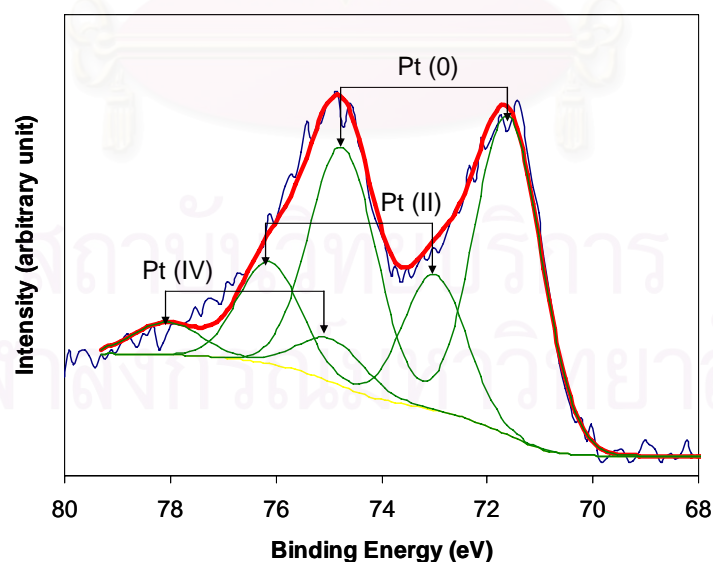


Figure 5.9 Pt4f XPS spectra of platinum co-precipitated with iron(II) at pH 6.

The reduction of platinum was confirmed from the both results shown in figures 5.4 and 5.5. However, the mechanism of reduction of platinum is likely to be different

judging from the Fe-bearing products as a co-precipitate. In the case of the co-precipitation with iron (III) hydroxide, the co-precipitation behavior of platinum is similar to that of gold (III) ions (Uchida et al., 2002), suggesting that the reduction process is also the same as that of gold (III) ions. Therefore, the reduction of platinum might be considered to be a result of Fe-O-Pt bonding, distortion of the bonding due to the same mechanism as described in Uchida et al., 2002. In the case of the co-precipitation with iron (II) hydroxide, iron(II) is actually not precipitated as mere iron(II) hydroxide. As the precipitate showed the black color and magnetism, it may form iron oxide by oxidation. Iron (II) hydroxide is well known to be reduced easily, therefore, the redox reaction between platinum (IV) and iron (II) ions are reasonably concluded as a reduction mechanism of platinum unless dissolved oxygen is superior to platinum (IV) as an oxidizing reagent.

5.3 Co-precipitation experiment of the synthetic leachate from aqua regia leaching

In order to see the influence of metal ions in combination in aqua regia leachate in co-precipitation, next experiment was conducted with synthetic leachate from aqua regia leaching and the effect of adding reducing agent (Fe^{2+}) was also investigated.

5.3.1 Experimental

5.3.1.1 Instruments

1. 1000 ml Pyrex beaker
2. 500 ml Pyrex volumetric flask
3. Magnetic stirrer
4. pH meter (Horiba F-21 Tou pH Series)
5. Vacuum filter kit
6. 0.45 μm membrane filter
7. Glass pipette
8. Parafilm

9. SEIKO / VISTA-MPX inductively coupled plasma atomic emission spectroscopy (ICP-AES)
10. NIPPON Jarrel Ash AA-835 flame atomic absorption spectrometer (AAS)

5.3.1.2 Chemical reagents

1. Platinum standard solution for atomic absorption spectrometry (Wako Chemical)
2. $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ analytical grade (Wako Chemical)
3. $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ analytical grade (Wako Chemical)
4. $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ analytical grade (Wako Chemical)
5. HCl analytical grade (Wako Chemical)
6. NaOH analytical grade (Wako Chemical)
7. NaCl analytical grade (Wako Chemical)
8. Ultra pure water

5.3.1.3 Procedure

Synthetic aqua regia leachates prepared in this study contain 1,500, 50, 10 and 20 ppm of aluminum, magnesium, iron and platinum respectively (see table 5.9). The concentrations were determined from the ICP-AES analysis from aqua regia leaching (chapter 4). According to the result from the preliminary co-precipitation experiment, iron ions are recognized as the best carrier of platinum during co-precipitation. In addition, iron (II) ions are expected to be a not only carrier of platinum but also reducing agent. As co-precipitation of platinum with iron ions is considered to be retarded by the coexistence of aluminum, therefore, the optimum leaching condition for the most effective platinum co-precipitation with iron (II) ions here is determined as at 90°C for 1 hours, which provide the concentration ratio as mentioned above, instead of the highest amount of aluminum, iron, magnesium and platinum concentration at 90°C after 6 hours.

Table 5.9 Effect of time on metal leached by aqua regia at 90 °C

Time	Metal leached by aqua regia at 90 °C ± S.D. (ppm)			
	Al	Mg	Fe	Pt
30 min	2,685±153	88.23±1.91	18.35±0.65	50.95±1.17
1 hour	3,060±156	102.00±2.67	20.18±0.78	58.41±1.41
3 hours	5,142±183	140.53±3.48	50.23±1.48	60.65±2.07
6 hours	7,513±168	211.73±5.10	74.31±2.64	65.09±1.65

In order to investigate the effect of iron (II) ions as a reducing agent, two systems of the sample solution were prepared; the first one is with the addition of iron (II) ions, another is without iron (II) addition. The concentration ratio of iron (II) ions and platinum (IV) ions in the sample solution is kept 115, which is determined from the optimum result from the preliminary co-precipitation experiment. All experiments were conducted at ambient temperature and magnetically stirred. The sample solutions were adjusted to pH 6 by dropping NaOH solution. The ionic strength of the sample solutions was adjusted to 0.12 mol dm⁻³ with NaCl solution, in order to stabilize the pH of the sample solution. During the experiment, the pH was continuously monitored and maintained within ± 0.1 with NaOH and HCl solution. After 0.5, 1, 3 and 6 hours, the aliquots of the sample solutions were collected and filtered with 0.45 µm membrane filter. The concentration of platinum and other metals (aluminum, magnesium and iron) in the filtrates were determined by SEIKO / VISTA-MPX inductively coupled plasma atomic emission spectroscopy (ICP-AES) and AAS (Jarrel Ash AA-835) at the Department of Earth Resources Engineering, Kyushu University, Japan.

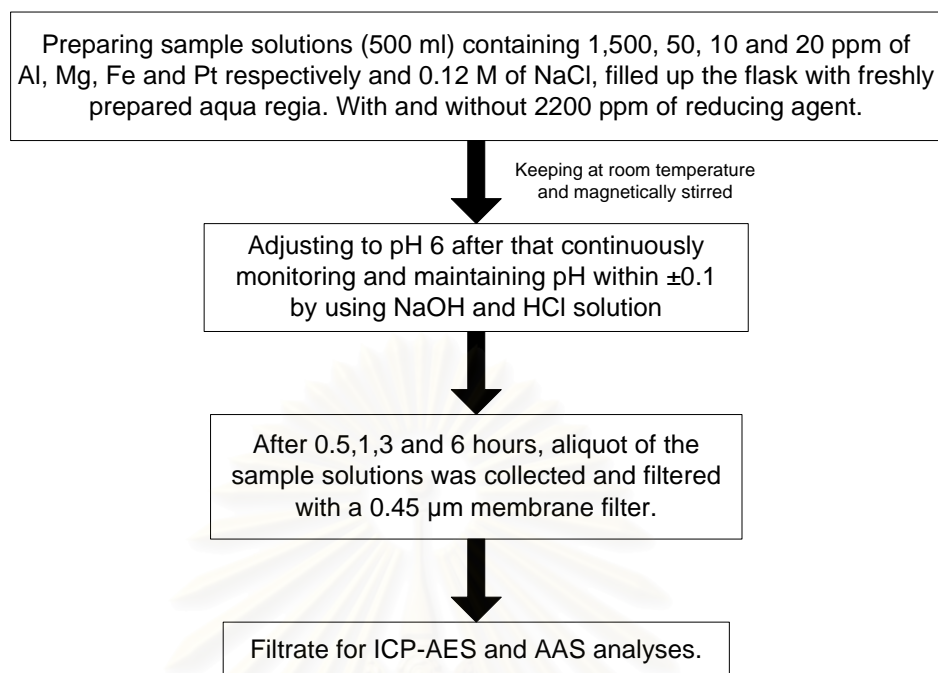


Figure 5.10 Schematic flow chart of co-precipitation experiment of the leachate from aqua regia leaching

As a final step of platinum recovery, platinum separation from Fe(II) hydroxides was conducted by dissolving with hydrochloric acid. The liquid-solid ratio is approximately 100 with 100 ml of 1M HCl and 1.16 g. of the residue from co-precipitation method. This experiment was conducted at room temperature and magnetically stirred. After 0.5, 1 and 3 hours, the aliquots of the sample solutions were collected and filtered with 0.45 µm membrane filter. The concentration of platinum and other metals (aluminum, magnesium and iron) in the filtrates were determined by SEIKO / VISTA-MPX inductively coupled plasma atomic emission spectroscopy (ICP-AES) at the Department of Earth Resources Engineering, Kyushu University, Japan.

5.3.2 Results and discussion

Figure 5.11 shows the effect of time on platinum co-precipitation from synthetic leachates at pH 6, with or without iron (II) ion addition. After 30 minutes, the percentage of co-precipitated platinum with the agent reached the maximum and maintained the constant value around 85% until 6 hours. On the other hand, the percentage of co-

precipitated platinum without iron (II) ion addition, showed around 55% as a constant value. It is clear that the difference of co-precipitation capacity is derived from the added iron (II) ion which is not initially contained in the leachate. As aluminum is the major component in the synthetic leachate, the co-precipitation behavior shown in figure 5.11 (without iron (II) ion addition) is mainly contributed by that with aluminum hydroxide shown in figure 5.5 , and minor contribution from iron (III) ions. It is obvious that the addition of iron (II) ion is required for effective platinum co-precipitation from the leachate. However, iron (II) ion cannot survive in the aqua regia, nitrogen gas may be added in order to retard the oxidation of iron (II) to iron (III) ions.

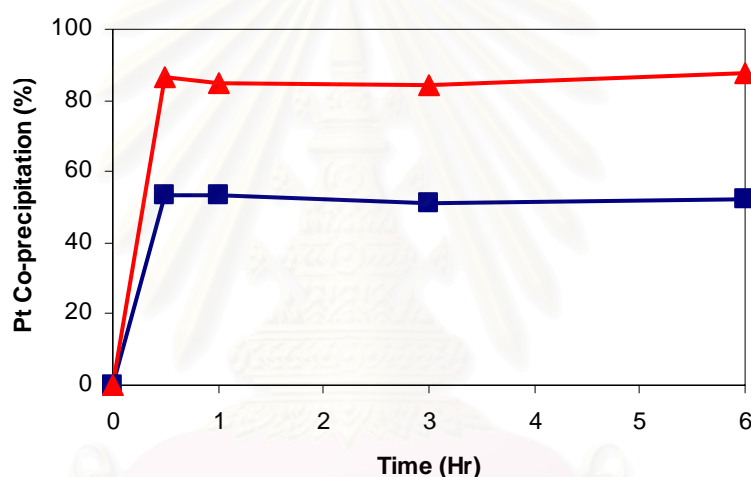


Figure 5.11 The effect of time on platinum co-precipitation at pH 6 with (▲) and without (■) iron(II) ions addition

Table 5.10 The effect of time on Pt co-precipitation with additional reducing agent

Time	Pt co-precipitation±S.D. with add. Reducing agent at pH 6	
	Pt concentration in solution	% Pt co-precipitation
initial	20.03±0.12	0%
30 min	2.60±0.03	87%
1 hour	3.00±0.04	85%
3 hours	3.20±0.05	84%
6 hours	2.40±0.03	88%

Table 5.11 The effect of time on Pt co-precipitation without additional reducing agent

Time	Pt co-precipitation \pm S.D. without add. Reducing agent at pH 6	
	Pt concentration in solution	% Pt co-precipitation
initial	20.03 \pm 0.12	0%
30 min	9.41 \pm 0.04	53%
1 hour	9.21 \pm 0.03	54%
3 hours	9.80 \pm 0.05	51%
6 hours	9.40 \pm 0.03	53%

The effect of time on Pt(II) and Pt(IV) ions dissolution by HCl is shown in figure 5.12. The amount of platinum dissolved in HCl reached the maximum at 35% after 30 minutes and maintained the constant value until 3 hours. Generally Pt(II) and Pt(IV) are dissolved by HCl, while Pt(0) is not. The result indicated that the dissolved platinum were Pt(II) and Pt(IV) (approximately 35%), while approximately 65% were remained in residue as Pt(0).

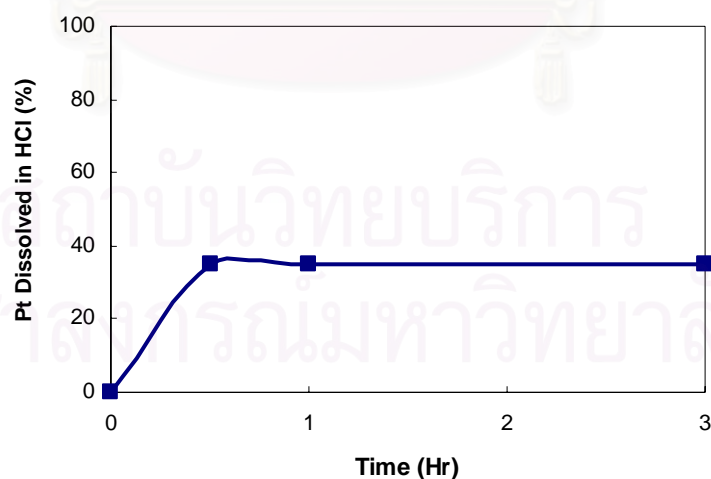


Figure 5.12 The effect of time on Pt(II) and Pt(IV) ions dissolution by HCl

Table 5.12 The effect of time on Pt(II) and Pt(IV) ions dissolution by HCl

Time	Pt(0) separation from Pt(II) and Pt(IV) by HCl dissolution	
	Pt dissolved in HCl (mg/l)	% Pt Metal
Initial	0	0%
30 min	3.69±0.05	65%
1 hour	3.81±0.03	64%
3 hours	3.70±0.03	65%
6 hours	3.71±0.01	65%

5.4 Conclusion

The co-precipitation behavior of platinum with aluminum, magnesium, iron (II) and iron (III) hydroxides are investigated. Iron (II) and iron (III) hydroxides can bring to better co-precipitation of platinum than aluminum and magnesium hydroxides. The percentage of co-precipitation of platinum with iron (III) hydroxide at pH 6 is closed to 100% within 1 hour, while that with iron (II) hydroxide at pH 6 attains nearly 100 % within 30 minutes. In terms of the chemical state of co-precipitated platinum, platinum (IV) species is partly reduced to platinum (II) species after co-precipitation with iron (III) hydroxide. In addition, the chemical state of platinum changes from platinum (IV) species to platinum (II) species and even to platinum (0) after co-precipitation with iron (II) hydroxide. Iron (II) ions can also react as a reducing agent. The reduction of platinum with iron (III) hydroxide might be caused by the spontaneous reduction due to the distortion of the coordination structure of platinum (IV) ions as suggested by Uchida et al., 2002 in the case of gold (III) and iron (III) ions, while the reduction of platinum by iron (II) hydroxide would result from the redox reaction between platinum (IV) and iron (II) ions.

Based on the result mentioned above, in order to design the platinum recovery process of spent automobile catalytic converters, co-precipitation method is applied to recovery of platinum from them after leaching by aqua regia. The percentage of

platinum co-precipitation reached 53% mainly due to uptake of aluminum hydroxide originally contained, while it reached 88% with iron (II) ions addition as a co-precipitation carrier and also reducing agent for platinum ion. Hence, iron (II) ions are considered to be an important agent to assist co-precipitation of platinum and to achieve platinum recovery in metal form. However, due to Fe (II) ion tends to be oxidized to Fe (III) ion and give mix products of both Pt (II) and Pt (0). Therefore, it is suggested to use only Fe (III) and separate Pt (II) from the solution prior to further reduction to Pt metal.



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CHAPTER VI

CONCLUSION

6.1 Conclusion

Automobile catalytic converter is mainly consisted of cordierite and alumina including lanthanum and cerium oxide with honeycomb structure. Platinum is observed only on the surface of alumina not cordierite. The determination of platinum in this spent automobile catalytic converter by decomposition method showed the platinum content of 754 ± 19 mg/kg.

Aqua regia leaching is selected for platinum extraction in the present study. The platinum extraction rate increases with the leaching time and temperature. The highest platinum leached is 86% at 90°C after 6 hours. Aluminum, magnesium and iron, which are the major elements in automobile catalytic converter, are also dissolved in aqua regia.

Co-precipitation method is applied in this present study to separate platinum from the major elements in the leachate with the green chemistry and easy operation point of view. Preliminary co-precipitation experiments of platinum were conducted separately with aluminum, magnesium, iron (II) and iron (III) ions. This is because these metal ions are the major component in the catalytic converter and they are also dissolved by aqua regia. The study results show that almost all platinum can co-precipitate with iron (II) and iron (III) hydroxides at pH 6 within 1 hour. Moreover, the XPS (X-ray photoelectron spectroscopy) analysis of solid sample shows that the chemical state of co-precipitated platinum was partly reduced to platinum (II) by iron (III) hydroxide and some are reduced to metallic platinum with iron (II) hydroxide. It is also found that co-precipitation of platinum with iron ions is retarded by the coexistence of aluminum; therefore the optimum leaching condition in this study is determined as at 90°C for 1 hours, where less aluminum is dissolved in the leachate.

Co-precipitation experiment of the synthetic aqua regia leachate was conducted with and without iron (II) ion addition. The result shows that platinum co-precipitation rate reached 88% with iron (II) ion addition and only 53% without iron (II) ion addition. It is clear that the difference of co-precipitation capacity is derived from the added iron (II) ion. However, due to Fe (II) ion tends to be oxidized to Fe (III) ion and give mix products of both Pt (II) and Pt (0). Therefore, it is suggested to use only Fe (III) in the co-precipitation and separate Pt (II) and Pt (IV) from the solution prior to further process to metallic Pt.

As a final step of platinum recovery process, platinum separation from the residue after co-precipitation was conducted by HCl dissolution. Approximately 35% of platinum, which were platinum (II) and platinum (IV) ions in the residues after co-precipitation was dissolved by HCl, while 65% of platinum (Pt(0)) was not dissolved by HCl and remained in solid after the dissolution. Platinum (II) and platinum (IV) ions dissolved in HCl were H_2PtCl_4 and H_2PtCl_6 , which can be used for the production of platinum sponge and platinum salts.

It can be concluded that the platinum recovery process, 68% of platinum was recovered by co-precipitation method, while 45.5% was recovered as Pt(0) after HCl dissolution.

All the process of platinum recovery from spent catalytic converter can be summarized in the flow chart below.

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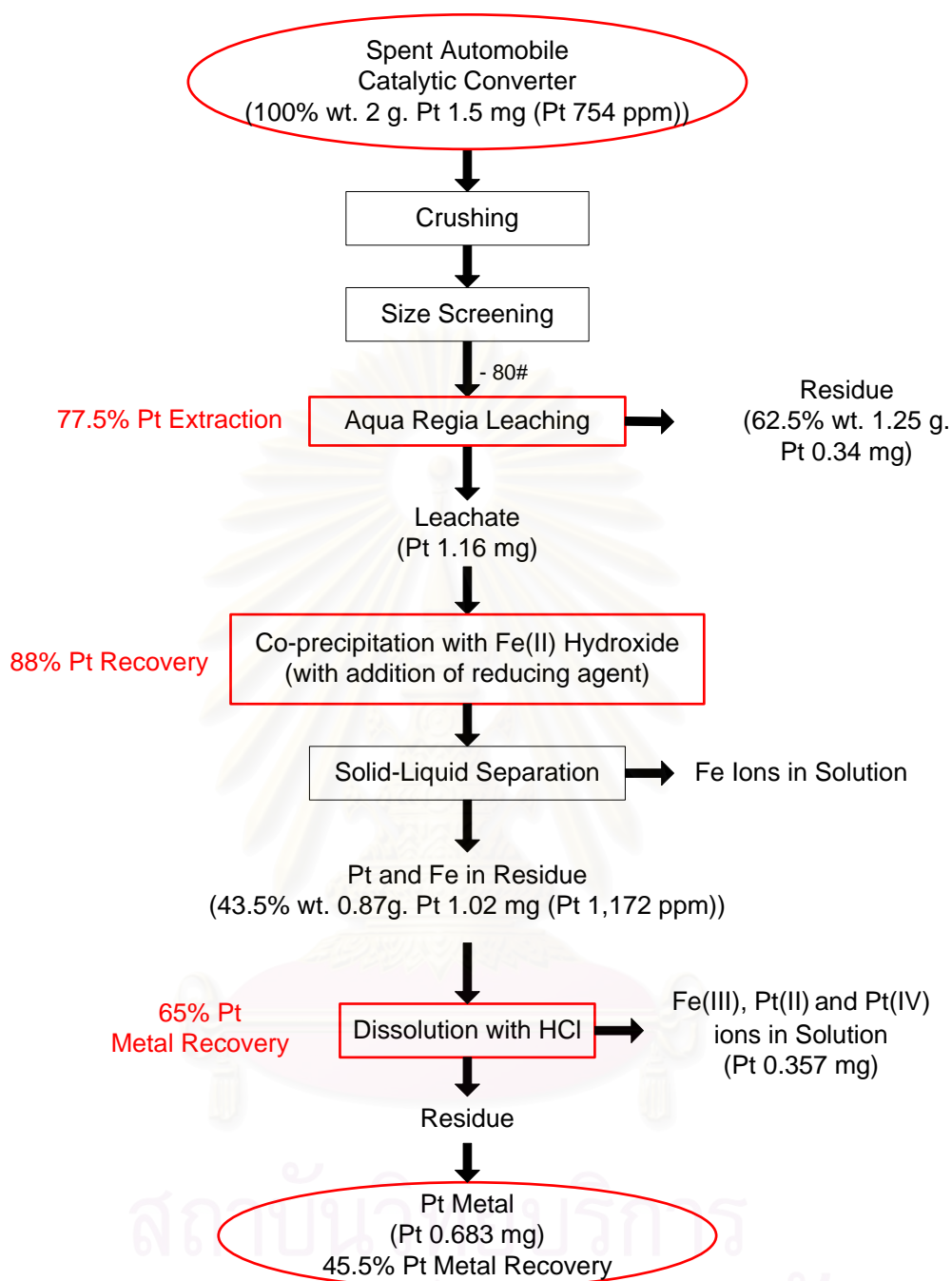


Figure 6.1 Variation of total amount of spent automobile catalytic converter and platinum concentration in every stage of platinum recovery

6.2 Recommendation and suggestion

More platinum extraction rate is required for more platinum recovery from spent automobile catalytic converter. Microwave assisted leaching and smaller particle size of crushed catalytic converter samples are recommended for more platinum extraction.

Aqua regia extraction of platinum is suggested to be done with the original honeycomb structure of spent automobile catalytic converter (without crushing) for the potential reuse of the honeycomb structure of spent automobile catalytic converter in automobile catalyst industry.

For more platinum recovery rate from co-precipitation method, aluminum elimination, for example sulphation roasting, is required.

The leachate after HCl dissolution in platinum separation still contained platinum (II) and platinum (IV) ions; hence, it is suggested to be used for co-precipitate again.

It is also suggested that platinum co-precipitation with Fe (III) hydroxide could be a better method for platinum recovery in recycling industry than platinum co-precipitation with Fe (II) hydroxide, due to the fact that the latter method requires 2 processes to obtain metallic platinum, i.e., HCl dissolution (in order to dissolve Pt^{4+} and Pt^{2+} , and also to obtain metallic Pt in residue) and then precipitation of Pt^{4+} and Pt^{2+} with NH_4Cl (in order to precipitate Pt^{4+} and Pt^{2+}). Whilst, co-precipitation of platinum with Fe (III) hydroxide requires only 1 process, i.e., precipitation of Pt^{4+} and Pt^{2+} with NH_4Cl to achieve metallic Pt.

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APPENDICES

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Appendix

Analytical machines in this study

X-Ray Fluorescence (XRF) Spectrometry

XRF Spectrometry is used to identify elements in a substance and quantify the amount of those elements present to ultimately determine the elemental composition of a material. An element is identified by its characteristic X-ray emission wavelength (λ) or energy (E). The amount of an element present is quantified by measuring the intensity (I) of its characteristic emission.

All atoms have a fixed number of electrons (negatively charged particles) arranged in orbitals around the nucleus. Energy Dispersive (ED) XRF and Wavelength Dispersive (WD) XRF Spectrometry typically utilize activity in the first three electron orbitals, the K, L, and M lines, where K is closest to the nucleus.

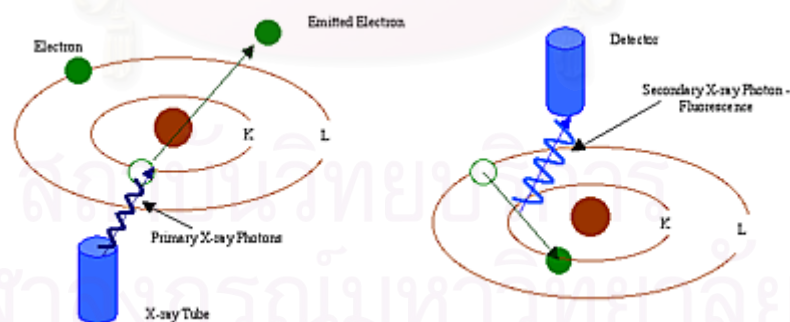


Figure A-1 Schematic of X-ray fluorescence spectrometry

In XRF Spectrometry, high-energy primary X-ray photons are emitted from a source (X-ray tube) and strike the sample. The primary photons from the X-ray tube have enough energy to knock electrons out of the innermost, K or L, orbitals. When this occurs, the atoms become ions, which are unstable. An electron from an outer orbital, L

or M, will move into the newly vacant space at the inner orbital to regain stability. As the electron from the outer orbital moves into the inner orbital space, it emits an energy known as a secondary X-ray photon. This phenomenon is called fluorescence. The secondary X-ray produced is characteristic of a specific element. The energy (E) of the emitted fluorescent X-ray photon is determined by the difference in energies between the initial and final orbitals of the individual transitions.

This is described by the formula

$$E=hc\lambda^{-1}$$

Where h is Planck's constant; c is the velocity of light; and λ is the characteristic wavelength of the photon.

Energies are inversely proportional to the wavelengths; they are characteristic for each element. For example the $K\alpha$ energy for Iron (Fe) is about 6.4keV. Typical spectra for EDXRF Spectrometry appear as a plot of Energy (E) versus the Intensity (I).

XRF Spectrometry is the choice of many analysts for elemental analysis. XRF Spectrometry easily and quickly identifies and quantifies elements over a wide dynamic concentration range, from PPM levels up to virtually 100% by weight. XRF Spectrometry does not destroy the sample and requires little, if any, sample preparation. It has a very fast overall analysis turnaround time. These factors lead to a significant reduction in the per sample analytical cost when compared to other elemental analysis techniques. Aqueous elemental analysis instrument techniques typically require destructive and time-consuming specimen preparation, often using concentrated acids or other hazardous materials. Not only is the sample destroyed, waste streams are generated during the analysis process that need to be disposed of, many of which are hazardous. These aqueous elemental analysis techniques often take twenty minutes to several hours for sample preparation and analysis time. All of these factors lead to a relatively high cost per sample. However, if PPB and lower elemental concentrations are the primary measurement need, aqueous instrument elemental analysis techniques are necessary.

All elemental analysis techniques experience interferences, both chemical and physical in nature, and must be corrected or compensated for in order to achieve adequate analytical results. Most aqueous instrument techniques for elemental analysis suffer from interferences that are corrected for by extensive and complex sample preparation techniques, instrumentation modifications or enhancements, and by mathematical corrections in the system's software. In XRF Spectrometry, the primary interference is from other specific elements in a substance that can influence (matrix effects) the analysis of the element(s) of interest. However, these interferences are well known and documented; and, instrumentation advancements and mathematical corrections in the system's software easily and quickly correct for them. In certain cases, the geometry of the sample can affect XRF analysis, but this is easily compensated for by selecting the optimum sampling area, grinding or polishing the sample, or by pressing a pellet or making glass beads.

Quantitative elemental analysis for XRF Spectrometry is typically performed using Empirical Methods (calibration curves using standards similar in property to the unknown) or Fundamental Parameters (FP). FP is frequently preferred because it allows elemental analysis to be performed without standards or calibration curves. This enables the analyst to use the system immediately, without having to spend additional time setting up individual calibration curves for the various elements and materials of interest. The capabilities of modern computers allow the use of this no-standard mathematical analysis, FP, accompanied by stored libraries of known materials, to determine not only the elemental composition of an unknown material quickly and easily, but even to identify the unknown material itself.

Atomic-Absorption Spectroscopy (AAS)

Atomic-absorption (AA) spectroscopy uses the absorption of light to measure the concentration of gas-phase atoms. Since samples are usually liquids or solids, the analyze atoms or ions must be vaporized in a flame or graphite furnace. The atoms absorb ultraviolet or visible light and make transitions to higher electronic energy levels. The analyze concentration is determined from the amount of absorption. Applying the Beer-Lambert law directly in AA spectroscopy is difficult due to variations in the atomization efficiency from the sample matrix, and no uniformity of concentration and path length of analyze atoms (in graphite furnace AA). Concentration measurements are usually determined from a working curve after calibrating the instrument with standards of known concentration.

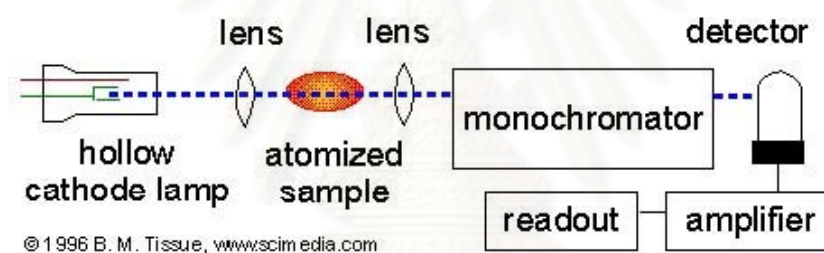


Figure A-2 Schematic of an atomic-absorption experiment

Instrumentation

Light source

The light source is usually a hollow-cathode lamp of the element that is being measured. Lasers are also used in research instruments. Since lasers are intense enough to excite atoms to higher energy levels, they allow AA and atomic fluorescence measurements in a single instrument. The disadvantage of these narrow-band light sources is that only one element is measurable at a time.

Atomizer

AA spectroscopy requires that the analyte atoms be in the gas phase. Ions or atoms in a sample must undergo desolvation and vaporization in a high-temperature

source such as a flame or graphite furnace. Flame AA can only analyze solutions, while graphite furnace AA can accept solutions, slurries, or solid samples.

Flame AA uses a slot type burner to increase the path length, and therefore to increase the total absorbance (see Beer-Lambert law). Sample solutions are usually aspirated with the gas flow into a nebulizing/mixing chamber to form small droplets before entering the flame.

The graphite furnace has several advantages over a flame. It is a much more efficient atomizer than a flame and it can directly accept very small absolute quantities of sample. It also provides a reducing environment for easily oxidized elements. Samples are placed directly in the graphite furnace and the furnace is electrically heated in several steps to dry the sample, ash organic matter, and vaporize the analyze atoms.

Light separation and detection

AA spectrometers use monochromators and detectors for uv and visible light. The main purpose of the monochromator is to isolate the absorption line from background light due to interferences. Simple dedicated AA instruments often replace the monochromator with a bandpass interference filter. Photomultiplier tubes are the most common detectors for AA spectroscopy.

Metals in solution may be readily determined by flame (direct aspiration) atomic absorption spectrophotometry. The method is simple, rapid, and applicable to a large number of environmental samples including, but not limited to, ground water, aqueous samples, extracts, industrial wastes, soils, sludges, sediments, and similar wastes. With the exception of the analyses for dissolved constituents, all samples require digestion prior to analysis. Analysis for dissolved elements does not require digestion if the sample has been filtered and then acidified.

ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectrometry)

ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectrometry) is an emission spectrophotometric technique, exploiting the fact that excited electrons emit energy at a given wavelength as they return to ground state. The fundamental characteristic of this process is that each element emits energy at specific wavelengths peculiar to its chemical character. Although each element emits energy at multiple wavelengths, in the ICP-AES technique it is most common to select a single wavelength (or a very few) for a given element. The intensity of the energy emitted at the chosen wavelength is proportional to the amount (concentration) of that element in the analyzed sample. Thus, by determining which wavelengths are emitted by a sample and by determining their intensities, the analyst can quantify the elemental composition of the given sample relative to a reference standard.

ICP-AES analysis requires a sample to be in solution. Thus, interstitial waters can be analyzed simply, requiring only dilution in most cases. Igneous rocks, sedimentary rocks, and sediments, however, must be dissolved. This can be achieved either by a combined acid attack employing HF, HNO₃, and HCl acids, or by a LiBO₂ flux-fusion technique similar to that used for XRF preparation. In addition to being somewhat dangerous for routine shipboard work (because of the highly reactive nature of HF), the acid attack is not able to generate consistent and reliable data for Si because it volatilizes in the presence of HF. The acid digestion procedure also often results in incomplete analysis of refractory elements such as Ti, Cr, and Zr because their host minerals are often difficult to dissolve. The flux-fusion approach is employed on board the *Resolution* for several reasons: (1) it is safer because HF is not involved; (2) it is a complete dissolution technique, allowing determination of all elements, including Si and the refractory elements; (3) the resultant solutions are similar in composition (or matrix) because they are dominated by the presence of the LiBO₂ flux; and (4) the solutions are stable in dilute HNO₃ acid and can be transported safely back to the scientist's laboratory for further shore-based study.

All ICP-AES systems consist of several components, namely on three main aspects: the sample introduction system, the torch assembly, and the spectrometer. The sample introduction system on the ICP-AES consists of a peristaltic pump, Teflon tubing, a nebulizer, and a spray chamber. The fluid sample is pumped into the nebulizer via the peristaltic pump. The nebulizer generates an aerosol mist and injects humidified Ar gas into the chamber along with the sample. This mist accumulates in the spray chamber, where the largest mist particles settle out as waste and the finest particles are subsequently swept into the torch assembly. Approximately 1% of the total solution eventually enters the torch as a mist, whereas the remainder is pumped away as waste.

Humidification of the Ar gas injected into the nebulizer is important when analyzing samples with high dissolved solids, as is often the case with analysis of ODP rocks, sediments, and interstitial waters. Humidification takes place in the Ar humidifier, where Ar is bubbled through deionized water prior to its expulsion in the nebulizer.

The fine aerosol mist containing Ar gas and sample is injected vertically up the length of the torch assembly into the plasma. There are several recommended Ar flow rates used in the torch, as described in detail in the owner's manual and in the various publications provided. The radio frequency-generated and maintained Ar plasma, portions of which are as hot as 10,000 K, excites the electrons. When the electrons return to ground state at a certain spatial position in the plasma, they emit energy at the specific wavelengths peculiar to the sample's elemental composition.

The plasma is viewed horizontally by an optical channel. Light emitted from the plasma is focused through a lens and passed through an entrance slit into the spectrometer. There are two types of spectrometers used in ICP-AES analysis: sequential (monochromator) and simultaneous (polychromator). The JY2000 has a sequential spectrometer. This means that the diffraction grating in the spectrometer is analogous to a prism that refracts visible light into its component colors. The detector (photomultiplier tube) is fixed in space at the far end of the spectrometer. Rotation of the diffraction grating sequentially moves each wavelength into the detector. The computer

control ensures that the detector is synchronized with the grating so that the intensity at the detector at any given time is correlated with the wavelength being diffracted by the grating. The operator enters the wavelengths that he or she wishes to detect into the computer, the grating sequentially moves to the specified wavelengths, and the energy intensity at each wavelength is measured to provide a quantitative result that can be compared to a reference standard. Using standard spectroscopic techniques (e.g., background corrections), sequential ICP-AES can provide extremely flexible and rapid analysis of a number of chemical elements. The spectrometer is flushed with N₂ gas to improve the detection limits of elements with emission wavelengths that are severely compromised by interference with air (e.g., P). This N₂ flush, which is constantly maintained in the instrument regardless of whether such elements are being analyzed, also protects the optics from the corrosive aspects of the atmosphere, which are particularly acute at sea.



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Scanning Electron Microscope with Energy Dispersive X-Ray Spectrometer (SEM-EDX)

SEM is essentially a high magnification microscope, which uses a focussed scanned electron beam to produce images of the sample, both top-down and, with the necessary sample preparation, cross-sections. The primary electron beam interacts with the sample in a number of key ways:

- Primary electrons generate low energy secondary electrons, which tend to emphasise the topographic nature of the specimen
- Primary electrons can be backscattered which produces images with a high degree of atomic number (Z) contrast
- Ionized atoms can relax by electron shell-to-shell transitions, which lead to either X-ray emission or Auger electron ejection. The X-rays emitted are characteristic of the elements in the top few μm of the sample.

Magnification achievable is about 200,000x to 400,000x magnification. Comparing with optical microscope, SEM also provides much superior depth of field, unflat specimens can still be focused all around. In SEM, we use electron beam to bombard on a sample, which generates secondary electrons (that reveals surface morphology), backscattered electrons (that reveals composition contrast), characteristic Xray (use in elemental analysis), etc. All the signals generated are detected simultaneously by the individual detectors that are currently mounted on Scanning Electron Microscope (SEM)

Typical applications are in materials research, quality control, failure analysis, and forensic science. Industries that commonly use this technique include: semiconductor and electronics, metals, ceramics, minerals, manufacturing, engineering, nuclear, paper, petroleum, bio-science, and the motor industry.

EDX is the measurement of X-rays emitted during electron bombardment in an electron microscope (SEM or TEM) to determine the chemical composition of materials on the micro and nano- scale. By determining the energies of the X-rays emitted from

the area being excited by the electron beam, the elements present in the sample are determined (qualitative analysis). The rate of detection of these characteristic X-rays is used to measure the amounts of elements present (quantitative analysis). If the electron beam is raster over an area of the sample then EDX systems can also acquire X-ray maps showing spatial variation of elements in the sample. It can detect the full range of elements from Boron (atomic no. 5) to Uranium (atomic no. 92).



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X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) is a quantitative spectroscopic technique that measures the elemental composition, empirical formula, chemical state and electronic state of the elements that exist within a material. XPS spectra are obtained by irradiating a material with a beam of aluminum or magnesium X-rays while simultaneously measuring the kinetic energy (KE) and number of electrons that escape from the top 1 to 10 nm of the material being analyzed. XPS requires ultra-high vacuum (UHV) conditions.

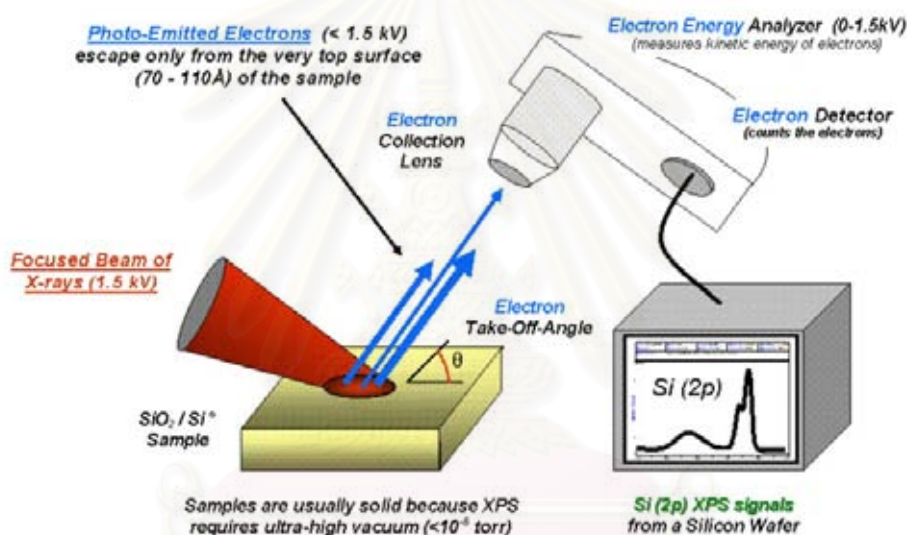


Figure A-3 Basic components of a monochromatic XPS system

XPS is a surface chemical analysis technique that can be used to analyze the surface chemistry of a material in its "as received" state, or after some treatment such as: fracturing, cutting or scraping in air or UHV to expose the bulk chemistry, ion beam etching to clean off some of the surface contamination, exposure to heat to study the changes due to heating, exposure to reactive gases or solutions, exposure to ion beam implant, exposure to ultraviolet light, for example.

XPS is also known as ESCA, an abbreviation for Electron Spectroscopy for Chemical Analysis. XPS detects all elements with an atomic number (Z) between those

of lithium ($Z=3$) and lawrencium ($Z=103$). This limitation means that it cannot detect hydrogen ($Z=1$) or helium ($Z=2$). Detection limits for most of the elements are in the parts per thousand range. Detection limits of parts per million (ppm) are possible, but require special conditions: concentration at top surface or very long collection time (overnight).

XPS is routinely used to analyze inorganic compounds, metal alloys, semiconductors, polymers, elements, catalysts, glasses, ceramics, paints, papers, inks, woods, plant parts, make-up, teeth, bones, medical implants, bio-materials, viscous oils, glues, ion modified materials and many others.

XPS is generally used to measure:

- elemental composition of the surface (1–10 nm usually)
- empirical formula of pure materials
- elements that contaminate a surface
- chemical or electronic state of each element in the surface
- uniformity of elemental composition across the top surface (aka, line profiling or mapping)
- uniformity of elemental composition as a function of ion beam etching (aka, depth profiling)

XPS can be performed using either a commercially built XPS system, a privately built XPS system or a Synchrotron-based light source combined with a custom designed electron analyzer. Commercial XPS instruments in the year 2005 used either a highly focused 20 to 200 micrometer beam of monochromatic aluminum K-alpha X-rays or a broad 10-30 mm beam of non-monochromatic (polychromatic) magnesium X-rays. A few, special design XPS instruments can analyze volatile liquids or gases, materials at low or high temperatures or materials at roughly 1 torr vacuum, but there are relatively few of these types of XPS systems.

Because the energy of a particular X-ray wavelength equals a known quantity, we can determine the electron binding energy (BE) of each of the emitted electrons by using an equation that is based on the work of Ernest Rutherford (1914):

$$E_{\text{binding}} = E_{\text{photon}} - E_{\text{kinetic}} - \Phi$$

Where E_{binding} is the energy of the electron emitted from one electron configuration within the atom, E_{photon} is the energy of the X-ray photons being used, E_{kinetic} is the kinetic energy of the emitted electron as measured by the instrument and Φ is the work function of the spectrometer (not the material).



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VITA

The author of this thesis was born on 9 March 1984, in Bangkok, Thailand. After receiving her bachelor's degree of engineering on geo-resources from the Department of Mining and Petroleum Engineering, Faculty of Engineering, Chulalongkorn University in 2006, she continuously started her geo-resources engineering master's study, which is presented in this thesis book in the Department of Mining and Petroleum Engineering, Faculty of Engineering, Chulalongkorn University. She was granted friendship scholarship to do this thesis during October 2006 - September 2007 from Earth Resources Engineering, Kyushu University, Fukuoka, Japan.



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