การเก็บกลับคืนโลหะทองคำและโลหะเงินในตะกรันทุติยภูมิจากกระบวนการทำให้ทองคำบริสุทธิ์โดยการตกตะกอนร่วมกับโลหะไฮดรอกไซด์

นางสาวร่มฉัตร ไชยรักษา

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
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RECOVERY OF GOLD AND SILVER IN SECONDARY SLAG FROM GOLD REFINING PROCESS BY CO-PRECIPITATION WITH METAL HYDROXIDES

Miss Romchat Chairaksa

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering Program in Mining Engineering
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ร่มฉัตร ไชยรักษา : การเก็บกลับคืนโลหะทองคำและโลหะเงินในตะกรันทุติยภูมิจากกระบวนการทำให้ทองคำบริสุทธิ์โดยการตกตะกอนร่วมกับโลหะไฮดรอกไซด์ (RECOVERY OF GOLD AND SILVER IN SECONDARY SLAG FROM GOLD REFINING PROCESS BY CO-PRECIPITATION WITH METAL HYDROXIDES) อ. ที่ปรึกษา: รศ.ดร. ขวัญชัย ลีเผ่าพันธุ์, อ.ที่ปรึกษาร่วม: รศ.ดร. ดาวัลย์ วิวรรธนะเดช , 82หน้า. ISBN 974-142-425-6.

กระบวนการทำให้ทองคำบริสุทธิ์โดยใช้ก๊าซคลอรีนเป็นสารแยกสกัด (Miller Chlorination Process) เป็นกรรมวิธีที่เก่าแก่และมีการใช้อย่างแพร่หลายในกระบวนการผลิตทองคำขนาดใหญ่ ตะกรันที่เกิดจากกระบวนการดังกล่าวเรียกว่า ตะกรันปฐมภูมิ (Primary Slag) มักมีปริมาณโลหะมีค่าทองคำหลงเหลืออยู่ 5-10% โดยน้ำหนัก หากนำตะกรันดังกล่าวไปทำให้บริสุทธิ์โดยวิธีการเผาถลุงจะได้ตะกรันทุติยภูมิ (Secondary Slag) ซึ่งยังมีโลหะมีค่าทองคำหลงเหลืออยู่ประมาณ 150-200 ppm และ โลหะเงินอยู่อีกประมาณ 1500 ppm ซึ่งยังมีศักยภาพที่จะเก็บกลับคืนโลหะมีค่า(ทองคำและเงิน) งานวิจัยนี้จึงทำการศึกษาการเก็บกลับคืนโลหะทองคำและเงินในตะกรันทุติยภูมิโดยวิธีการทางกายภาพ (บดแยกและโต๊ะสั่น) แล้วตามด้วยวิธีการแยกสกัดทางเคมีโดยใช้กรดไนตริกและกรดกัดทองตามลำดับ จากนั้นทำการตกตะกอนแยกทองคำและเงินออกจากสารละลายกรดกัดทองด้วยเทคนิคการตกตะกอนร่วมกับโลหะไฮดรอกไซด์ แล้วทำให้บริสุทธิ์อีกครั้งโดยละลายตะกอนด้วยกรดไนตริกเปรียบเทียบกับกรดไฮโดรคลอริก

ผลการศึกษาพบว่าการแยกทางกายภาพโดยวิธีบดแยกพบอัลลอยด์ของทองคำ-เงิน-ทองแดงแยกตัวออกมาที่ขนาด 70 เมช หลังจากนำไปผ่านโต๊ะสั่น สามารถเพิ่มความเข้มข้นของทองคำและเงินในตะกรันเป็น 0.126% และ 1.56% ตามลำดับ จากตะกรันเริ่มต้นซึ่งประกอบด้วย 0.015% ของทองคำ และ 0.174% ของเงิน เมื่อนำตะกรันที่ผ่านโต๊ะสั่นไปผ่านกระบวนการทางเคมีโดยการสกัดแยกด้วยกรดไนตริก ตามด้วยกรดกัดทอง แล้วตกตะกอนทองคำและเงินร่วมกับโลหะไฮดรอกไซด์ที่ pH~6 จะสามารถเก็บกลับคืนทองคำได้เกือบ 100% และเก็บกลับคืนเงินได้ประมาณ 80% หลังจากทำให้ทองคำบริสุทธิ์โดยวิธีละลายตะกอนด้วยกรดไนตริกเปรียบเทียบกับกรดไฮโดรคลอริก พบว่ากรดไนตริกเข้มข้น 1 โมลาร์ มีประสิทธิภาพในการทำให้ทองคำบริสุทธิ์สูงกว่ากรดไฮโดรคลอริกเข้มข้น 1 โมลาร์

ภาควิชา..วิศวกรรมเหมืองแร่และปิโตรเลียม...ลายมือชื่อนิสิต..........ร่มฉัตร ไชยรักษา..........
สาขาวิชา..............วิศวกรรมเหมืองแร่.........ลายมือชื่ออาจารย์ที่ปรึกษา..............................
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ROMCHAT CHAIRAKSA: RECOVERY OF GOLD AND SILVER IN SECONDARY SLAG FROM GOLD REFINING PROCESS BY CO-PRECIPITATION WITH METAL HYDROXIDES. THESIS ADVISOR: ASSOC.PROF.QUANCHAI LEEPOWPANTH, Ph.D., THESIS COADVISOR : ASSOC.PROF. DAWAN WIWATTANADATE, 82 pp. ISBN 974-14-2425-6.

Purification of gold using chlorine gas as an extracting agent is one of the oldest and most widely used process in large scale gold refining, so called "Miller Chlorination Process". Slag derived from this process is usually called "Primary slag" generally containing 5-10 wt% gold. Secondary slag produced after smelting of the primary slag generally contains approximately 200-300 ppm gold and 1000 ppm silver, which indicates the high potentiality for further recovery of precious metals (Au and Ag).

The aim of this study is to develop an effective recovery system for gold and silver, from secondary slag during gold refining process. The recovery process consists of both physical process (comminution and shaking table) and chemical separation (extraction with nitric acid and aqua regia respectively). The extracted gold and silver were recovered by co-precipitation with metal (e.g. Fe, Cu) hydroxides at pH 6, and then, the co-precipitation including gold was dissolved with 1 M hydrochloric acid or 1 M nitric acid. The result of physical separation process showed alloy of Au-Ag-Cu was liberated from the slag under the size of 70 Mesh. After passing the shaking table, the concentration of slag was upgraded from 0.015% to 0.126% of gold and from 0.174% to 1.56% of silver. Then, the two-stage leaching with nitric acid and aqua regia was applied to recover silver as AgCl precipitate, and gold as $[AuCl_2]^-$ with $AgNO_3$ impurities. Then, the solution or leachate was further concentrated by co-precipitation with metal (Fe, Cu) hydroxides at pH 6. The chlorohydroxy Au (III) complexes co-precipitated on metal hydroxides are reduced to elemental gold (Au^0) without adding any reducing reagents. The gold and silver was further purified by (comparatively) dissolved using 1M HNO_3 and 1M HCl. The results showed that gold and silver could be effectively purified by treatment of 1M HNO_3 rather than that of 1M HCl.

Department... Mining and Petroleum Engineering...Student's signature....ร่มฉัตร ไชยรักษา...
Field of study... Mining Engineering......................Advisor's signature.Q. Leepowpanth
Academic year...............2005............................Co-advisor's signature.........................

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CHAPTER I

INTRODUCTION

1.1 General introduction

The processing of industrial wastes containing substantial quantities of valuable components often becomes an absolute necessity for their recovery or separation. In addition, even secondary slag passed refining process once still contains much valuable elements. Therefore, it is important to develop a more efficient and effective method to recover precious metals, especially gold and silver, from the secondary slag by physical separations *(Delfini, 2000)* followed with chemical extractions. Recovery of metals from the slag and its utilization are quite important in terms of not only for saving metal resources but also for environmental protection.

According to the World Gold Council, demand and price of gold gradually increase during the last decade (Figure 1.1). This is due to not only the jewelry market, but also the increasing uses of gold in industries, as well as medical applications *(Aworn, 2005)*. Gold and silver are relatively rare precious metals with a particular beauty *(Marcos, 2004)*. Furthermore, it is still largely consumed in jewelry manufacturing. Therefore, gold and silver recycling from scraps and residues has also raised much interest *(Manni, 2001)*. Some wastes actually contain extractable valuable metals such as gold, silver and copper. Demand for gold and silver will continue to increase in coming near future, therefore, it is important and essential to investigate the recovery of gold and silver from secondary slag as recycling system of precious metals.

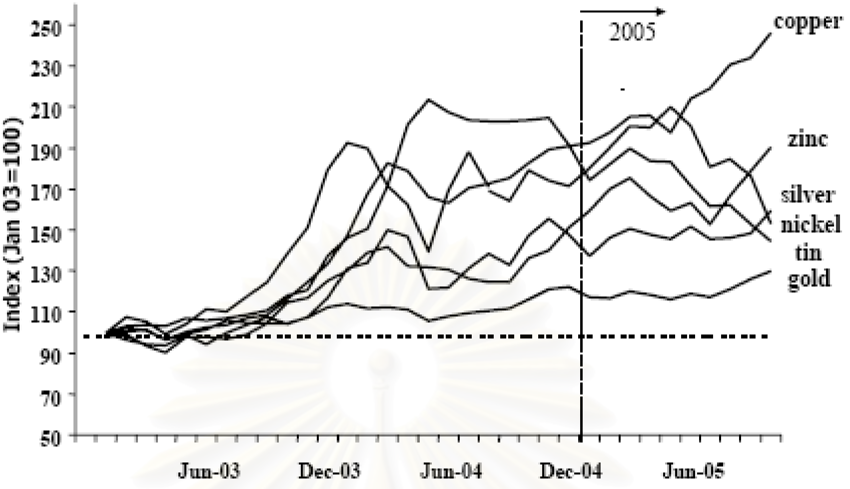


Figure 1.1 Gold, silver and base metals prices.

(reference www.gold.org)

Various kinds of slag are produced as by-products in metallurgical processes or as residues in incineration processes. The primary slag is classified as the waste, that is after the refining procedure of precious metals using chloride re-leach method (Miller process). This primary slag usually contains approximately 5-10 percent gold. The secondary slag is produced after smelting of the primary slag. This contains about 200-300 ppm gold and 1000 ppm silver (see the Figure1.2).

There are three main methodologies for extraction and refining process of gold as follows:

1. Miller Process: Using chlorine gas
2. Wohlwill Process: Using electrolysis
3. Chemical Refining Process: Using nitric acid and aqua regia

As each methodology utilizes the different properties of gold, the three methodogies provide different results. The Miller process is usually used for the primary refining. While the Wohlwill process and the chemical process are applied to purify gold. Figure 1.2 shows a flowchart for chemical refining process of gold slag.

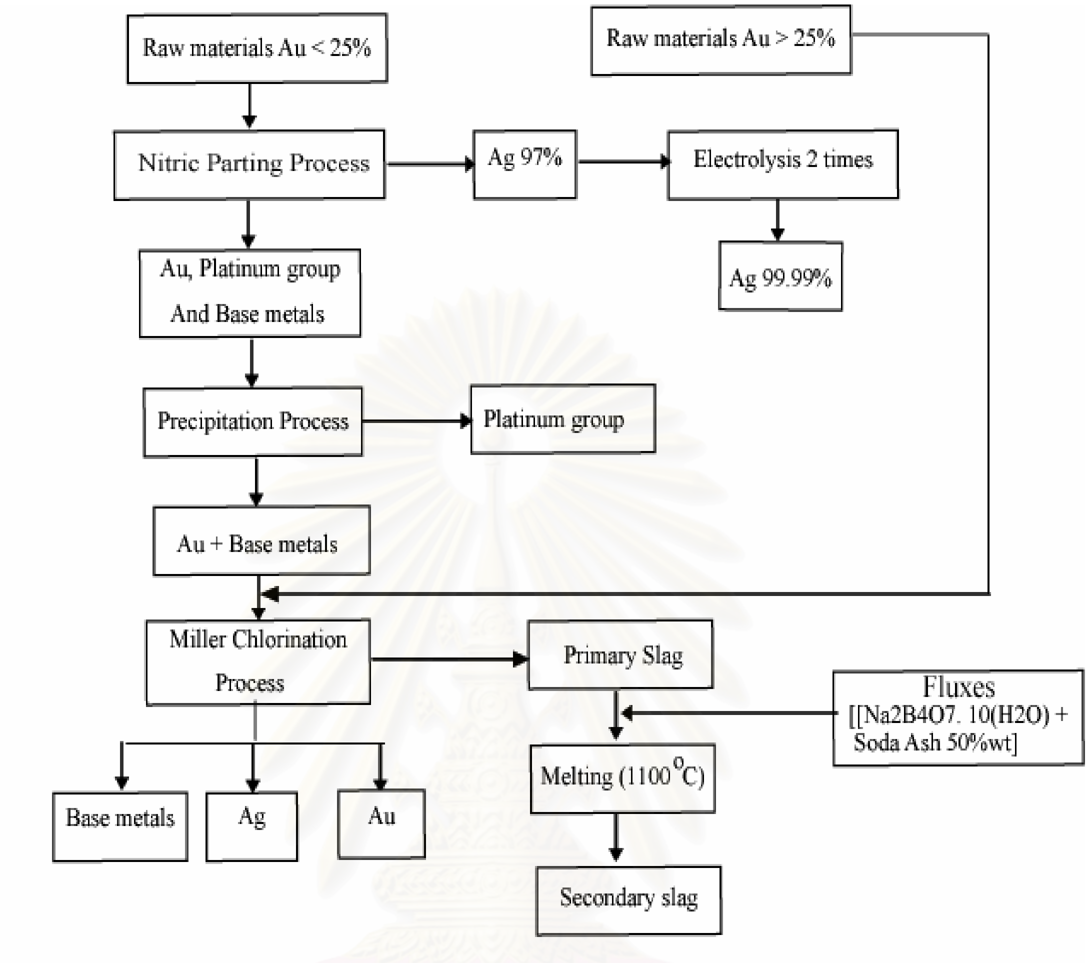


Figure 1.2 Flowchart of gold refining process.

The purpose of this work is to recover precious metals, especially gold and silver, from jewelry secondary slag by physical and chemical separation and then applying co-precipitation method and purification operation.

1.2 Objectives of this study

The objective of this study is to develop a recycling system and recover precious metals, especially gold and silver, from secondary slag produced in precious metal refining. The chemical separation study is firstly focused on the leaching by aqua regia, followed with the co-precipitation of gold and silver from leachate with metal hydroxides, and then focusing on purification of gold and silver by dissolving with acidic reagent.

1.3 Outline of this study

The process for recovery gold and silver of this study is shown in the flowchart below.

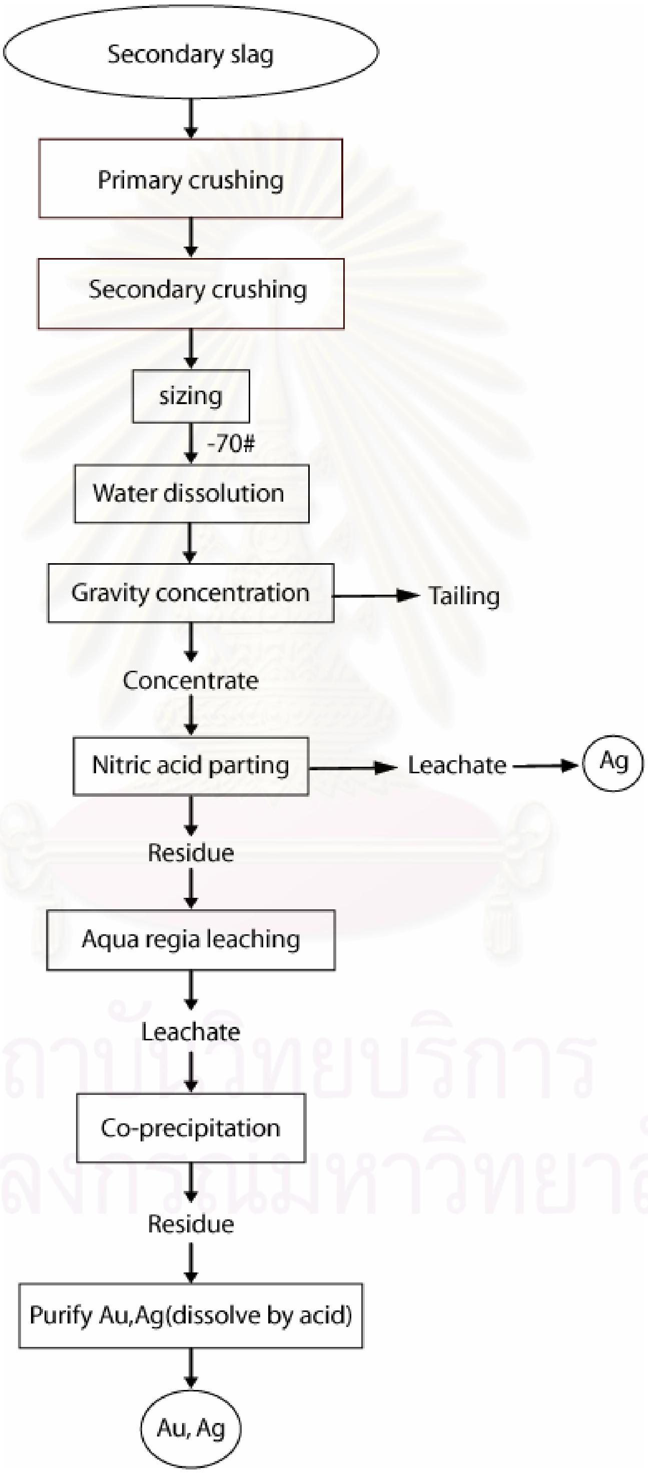


Figure 1.3 Outline of the process.

1.4 Expected benefits

It is to provide a new, simpler, harmless and efficient alternative system for recycling to recover precious metals and the system which can be applied for industry with scaling up in practice.

1.5 Order of presentation

In order to present this research, the author separated the contents in 6 chapters as follows;

Chapter 1: Introduction, objective of this study, outline of the experiments and expected benefits.

Chapter 2: Literature review, background of this study, rationales and related research.

Chapter 3: The physical concentration by comminution and gravity concentration to recover gold and silver from secondary slag.

Chapter 4: The hydrometallurgy recovery of gold and silver by nitric acid parting and aqua regia leaching in terms of two parameters; 1) reaction time and 2) the solid-liquid ratio (the weight of residue/ the volume of aqua regia).

Chapter 5: Gold and silver co-precipitation with metal hydroxides from aqueous solution (after aqua regia leaching in chapter 4), a comparison of the efficiency of purification between 1M HCl and 1M HNO_3.

Chapter 6: Conclusion of this study and suggestion as to improvement.

CHAPTER II

BACKGROUNDS AND LITERATURE REVIEWS

2.1 Properties and used of gold and silver

2.1.1 Gold

Gold is used in coinage and is the standard for many monetary systems. Gold is used for jewelry, dental work, plating, and reflectors. The melting point of gold is1064.43°C, boiling point is 3080°C, specific gravity is 18.88 (20°C), with a valence of 1 or 3. The melting point of gold is 1064 Degree Celsius. In mass, gold is a yellow-colored metal, although it may be black, ruby, or purple when finely divided. Gold is the most malleable and ductile metal. One ounce of gold can be beaten out to 300 ft^2. Gold is a good conductor of electricity and heat. It is not affected by exposure to air or to most reagents. It is inert and a good reflector of infrared radiation.

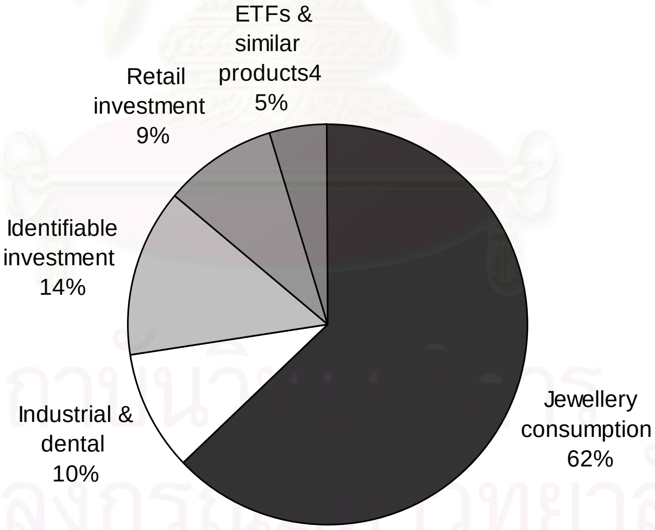


Figure 2.1 End-use gold demands (2005).

(reference www.gold.org)

Gold is found as the free metal and in telluride. It is widely distributed and almost always associated with pyrite or quartz. Gold is found in veins and in alluvial deposits. Gold occurs in sea water in the amount of 0.1 to 2 mg/ton, depending on the location of the sample.

Gold is usually alloyed to increase its strength. Pure gold is measured in troy weight, but when gold is alloyed with other metals such as copper, nickel, palladium, silver and zinc. The term karat is used to express the amount of gold present. The yellow, red and green gold alloys are basically ternary alloys of gold, silver and copper. Figure 2.2 shows the composition ranges of the various colors. Ternary (triangular) diagrams are useful to obtain information on the melting temperature, hardness and color of any of these alloys.

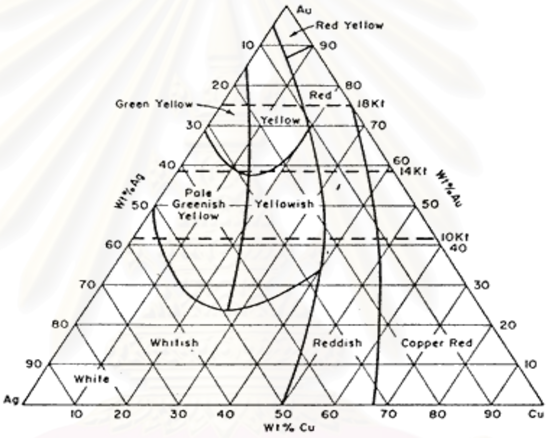


Figure 2.2 Weight percent composition ranges for various colors of Ag-Ag-Cu.

(Marden, J. & House, I, 1992)

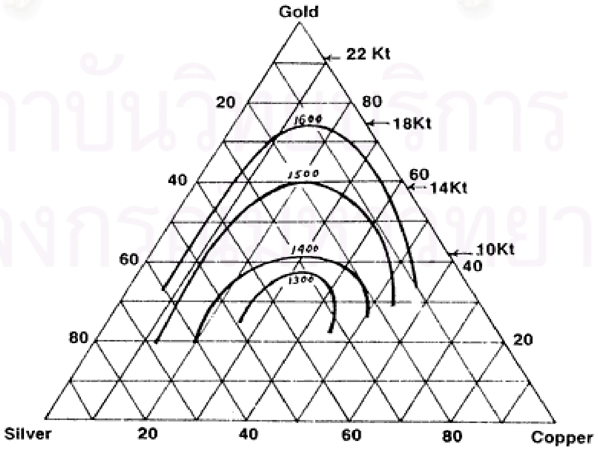


Figure 2.3 Solidus of Au-Ag-Cu Alloys.

(Marden, J. & House, I, 1992)

2.1.2 Silver

Together with gold, and the platinum-group metals, silver is one of the so-called precious metals. Because of its comparative scarcity, brilliant white color, malleability, and resistance to atmospheric oxidation, silver has long been used in the manufacture of coins, ornaments, and jewelry. Silver has the highest known electrical and thermal conductivity of all metals and used in fabricating printed electrical circuits and as a vapor-deposited coating for electronic conductors. Historically, a major used of silver has been monetary, in the term of reserves of silver bullion and in coins. By the 1960s, however, the demand of silver for industrial purpose, in particular the photographic industry, exceeded the total annual world production.

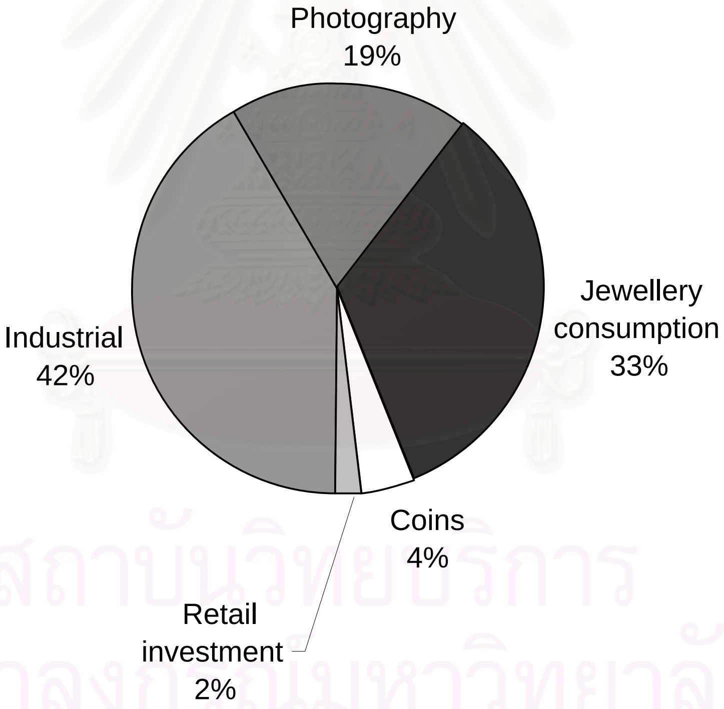


Figure 2.4 End-use silver demands (2005).

(reference www.silverinstitute.org)

Silver is widely distributed in nature but the total amount is quite small when compared with other metals; the metal constitutes 0.05 parts per million of the Earth’s crust. Practically all sulfides of lead, copper, and zinc contain some silver. Silver-bearing ores may contain amounts of silver from a trace to several thousand troy ounces per ton, or about 10 percent.

Alloys of silver with copper are harder, tougher, and more fusible than pure silver and are used for jewelry and coinage. The proportion of silver in these alloys is stated in terms of fineness. Most of the silver alloys used in jewelry are binary silver-copper alloys with a higher percentage of silver (80% or more). Figure 2.5 shows the copper-silver phase diagram.

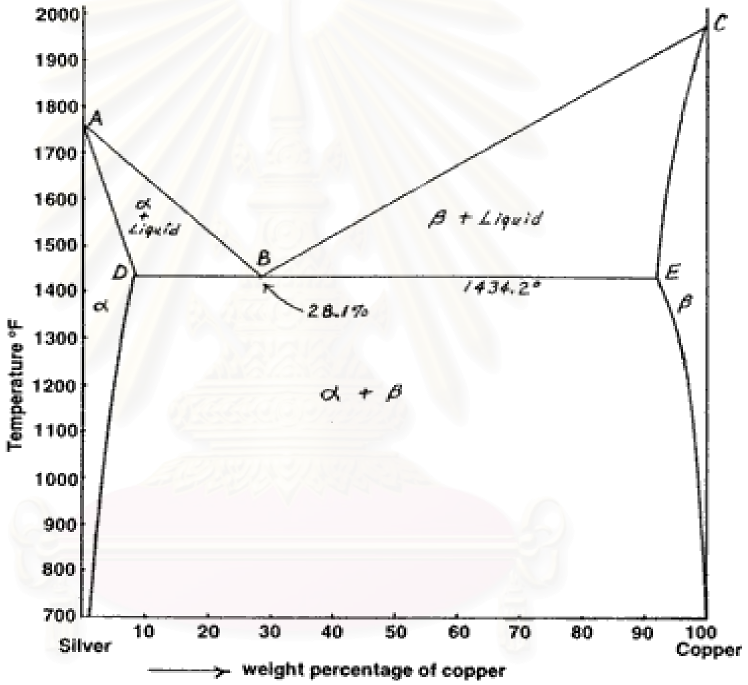


Figure 2.5 Ag - Cu Phase Diagram.

(Marden, J. & House, I, 1992)

2.2 Gold refining process

As a precious metal, gold is intensively recycled from any and every collectable waste. Many of the processes used for primary gold extraction are applicable to its secondary recovery. Refining is a practice that must be done precisely and methodologically to ensure the full recovery of gold, as well as an end product that is free of impurities, which can lead to quality problems when the metal is reused in production. But refining doesn’t have to be a mystery to manufacturers.

There are several methods commonly used to recover metals. Some operations are suitable for manufacturers and jewelers who wish to refine in-house, while others are designed for commercial refiners who handle large lots. The following are the most common methods used in the jewelry and gold refining process.

1. Miller Chlorination Process

The Miller chlorination process is one of the oldest and most widely used processes in large scale gold refining. It involves bubbling chlorine gas through molten bullion. The base metals and silver are removed as chlorinated compounded, which either volatilize or form a molten slag on the surface of the melt. The process is complete when purple fumes of gold chloride start to form, usually when the gold content reaches a purity of 99.6 to 99.7 percent. Any PGMs present are not removed, and futher refining is necessary if pure gold is required.

The typical gold purity achieved by this process is 99.5 percent, with silver as the main impurity. The process has the advantage of being quick and is widely used for primary refining of gold from the mines.

Considerable technical skills are required for the process, and there are a number of health and safety implication in the use of chlorine gas. Expensive fume extraction and treatment facilities are essential. Consequently, this process is not suited for small to medium scale refining by jewelers.

The Miller chlorination process is used to remove silver and other metal impurities from gold by bubbling chlorine gas into the molten metal at 1150 ^{0}C. Under these conditions iron, zinc and lead form gaseous chlorides, while copper and silver form liquid chlorides, as reactions shown below:

$$\mathrm{Fe} + \mathrm{Cl_2} \leftrightarrow \mathrm{FeCl_2} \quad : \quad \Delta G^0 = -200.6 \text{ kJ mol}^{-1}$$

$$\mathrm{Zn} + \mathrm{Cl_2} \leftrightarrow \mathrm{ZnCl_2} \quad : \quad \Delta G^0 = -288.8 \text{ kJ mol}^{-1}$$

$$\mathrm{Pb} + \mathrm{Cl_2} \leftrightarrow \mathrm{PbCl_2} \quad : \quad \Delta G^0 = -200.6 \text{ kJ mol}^{-1}$$

$$\mathrm{2Cu} + \mathrm{Cl_2} \leftrightarrow \mathrm{2CuCl_2} \quad : \quad \Delta G^0 = -125.6 \text{ kJ mol}^{-1}$$

$$\mathrm{2Ag} + \mathrm{Cl_2} \leftrightarrow \mathrm{2AgCl_2} \quad : \quad \Delta G^0 = -138.1 \text{kJ mol}^{-1}$$

$$\mathrm{2Au} + \mathrm{3Cl_2} \leftrightarrow \mathrm{AuCl_2} \quad : \quad \Delta G^0 = \text{positive}$$

The metals are converted to their respective chlorides in the sequence Fe > Zn > Pb > Cu > Ag >>> Au, as illustrated graphically in Figure 2.6

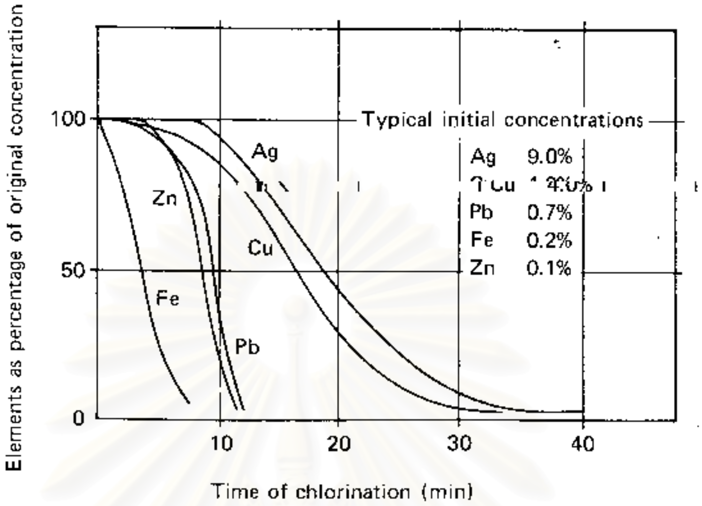


Figure 2.6 The effect of chlorination time on metal removal.

(Marden, J. & House, I, 1992)

2. Wohlwill Electrolytic Process

An old and well-established process, the Wohlwill method is widely used in major gold refineries, often in conjunction with the Miller process. (For typical jeweler’s scraps and wastes, a preliminary refining step, such as the Miller or inquartation process, is required.) An electrolytic refining technique, it entails the electrolytic dissolution of an impure gold anode in a hydrochloric acid-based electrolyte. The process results in a deposition of 99.99 percent pure gold at the cathode. The silver and insoluble PGMs (along with a little gold) fall out as anode slimes, with the silver precipitated out as silver chloride, and all are recovered later. Any base metals, platinum, and palladium remain in solution and can be treated later to recover the PGMs.

Gold with purity at least 98.5 percent is normally required for the anode, as too much silver will result in silver chloride building up on the anode surface and preventing dissolution of the gold. Typically, the input material for the anode is the gold from the Miller process, described previously.

Because it is time consuming-typically 24 hours or more and suffers from the lock-up of gold inventory in the electrodes and electrolyte, the Wohlwill process is not suitable for small-scale refining

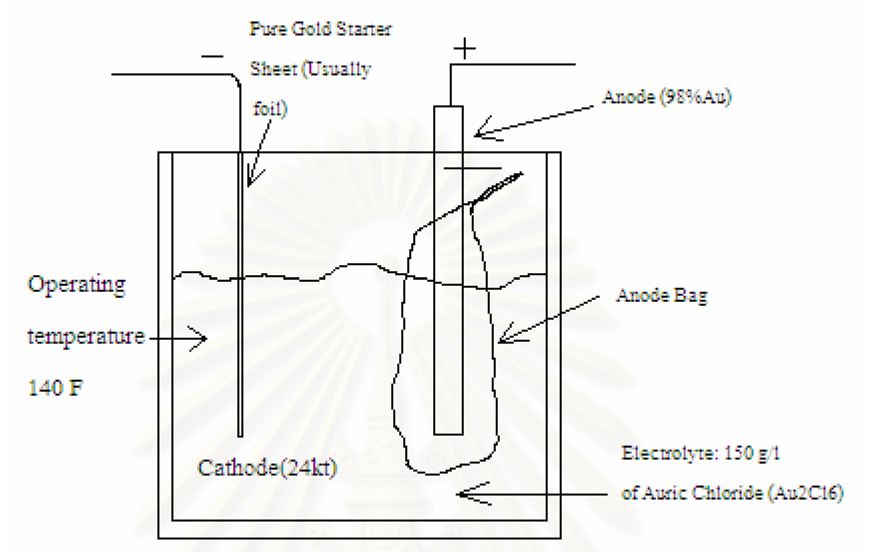


Figure 2.7 Basic gold electrorefining cell (Wohlwill cell).

(Ammen C.W., 1997)

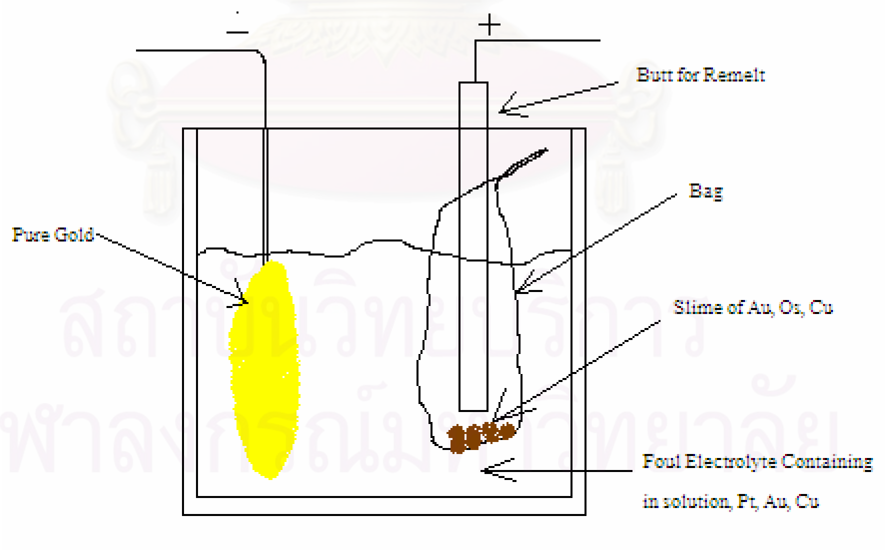


Figure 2.8 End products of Wohwill cell.

(Ammen C.W., 1997)

3. Chemical Refining Process

The Agua Regia process can produce gold of up to 99.99 percent purity. It is based on the fact that Aqua Regia (a mixture of hydrochloric and nitric acids in a 3:1 ratio) can dissolve gold into soluble gold chloride. The process is most suited to medium to large-scale operation. A typical batch size is 4 kg of scrap, and equipment in a range of capacities is commercially available from several suppliers.

The main limitation of the process is that the feed material should have a silver content of 10 percent or less to avoid blocking up the dissolution of the scrap. Because of this, pretreatment by the inquartation process to reduce the silver content may be necessary. Alternatively, the low silver content may be achieved by a judicious blending of batches of scrap. Thus, the process is more suited for medium to high karat gold scrap refining.

In practice, the scrap is grained to increase surface area and treated with a series of Aqua regia acid additions. Gentle heating speeds up dissolution.

Copious brown fumes of nitrogen oxide are emitted while the gold is being dissolved. Fume abatement systems are required to stop emission of these toxic fumes and to comply with pollution laws. It is also worth nothing that these strong acids require suitable storage and safety procedures.

Once the gold is dissolve, the yellow-green solution must be filtered to remove the insoluble silver chloride, the insoluble PGMs, and any non-metallic, such as abrasives and inclusions. The gold can then be selectively precipitated using a number of reducing agents, such as ferrous (also known as Copperas), sodium bisulphate and sulphur dioxide gas. Other less frequently used agents include hydrazine, oxalic acid, and hydroquinone. Some emit copious quantities of gas and some are carcinogenic.

2.3 Smelting with flux

The purpose of smelting is to remove base metal and other impurities from high grade concentrates to produce gold-silver bullion containing typically> 95% precious metals. The smelted product, called dore bullion.

The smelting process is achieved by heating the material in the presence of slag forming flux at temperatures in excess of the smelting point of all the components of the charge, typically between 1200°Cand 1400°C . The molten gold and silver form an alloy that is heavier than the slag and sinks to the bottom of the smelting vessel. The efficiency of separation depends on the quality of the slag that is formed, measured in terms of gold (and silver) grades in the slag and the recovery of the base metals(and other impurities) to the slag, The performance depends on the nature of the gold-bearing material smelted and the properties of the fluxes used. Silica usually forms the basis for the flux as it has the capability of dissolving most metal oxides. The metal oxides break up the silica lattice and are incorporated into the modified structure. Silica has a high melting point (1723°C) and the tends to form a highly viscous slag which may entrain precious metals. The addition of sodium and boron oxides (i.e. sodium borate, or “borax”, $Na_2B_4O_7 \cdot 10H_2O$) reduces both the melting point and viscosity. This is illustrated in the ternary phase diagram for the silica-sodium oxide-borate system, given in Figure 2.9. The reaction of sodium borate with the metal oxides is analogous to that of silica. Consequently, silica-sodium borate mixtures are commonly used as fluxes.

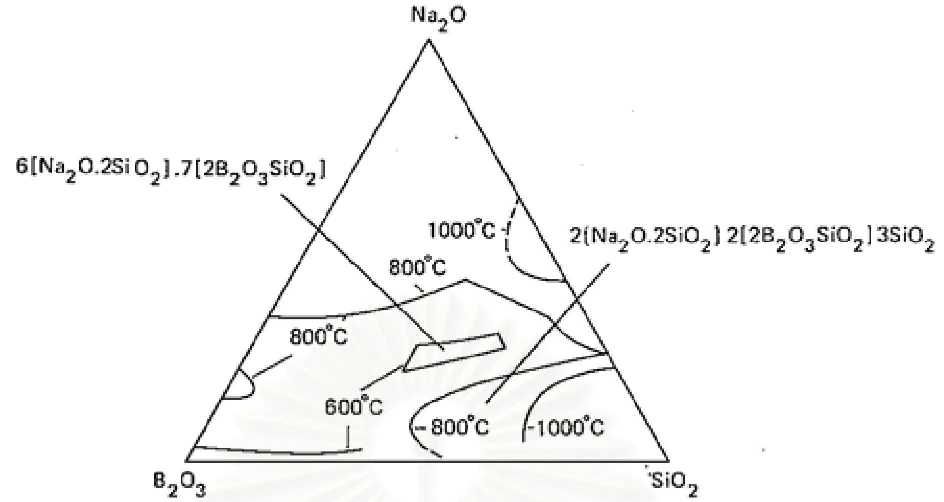


Figure 2.9 Na_2O - B_2O_3 - SiO_2 phase.

(Marden, J. & House, I, 1992)

Once smelting is complete the slag is poured off and the precious metal alloy is removed from the furnace. The metal are allowed to cool in bar or button moulds. Ideally the slag should be clear and uniform, with a grey-greenish coloration.

Direct smelting of steel wool cathodes requires the use of a strongly oxidizing flux to fully oxidize all the iron present and remove it in to the slag phase. The ternary phase diagram for the iron oxide-silica-sodium oxide system is shown in Figure 2.10.

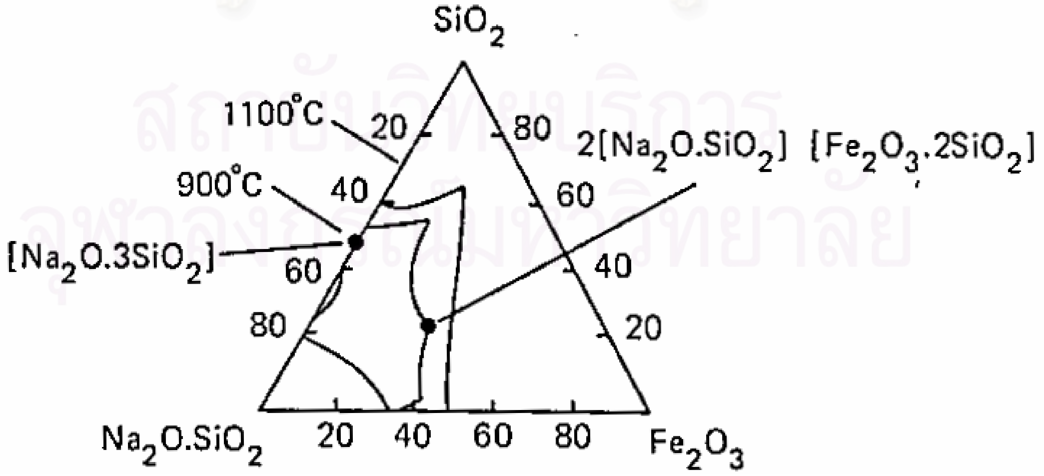


Figure 2.10 Na_2OSiO_2 – Fe_2O_3 – SiO_2 melting point diagram.

(Marden, J. & House, I, 1992)

2.4 Literature reviews

Apisit Namprasanthai (2003) studies the distribution of Precious Metals in secondary Slag from Gold Refining Process", there are two main categories of secondary slag

- Valuable materials

  Alloy of gold, silver and copper

- The composition materials of Borax (Na2B4O7.10H2O), containing

  Borax ($Na_2B_4O_7.10H_2O$)

  Sodium Aluminum Silicate ($NaAlSiO_4$)

  Hematite (Fe_2O_3)

  Sodium Zinc Silicate ($NaZnSiO_4$)

  Sodium Chloride (NaCl)

  Calcium Silicate (Ca_2SiO_4)

Precious metals in Secondary slag were recovered by physical separation. Alloy of Au-Ag-Cu liberated from secondary slag at size under 70 mesh and then concentrated by shaking table. Concentrate from the recovery with shaking table having percentage of 2% gold and 6% silver was suggested to use chemical process to upgrade and purify precious metals.

Theeraporn .R et.al. (2001) studies the recovery of silver from Thai industrial jewelry scrap. A study of silver leaching which is the first stag in hydrometallurgical recovery from Thai industrial jewelry scrap has been carried out using nitric acid as the leachant. The effects of temperature, particle size, stirring speed and concentration of nitric acid on the leaching rate of silver scrap have been investigated. The rate of dissolution increased with nitric acid concentration up to 7.92 M(40 wt%) and then decreased at 10.4 M(50wt%). The highest rate of dissolution occurs at the concentration between 7.92 and 10.4 M. From the result, it was concluded that the overall leaching rate of silver in jewelry scrap with nitric acid at 26 to 85 °C is described best by the surface chemical reaction limiting utilizing the shrinking core model. From this conclusion, the range of nitric acid parting is also able to apply in the section nitric acid parting, for remove base metals and recovery silver in the first stage before aqua regia leaching.

*Kitamoto S et.al. (2005)*The co-precipitation of Au (III) complex ions with iron (III) hydroxide was studied as a function of pH, electrolyte concentration, and iron concentration at 30 ^{o}C. Most of Au (III) complex ions were co-precipitate with iron (III) hydroxide under neutral pH, lower Cl concentration, and lower iron concentration. Au (III) complex ions were co-precipitated effectively with iron (III) hydroxide and were spontaneously reduced to elemental gold which grows to large colloid particles by aggregation. Iron (III) hydroxide with gold particles is dissolved with acid and filtered. The remaining gold particles are recovered. From the result of this study, it was concluded that co-precipitaion of Au (III) complex ions with iron hydroxide may be applied to gold recovery from solutions leached from electronic product wastes. From this conclusion, can be applied this method to recover Au (III) complex ions from aqua regia leached from secondary slag.

Uchida .A.et al. (2002) The adsorption of gold on iron (III) and aluminum hydroxides from solutions containing Au (III) complexes has been studied as a function of pH and chloride concentration at 30 ^{o}C. Iron (III) hydroxide was more effective in adsorbing gold from solution than aluminum hydroxide. However, both hydroxides controlled the behavior of Au (III) complex with very similar manner. The most effective gold adsorption occurred in aqueous solution with near neutral pH and low Cl concentration. In this solution condition, Au (III) complexes were mainly dissolved as $AuCl_2\ (OH)\ _2^-$ and $AuCl\ (OH)\ _3^-$, and the surface charge for both hydroxides was positive. In addition, the absorbed Au (III) complexes were spontaneously reduced to elemental gold in spite of the absence of a specific reducing agent.

CHAPTER III

PHYSICAL CONCENTRATION OF GOLD AND SILVER FROM SECONDARY SLAG

3.1 Introduction

The objective of this section is to apply the physical separation circuit for recovering precious metals from secondary slag. In order to produce a mineral concentrate of a sufficiently high grade, it is referred to the ore processing for initial treatment of mined material, and then the mineral concentrate is able to be satisfactorily processed further to the pure metal or other end product. Since particle size, shape and liberation degree play crucial roles in mechanical recycling processes, therefore, most of the mechanical recycling processes have a certain effective size range *(Forssberg and Cui, 2003).* For this reason, valuable minerals must be firstly separated from those of no commercial value, so called “gangue”.

Based on the process in this study, primary crushers are designed to reduce the size of secondary slag from 10-30 cm down to 100-200 mm. Machines such as jaw crushers apply a fracture force to the large particles and break into the secondary slag by compression. In a jaw crusher, ore falls into a wedge-shaped space between a fixed and a moving crushing plate. Fed material is nipped and squeezed until it breaks and released in the closed circuit. This operation is continued until it finally escapes through the gap set with further down size at the bottom while the jaws open and close.

In the same secondary slag, *Apisit Numprasanthai (2003)* has reported that the precious metals were liberated from the gangue at size 70 mesh. After that, gravity separation by shaking table was applied. In this study, jaw crusher and roller crusher are used for the primary and secondary crushing respectively. Then the gravity separation method by a shaking table is applied to the concentrated metallic particles out of the secondary slag.

3.2 Experimental

3.2.1 Materials

Samples of secondary slag used in this study were collected from smelting operations of Greatest Gold and Refining Co. Ltd., Bangkok, which is the biggest gold refining factory in Thailand. The amount of secondary slag collected was 200 Kg for the laboratory work.

The original secondary slag is classified into black and blue colored types by appearance and both types are shown in Figure 3.1. However, experiments were carried out on the mixture of both types of slag due to the difficulty in separating. The chemical composition of original secondary slag is given in Table 3.1.

Figure 3.1 Original Secondary slag.

Table 3.1 Chemical composition of original secondary slag analyzed by XRF.

Sample Oxides and Elements	Secondary Slag (black color)	Secondary Slag (blue color)
SiO_2 (%)	38.3	15.7
Al_2O_3	38.9	1.89
Fe_2O_3	1.56	1.55
MnO	0.01	0.01
MgO	0.17	0.04
CaO	2.53	1.00
Na_2O	15.1	54.8
Cl	0.97	6.14
Ag(ppm)	**1650**	**455**
Au(ppm)	**238**	**n.d.**
Cu(ppm)	1310	483
Zn(ppm)	2860	31040

Table 3.1 shows the chemical composition of the original secondary slag for both black and blue color from gold refining process after melting with flux. The content of SiO_2 and Al_2O_3, in the black colored part is approximately 2.5 and 20 times more than the blue one, respectively. Whereas that of Na_2O and Cl in the blue colored part is 3.5 and 6 times more than the black one. Again, the content of **Ag** in the black colored part is approximately 4 times more than the blue one, on the other hand, **Au** is contained only in the black part.

3.2.2 Instruments

1. Hammer mill
2. Jaw crusher
3. Sieve
4. Shaking Table
5. Nikon polarization microscope E6TP-M61
6. Shimudsu Superscan SS-550 scanning Electron microscopy (SEM-EDX)
7. Rigaku RIX 3100 X-ray Fluorescence Spectrometer (XRF)

3.2.3 Procedure of Comminution and size separation

The comminution circuit is designed to produce a crushed secondary slag with a narrow size distribution and to minimize the production of fines. The amount of secondary slag is 200 kg. Both black and blue types of samples were comminuted by mixture in jaw crusher and roller crusher until the fractions reached smaller than 70mesh in particle sizes. They give a shearing action which helps to break the metal free at metallic alloy-slag boundaries.

The primary crusher in close circuit is a single-toggle jaw crusher which can reduce the size of the feed from 300 to 10 mm. The oversize (+10 mm) of secondary slag is fed back to the jaw crusher, and the undersize (-10 mm) of secondary slag is fed to the secondary crusher. The secondary crusher in close circuit is a roller crusher which can crush from 10 mm to 70mesh. The size under 70mesh product is then fed into the water soluble circuit.

3.2.4 Procedure of physical separation

The gravity separation method is used for separation of metallic alloy particles from secondary slag. A shaking table is used for this process to upgrade, because the density of the metallic alloy particles is higher than that of slag particles. The type of shaking table selected for this study is a wifly shaking table. The important requirement is that the shaking table should be able to handle a variable feed grade and produce a clean concentrate at high recovery. This middling is fed into shaking table again and tailing is discarded. The physical separation process is shown in Figure 3.2.

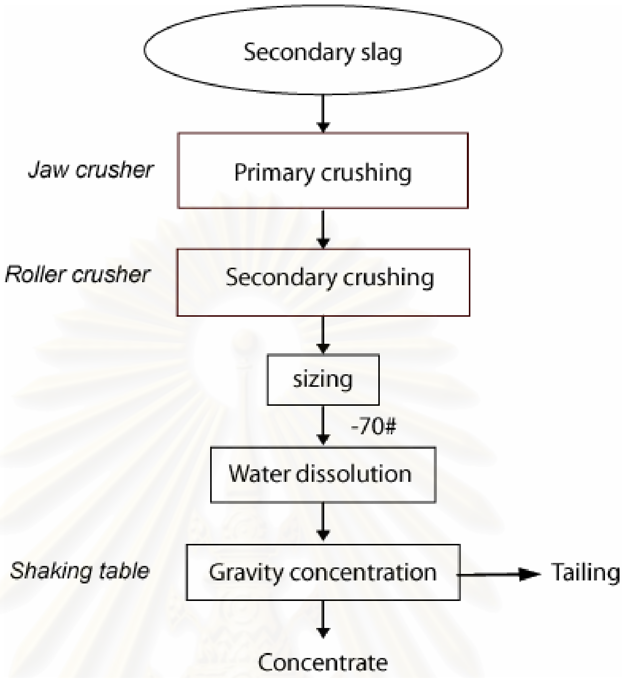


Figure 3.2 Physical concentrations to recovery gold and silver from secondary slag.

3.2.5 Analytical method

The bulk chemical composition of the secondary slags before and after physical concentration were determined using Rigaku RIX 3100 X-ray fluorescence spectrometer (XRF) at the Department of Earth Resources Engineering, Kyushu University, Japan. Compressed powder pellets were used to analyze major and trace elements.

To determine the chemical composition and textural characteristics of the metallic particles in secondary slag after gravity concentration, five polished sections were prepared and examined by an optical microscopy (Nikon polarization microscope E6TP-M61) at the Department of Earth Resources Engineering, Kyushu University, Japan and a Shimudsu Superscan SS-550 Scanning Electron Microscope (SEM-EDX) at the Analytical center, Kyushu University, Japan. Each metallic particle in the images is identified after threshold by color and shape analysis.

3.3 Results and Discussion

3.3.1 Recovery of gold and silver from shaking table

Table 3.3 and 3.4 represents the mass balance of secondary slag before and after the physical separation. The physical separation is quite practical for primary processing because the content of gold, silver in the concentrate is significantly increased by performing only the shaking table process. Twenty kilogram of concentrate is obtained from the shaking table.

Table 3.2 Chemical composition of secondary slag before and after gravity concentration

Sample Oxides And elements	Secondary Slag (black color)	Secondary Slag (blue color)	Concentrate after gravity concentration	Tailing after gravity concentration
SiO_2 (%)	38.3	15.7	34.9	42.9
Al_2O_3	38.9	1.89	15.9	9.79
Fe_2O_3	1.56	1.55	8.04	4.23
MnO	0.01	0.01	0.11	0.04
MgO	0.17	0.04	4.72	0.71
CaO	2.53	1.00	2.92	6.38
Na_2O	15.1	54.8	7.81	17.8
Cl	0.97	6.14	0.2	0.41
Ag(ppm)	**1650**	**450**	**15600**	**1830**
Au(ppm)	**240**	**n.d.**	**1260**	**260**
Cu(ppm)	1310	480	>100000	11810
Zn(ppm)	2860	31030	23300	42500

Table 3.3 Mass balance of gold after recovery by shaking table (Calculated from XRF result data after shaking table experiments from Table 3.2).

	Weight (kg)	Weight (%)	Assay (% Au)	Weight of Au(g)	%Distribution Au
Secondary slag (feed)	200	-	0.0152	30.4	-
Secondary slag (insoluble)	65.8	100	0.0462	30.4	100
Concentrate	20	30	0.126	25.2	83
Tailing	45.8	70	0.026	5.2	17

Table 3.4 Mass balance of silver after recovery by shaking table (Calculated from XRF result data of residue after leaching experiments from Table 3.1).

	Weight (kg)	Weight (%)	Assay (% Ag)	Weight of Ag (g)	%Distribution Ag
Secondary slag (feed)	200	-	0.174	348	-
Secondary slag (insoluble)	65.8	100	0.529	348	100
Concentrate	20	30	1.56	312	90
Tailing	45.8	70	0.183	36	10

3.3.2 Characteristic of metallic phase in secondary slag after gravity concentration

3.3.2.1 Optic Microscopic Observation

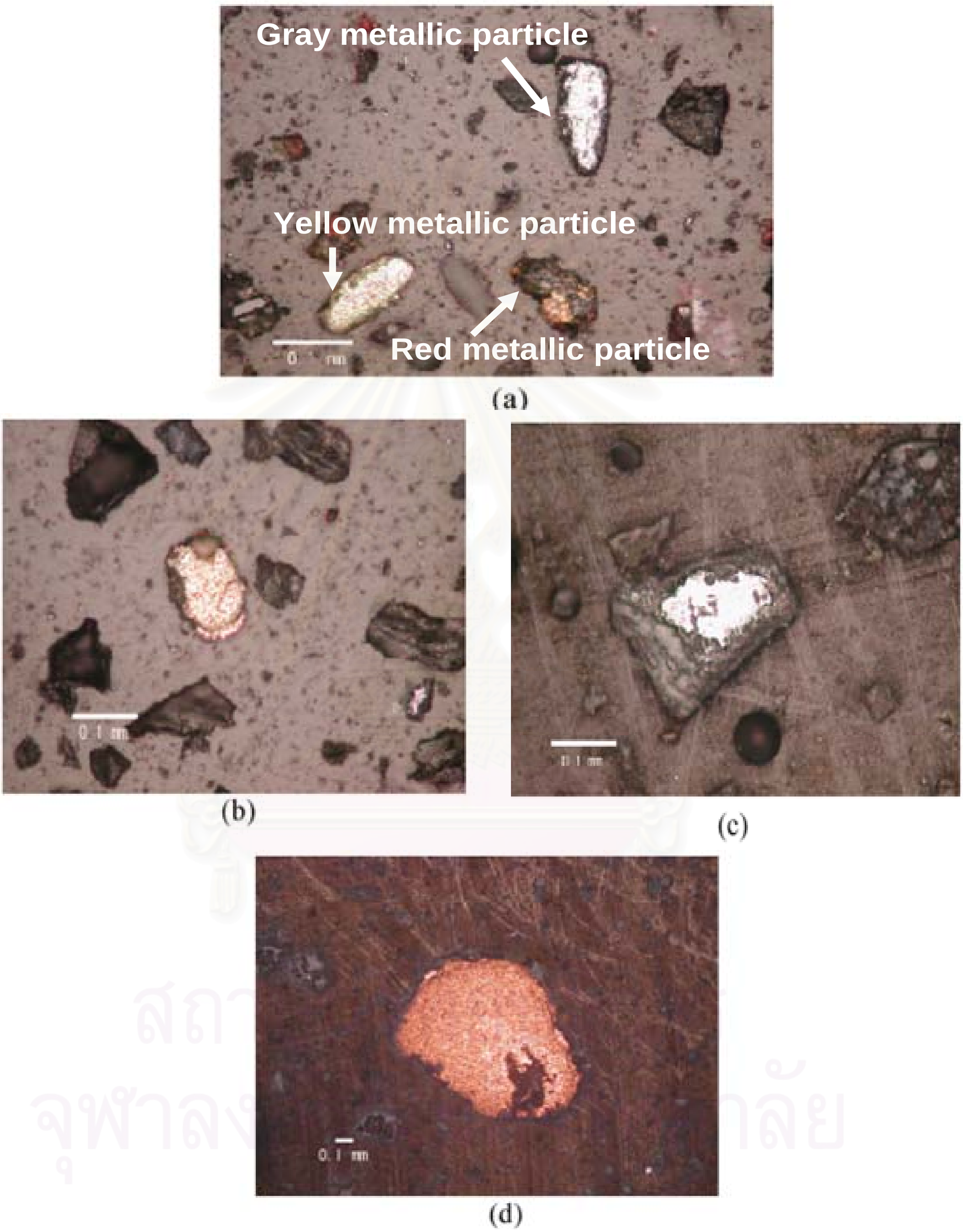


Figure 3.3 Photomicrographs of the concentrate after gravity concentration.

(a) The distribution of metal particles in secondary slag.

(b) Yellow color metallic particle.

(c) Grey color metallic particle.

(d) Red color metallic particle.

Mineralogical characteristics of the secondary slag (photomicrographs of particles in the concentrate after gravity concentration shown in Figure 3.3). The metallic particles are alloys and can be divided into three categories by the abundance in descending order 1) Gold > silver, copper (Figure 3.3 (B)), 2) silver > gold, copper (Figure 3.3 (C)), and c) copper > gold, silver Figure 3.3 (D)), The first category particles colored yellow contain the greater amount of gold than silver and copper, while the gray metallic particles contain the greater amount of silver than gold and copper. The red metallic particles have the greater amount of copper than gold and silver.

3.3.2.2 Scanning electron microscopy (SEM-EDX)

According to Table 3.1, secondary slags are composed of various silicate, oxide and metallic phases. For example, the distribution of Au, Ag, Cu, Fe, Zn and Si for a representative particle is displayed in Figure 3.4. The particle appears to be a spherical in shape. Two phases are probably present from the viewpoint of composition; (1) one phase consisting of Au, Ag and Cu, (2) and the other consisting of Fe.

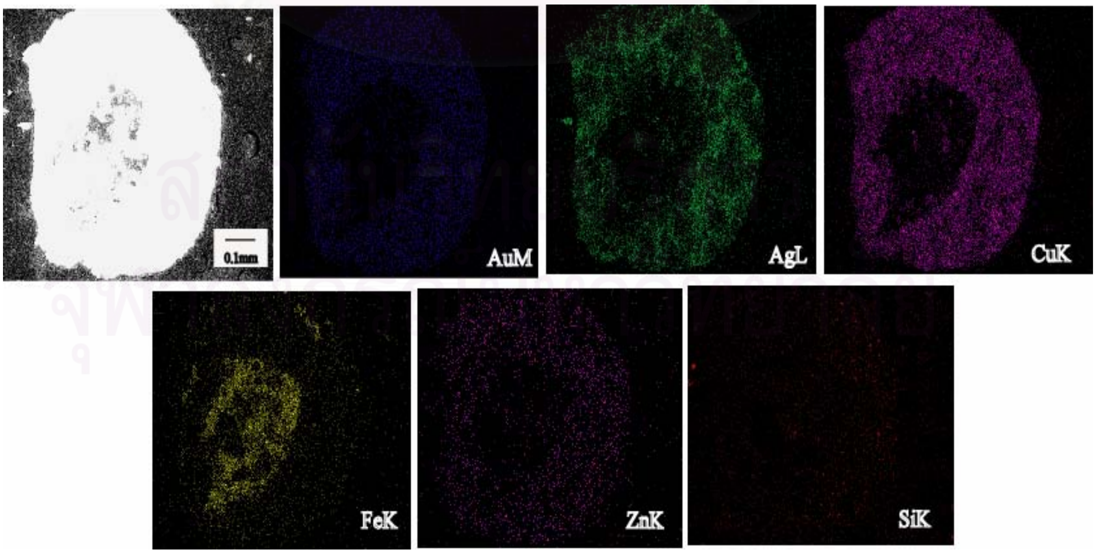


Figure 3.4 SEM photograph and X-ray images for AuMα, AgLα, CuKα, FeKα, ZnKα and SiKα of metallic particles in the concentrate after gravity concentration.

3.4 Conclusions

1) The content of gold, silver and copper in the concentrate are significantly increased by performing of the shaking table process. The percent recovery of gold is 83% and silver is 90%.

2) The metallic particles in secondary slag are liberated from slag phase and can be determined in spherical shape due to the chemical composition. The metallic particles exist as Au, Ag, Cu alloys and show various colors depending on the content of Au, Ag and Cu.

CHAPTER IV

NITRIC ACID PARTING AND AQUA REGIA LEACHING

4.1 Introduction

A hydrometallurgical process is based on the dissolution of metal contents into leaching solution (leachate) such as acid or alkaline. This technique has been also widely applied to metal recovery from industrial wastes because it is environmentally-benign and is an effective energy saving method. Aqua regia is widely used for the leaching of precious metals from solid substances, primarily focusing on the leaching of gold from industrial wastes such as PWBs, pulps and loaded activated carbon. Although this reagent is best for dissolution of gold from waste materials, its corrosive and poisonous properties require corrosion-proof equipment as well as complicated process operation *(Kinoshita et al., 2002).*

The chemical composition of concentrate after gravity concentration is shown as Table3.2 in chapter III. The metal contents are 1260 ppm of Au, 15600 ppm of Ag, more than 100000 ppm of Cu and 23300 ppm of Zn, respectively. The concentration of silver is much higher than that of gold. From the result in chapter III (Figure 3.3), we observed that the secondary slag obtained after the gravity concentrations is partially composed of gold, silver and copper alloys. Consequently, the process of dissolution of silver and base metal by nitric acid (see equation 1 and 2) was applied to remove them from secondary slag at first. Then, silver chloride is later obtained by adding sodium chloride (see equation 3) and silver chloride is melted by adding flux to get metallic silver.

Reaction equation:

$$Ag(s) + 2HNO_3\,(aq) \Rightarrow AgNO_3\,(aq) + H_2O\,(l) + NO_2\,(g) \qquad (1)$$

$$Cu(s) + 4HNO_3\,(aq) \Rightarrow Cu\,(NO_3)_2(aq) + 2H_2O\,(l) + 2NO_2\,(g) \qquad (2)$$

$$Ag^{+}\,(aq) + Cl^{-}(aq) \Rightarrow AgCl\downarrow\,(s) \qquad (3)$$

Aqua regia can dissolve gold because each of its two component acid carries out a different function. The nitric acid is a good oxidizing agent (see equation 4). Chloride ions from the hydrochloric acid form coordination complexes with the gold ions (see equation 5).Not only gold but also silver, copper and iron that still remains in the residue (after nitric acid parting) can be isolated in the form of aqueous solution.

Reaction equation:

$$Au(s) + 3NO_3^{-}(aq) + 6H^{+}(aq) \rightleftharpoons Au^{3+}(aq) + 3NO_2(g) + 3H_2O(l) \qquad (4)$$

$$Au^{3+}\,(aq) + 4Cl^{-}(aq) \rightleftharpoons AuCl_4^{-}(aq) \qquad (5)$$

$$Ag(s) + 2HNO_3\,(aq) \Rightarrow AgNO_3\,(aq) + H_2O\,(l) + NO_2\,(g) \qquad (6)$$

$$Cu(s) + 4HNO_3\,(aq) \Rightarrow Cu\,(NO_3)_2(aq) + 2H_2O\,(l) + 2NO_2\,(g) \qquad (7)$$

$$Fe(s) + 3HCl\,(aq) \Rightarrow Fe^{3+}\,(aq) + 3Cl^{-}\,(l) + 3/2H_2\,(g) \qquad (8)$$

In this study, the hydrometallurgy recovery of valuable metals, especially gold and silver, from secondary slag is investigated following the physical concentration. Nitric acid was adopted as a leaching solution since it can leave gold intact whereas dissolve other base metals. The gold remaining in the residue after the nitric acid parting is dissolved by using aqua regia in terms of two parameters; 1) reaction time and 2) the solid-liquid ratio (the weigh of residue / the volume of aqua regia).

4.2 Nitric acid parting

4.2.1 Instruments

1. 1000 ml Pyrex beaker
2. Magnetic Stirrer
3. Hot plate
4. Vacuum filter kit
5. 0.45 μm membrane filter
6. Rigaku RIX 3100 X-ray fluorescence spectrometer (XRF)

4.2.2 Chemicals and reagent

1. HNO_3 analytical grade (Wako Chemicals)
2. Distilled water

4.2.3 Procedure of nitric acid parting

Nitric acid parting experiment was carried out by immersing a given amount of the sample (500 gram of concentrate after gravity concentration) covered with a 1:1 solution of nitric acid and distilled water and placing it on a hot plate. The experiments were magnetically stirred and after the prescribed settling time, the solid residues were filtered out and the air-dried at ambient temperature. The silver ions in leachate were recovered by adding NaCl to precipitate all the silver as the form of silver chloride. The silver chloride was filtered out and was reduced to metallic silver by heat and a reducing flux.

The chemical composition of the solid residue after nitric acid parting (containing gold) was determined by XRF to confirm the efficiency of nitric acid parting. As shown in Table 4.1.

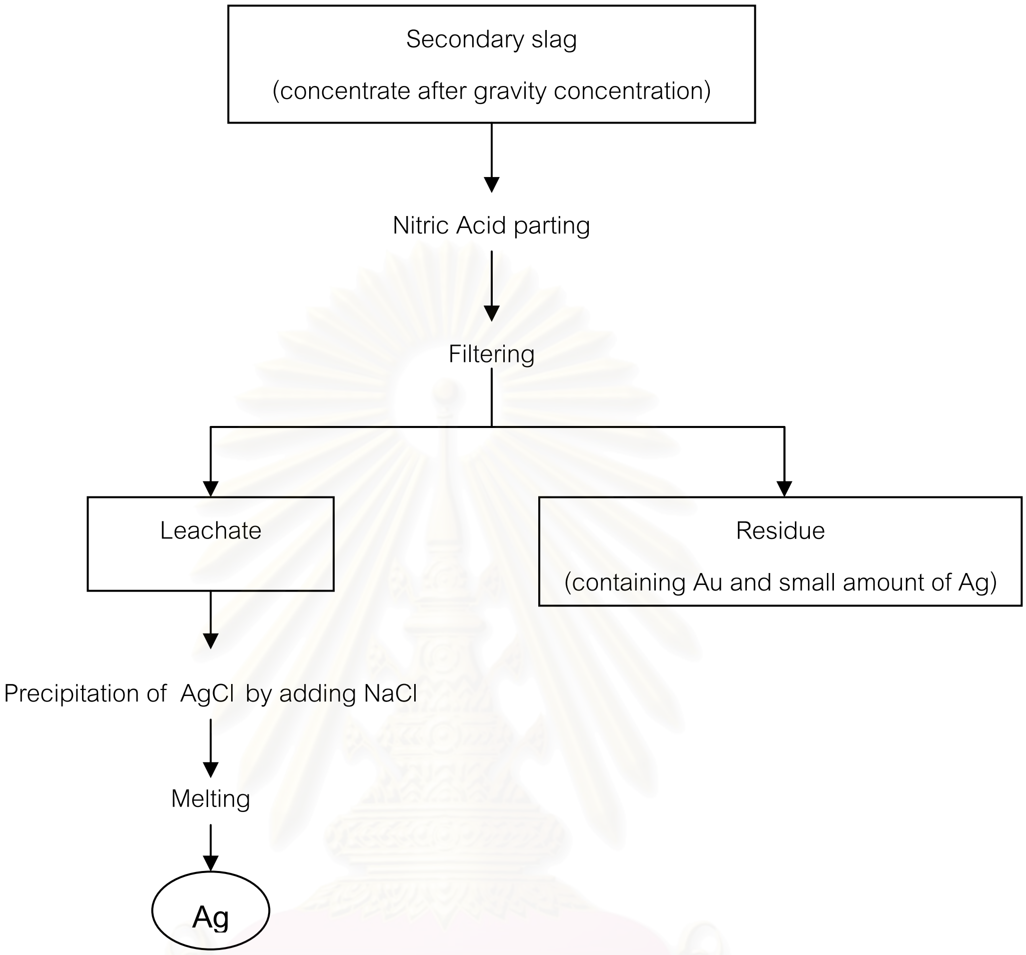


Figure 4.1 Nitric acid parting experiment procedure used for concentrate after gravity concentration.

4.2.4 Analytical method

The bulk chemical composition of the secondary slag after nitric acid parting was determined using Rigaku RIX 3100 X-ray fluorescence spectrometer (XRF) at the Department of Earth Resources Engineering, Kyushu University, Japan. Compressed powder pellets were used to analyze major and trace elements.

4.3 Aqua regia leaching

4.3.1 Instruments

1. 100 ml Pyrex beaker
2. Magnetic Stirrer
3. Vacuum filter kit
4. 0.45 μm membrane filter
5. Glass pipettes
6. NIPPON Jarrel Ash AA-835 flame atomic absorption spectrophotometer (AAS)
7. Rigaku RIX 3100 X-ray fluorescence spectrometer (XRF)

4.3.2 Chemicals and reagent

1. HCl analytical grade (Wako Chemicals)
2. HNO_3 analytical grade (Wako Chemicals)
3. Distilled water

4.3.3 Procedure of aqua regia leaching experiment

Aqua Regia is used for the leaching of gold and silver (residue from the nitric acid parting). The amount of solid sample (residue from nitric acid parting) used was 5 g and the volume of aqua regia used was 100 ml. All chemicals were analytical grade (Wako Chemicals). All experiments were conducted at room temperature and magnetically stirred during the experiments.

In this experiment, reaction time and solid–liquid (S/L) ratio (the ratio of the weight of sample to the volume of leaching solution) are variable parameters. Residue (after nitric acid parting) was treated by aqua regia for respectively 1, 3, 6, 12 and 24 hours to determine the optimum reaction time. The S/L ratio was ranged from 5 g/100 ml to 200 g/ 100 ml. The product is a solution that contains precious metals. At adequate intervals, aliquots of the suspensions were taken out with a glass pipette and filtered with a 0.45 μm membrane filter. The gold, silver, copper and iron concentration in the filtrate was determined by AAS. After batch experiments, each residue (after aqua regia leaching) on the filter were air-dried at ambient temperature and the chemical composition of each residue was also determined by XRF to confirm the efficiency of leaching. As shown in Table 4.3.

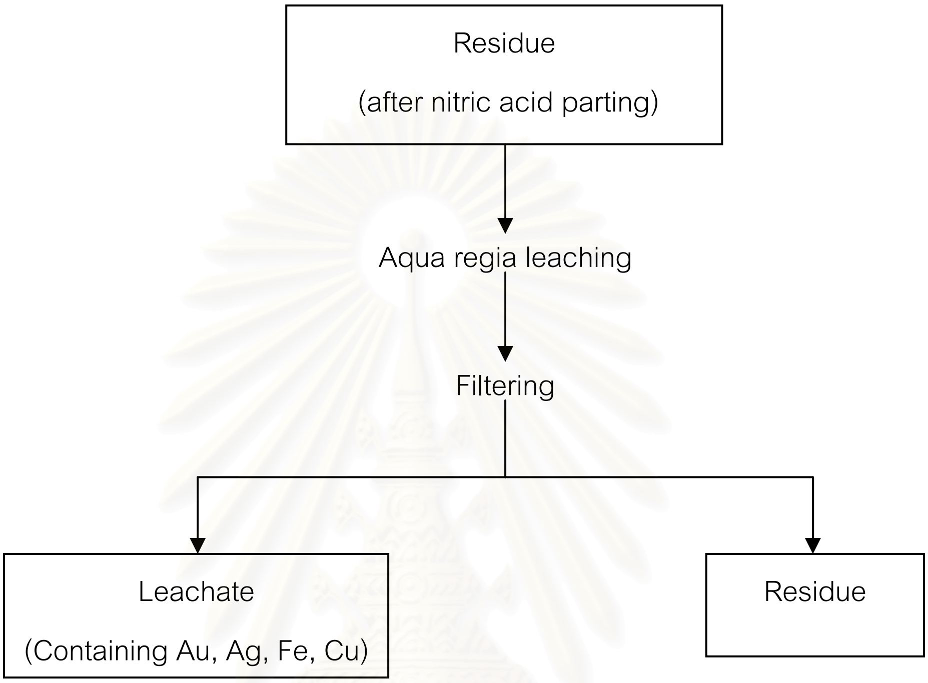


Figure 4.2 Aqua regia leaching experiment procedure used for residue after nitric acid parting.

4.3.4 Analytical method

The concentration of gold, silver, copper and iron in leachate was measured by NIPPON Jarrel Ash AA-835 flame atomic absorption spectrophotometer (AAS) after appropriate dilution at the Department of Earth Resources Engineering, Kyushu University, Japan.

The bulk chemical composition of the residue on the filter paper after aqua regia leaching was determined using Rigaku RIX 3100 X-ray fluorescence spectrometer (XRF) at the Department of Earth Resources Engineering, Kyushu University, Japan. Compressed powder pellets were used to analyze major and trace elements.

4.4 Results and Discussion

4.4.1 Nitric acid parting for the concentrate from gravity concentration

The following table tabulates chemical composition of concentrate before and after nitric acid parting.

Table 4.1 Chemical composition of secondary slag before and after nitric acid parting.

Samples Oxides and Elements	Concentrate before Nitric acid parting	Concentrate after Nitric acid parting
SiO_2(%)	34.9	57.0
Al_2O_3	15.9	15.8
Fe_2O_3	8.04	8.49
MgO	4.72	2.65
CaO	2.92	0.86
Na_2O	7.81	0.59
Cl	0.2	0.16
Ag(ppm)	**15600**	**10800**
Au(ppm)	**1260**	**2720**
Cu(ppm)	>100000	57400
Zn(ppm)	23300	20300

Since gold, silver and copper are present as a form of solid solution (alloy), some chemical processing is also effective to enrich the gold grade as much as possible. Nitric acid parting is the chemical processing that can indirectly concentrate gold. This process can remove some other elements such as silver and copper out of the sample.

From the assays of Au and Ag, percent recovery of Au and Ag by nitric acid parting method can be calculated. As shown in Table 4.2, the mass balance revealed that approximately 64% of silver have been leached. Hence, the gold is remained in residue without dissolution in nitric acid and relatively concentrated more than twice, from 0.126% to 0.293% of gold.

Table 4.2 Mass balance of secondary slag before and after nitric acid parting.

Au	Weight (kg)	Weight (%)	Assay (%Au)	Weight of Au (g)	%Distribution Au
Concentrate after shaking table	20	100	0.126	25.2	100
Residue after Nitric acid parting	8.6	43	0.293	25.2	100
Ag	Weight (kg)	Weight (%)	Assay (%Ag)	Weight of Ag (g)	%Distribution Ag
Concentrate after shaking table	20	100	1.56	312	100
Residue after Nitric acid parting	8.6	43	1.3	112	36
Leachate after Nitric acid parting	-	-	-	200	64

4.4.2 The effect of Aqua regia leaching time

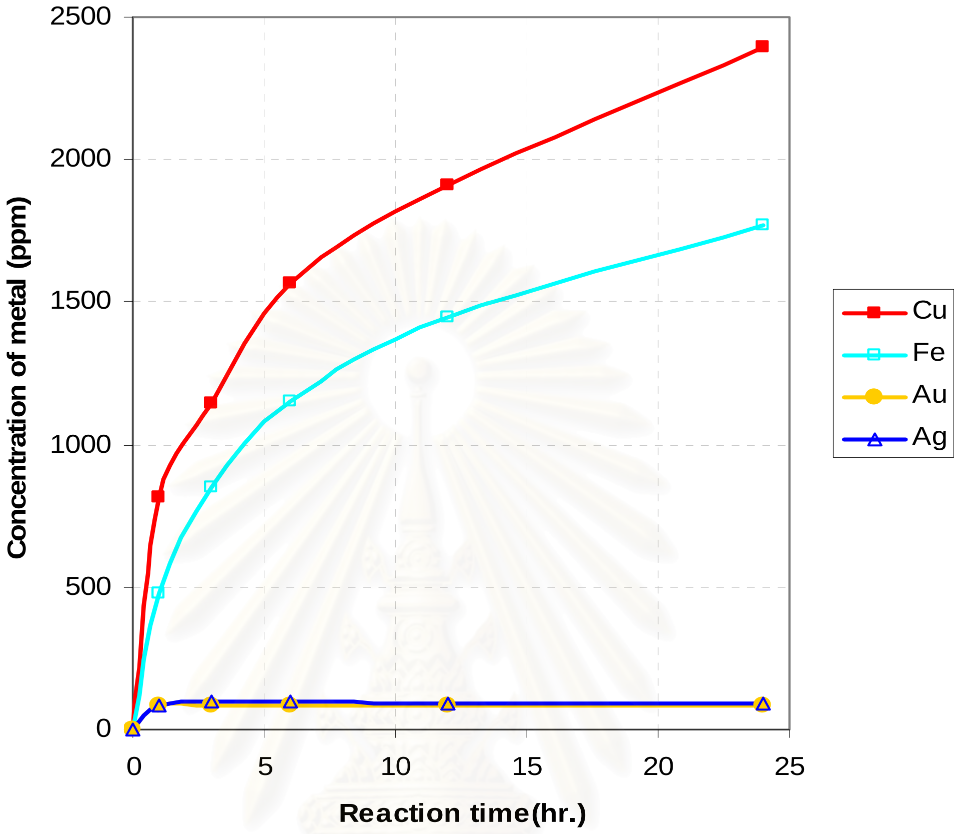


Figure 4.3 Metal dissolution in the leachate as a function of reaction time at room temperature, 5g. of sample(residue after nitric acid parting), 100 mL. of aqua regia

Figure 4.3 represents the variation of concentration of gold, silver, iron and copper in leachate with reaction time. Aqua regia was used to leach gold and silver out of the other metals, i.e., iron zinc and copper. The result can be concluded that gold and silver are selectively and completely leached out of the residue within 1 hour, while the other metals, iron and copper, are gradually leached. Most of gold and silver were dissolved by aqua regia in less than 1 hour. Otherwise, the longer time for leaching, the more iron and copper are dissolved into leachate.

This result shows that it is optimum for leaching gold and silver to take 1 hour or less.

Table 4.3 Chemical composition of the residue as a function of reaction time at room temperature, 5g. of sample(residue after nitric acid parting), 100 ml. of aqua regia, after aqua regia leaching 1 hr.

Residue samples / Chemical composition	Concentrate after Nitric acid parting	Leaching 1 hr.	Leaching 3 hr.	Leaching 6 hr.	Leaching 12 hr.	Leaching 24 hr.
SiO_2 (%)	57.00	57.20	77.00	75.80	76.50	59.80
Al_2O_3	15.80	17.70	14.00	14.33	11.30	20.10
Fe_2O_3	8.49	8.35	8.39	6.69	5.42	7.27
MnO	0.06	0.06	0.07	0.05	0.04	0.05
MgO	2.65	2.52	1.97	1.93	1.69	2.49
CaO	0.86	0.78	0.74	0.74	0.62	0.69
Na_2O	0.59	0.49	0.43	0.44	0.50	0.59
Cl	0.16	0.25	0.13	0.13	0.16	0.10
Ag(ppm)	**10800**	**325**	**363**	**383**	**1019**	**4740**
Au(ppm)	**2720**	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**n.d.**
Cu(ppm)	57400	48700	36020	31300	26200	35100
Zn(ppm)	20300	23200	19600	18500	16300	24020

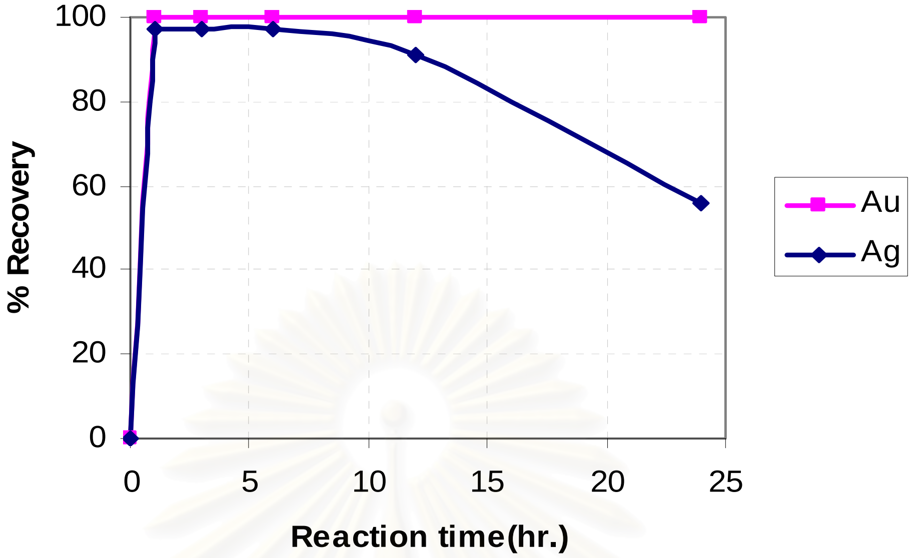


Figure 4.4 Percent recovery of gold and silver as a function of reaction time at room temperature, 5g. of sample(residue after nitric acid parting), 100 mL. of aqua regia.(Calculated from XRF result data of residue after leaching experiments from Table 4.3)

From the Figure 4.3, the concentration of the gold as well as the silver (over different time period of the test conducted) in the leachate is almost stable for each different time periods. The Figure 4.4 shows that the percent recovery of silver has a decreasing trend over time from 98% to 65%. The amount of Ag^+ (aq) from leaching process is constant, but that of resultant Ag in the residue is varied. It is reasonably concluded that Ag^+ (aq) easily reacts with Cl^- to form AgCl precipitate, whereas gold still remains in the leachate in the form of tetrachloroaurate(III) complex and 100% recovery from aqua regia leaching.

Table 4.4 Metal concentration in leachate as re-producibility 4 times, 5g. of sample(residue after nitric acid parting), 100 ml. of aqua regia, reaction time 1 hour, at room temperature.

Re-producibilities Metal concentration (ppm)	1	2	3	4
Au	91	87	91	89
Ag	84	125	96	147
Cu	647	626	698	773
Fe	428	406	444	576

As shown in previous paragraph, the most effective reaction time for leaching was determined to be 1 hour in terms of time saving for the practical experiments. In order to confirm the validity of the process, repetitive tests for this time duration were carried out. Four tests were carried out in total (Table 4.4) and although the variation of value for each element was recognized in a particular range, it does not affect significantly about the following experiments and system.

4.4.3 The effect of solid-liquid ratio

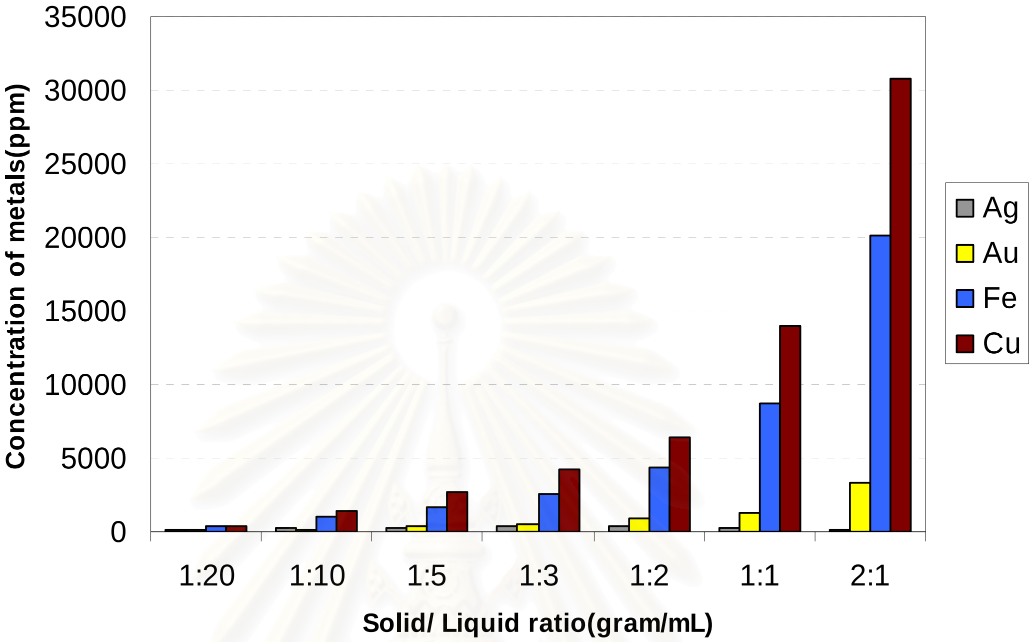


Figure 4.5 Metal concentration in the leachate as a function of ratio sample: aqua regia; reaction time 1 hr., volume of aqua regia 100mL.

Table 4.5 Metal concentration in leachate as a function of ratio sample : aqua regia; reaction time 1 hr., volume of aqua regia 100mL.

Solid/liquid ratio(gram/mL) Metal concentration(ppm)	1:20	1:10	1:5	1:3	1:2	1:1	2:1
Ag	171	213	299	408	436	214	144
Au	90	171	363	555	954	1310	3380
Fe	372	1040	1680	2530	4370	8720	20200
Cu	416	1360	2740	4180	6390	13990	30700

The leaching experiments were then conducted using different parameters, S/L ratio. The amount of sample was varied from 5 g to 200 g without changing the volume of aqua regia and then the experiments were conducted for the same time period (1 hr). The Figure 4.5 shows that the amount of silver in leachate did not increase much as comparative to the proportion of the sample used, but the concentration of the other metals increased in response to the amount increasing.

Table 4.6 Chemical composition of the residue after aqua regia leaching as a function of ratio sample: aqua regia (reaction time 1 hr., volume of aqua regia 100 mL.)

Weight of sample: volume of Aqua Regia / Chemical composition	1:20	1:10	1:5	1:3	1:2	1:1	2:1
SiO_2(%)	57.20	61.0	62.5	62.0	61.7	60.2	61.1
Al_2O_3	17.7	16.9	17.3	17.1	17.9	18.0	18.2
Fe_2O_3	8.35	8.05	8.36	7.82	7.91	8.02	7.88
MnO	0.06	0.07	0.07	0.07	0.06	0.06	0.06
MgO	2.52	2.67	2.55	2.65	2.63	2.71	2.52
CaO	0.78	0.84	0.75	0.87	0.81	0.84	0.76
Na_2O	0.49	0.55	0.55	0.57	0.54	0.55	0.56
Cl	0.25	0.08	0.03	0.05	0.05	0.07	0.05
Ag(ppm)	**425**	**1570**	**7780**	**8350**	**9400**	**9410**	**10030**
Au(ppm)	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**58**	**76**	**134**
Cu(ppm)	48700	48700	46300	47300	47300	47200	43800
Zn(ppm)	23200	22900	23900	22000	22700	22800	23200

The figure below shows that the percent recovery of silver has a decreasing trend with amount of sample, while Au is still 100% recovery and decrease only slightly. The reason for the decrease of silver concentration is that Ag^+ (aq) reacts with Cl^- to form AgCl in the solid residue. The most important result of this table is that all of gold was dissolved into the leachate even under the high S/L ratio condition. These results suggest that nitric acid parting is important for recovery of silver and aqua regia leaching is much effective for recovery of gold.

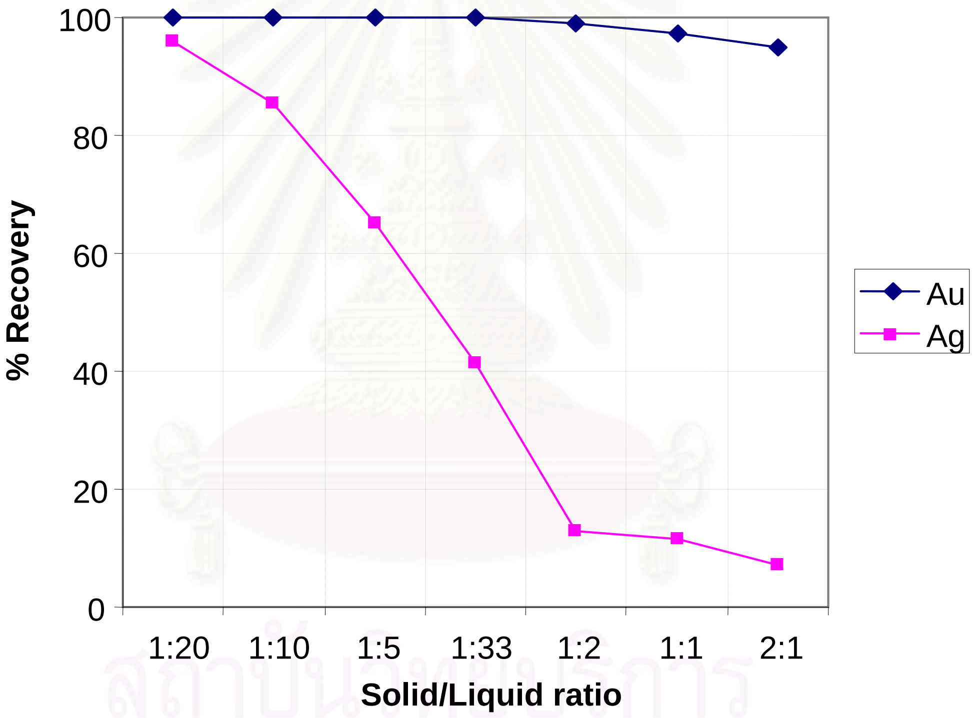


Figure 4.6 Percent recovery of gold and silver after aqua regia leaching as a function of ratio sample: aqua regia; reaction time 1 hr., volume of aqua regia 100mL.(Calculated from XRF result data of residue after leaching experiments from Table 4.6)

4.5 Conclusions

1) Nitric acid parting can remove base metals and silver out of the sample, and then silver can be recovered from leachate after nitric acid parting by precipitation with sodium chloride and then reduced to metallic silver by heat with a reducing flux.

2) Most of gold and silver in the sample are completely leached within 1 hour by the aqua regia. For silver, the longer reaction time is, the more AgCl precipitate is formed in the residue.

3) Aqua regia is effective to extract gold, but not silver, especially under the high S/L ratio condition.

CHAPTER V

RECOVERY OF GOLD AND SILVER FROM LEACHATE BY METAL HYDROXIDES CO-PRECIPITATION METHOD

5.1 Introduction

Recycling of valuable metals is one of the most important matters from the viewpoint of earth environment and economy. The wastes of electronic product and jewelry industrial slags are discarded in real even if they contain a large amount of valuables such as gold. According to the World Gold Council, the demand for gold has shown an increasing trend during the last decade and reached up to around 2500 t/year. This increase is due to not only from the jewelry market, but also the increasing use of gold in industry, as well as medical applications *(Aworn et al., 2005)*. Gold is a relatively rare precious metal with a singular beauty *(Marcos et al, 2004)*. Furthermore, it is still largely used in jewelry manufacturing. Therefore, gold recycling from scraps and residues has also raised much interest *(Manni et al., 2001)*.

The processing of industrial wastes containing valuables for their recovery often becomes an absolute necessity. Therefore, it is important to develop a more efficient and effective method to recover precious metals, especially gold and silver by the combination of physical separation *(Delfini et al., 2000)* and chemical extraction. To recover and concentrate precious metals, copper refining processing and cyanizing method is utilized in common. However, they are quite expensive or hazardous. Consequently, a more economical, efficient simpler and environment-friendly method is required to recover gold from the wastes.

In this study, in order to establish a recycling system, co-precipitation method is applied. The advantage of co-precipitation is ease for operation, cheapness and less hazardous effect. Chemical method such as co-precipitation is quite suitable for these reasons *(Uchida et al., 2002).* It is reported that Au (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 the recovery of gold from wastes of electronic products *(Kitamoto et al., 2004)*. Also it is reported that not only iron(III) hydroxide but also copper(II) and Al(III) hydroxide can be co-precipitated with gold under near neutral pH and low chloride concentration conditions *(Kitamoto. 2005 Master thesis written in Japanese)*.

$AuCl_4^-$ complex is generally known to hydrolyze to give various chloro-hydroxy forms, $AuCl_{4-n}(OH)_n^-$, in aqueous solution *(Baes and Mesmer, 1976)*, and *(Fedoseyeva and Zvonareva, 1988)* showed the equilibrium among $AuCl_{4-n}(OH)_n^-$ 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 $[AuCl_n(OH)_{4-n}]^-$ as follows *(Baes and Mesmer, 1976)*:

$$AuCl_4^- + n\,OH^- = AuCl4_{-n}(OH)_n^- + n\,Cl^- \quad (n = 0\text{-}4)$$

$AuCl_4^-$ was certainly hydrolyzed to form hydrolysis product species $AuCl_3(OH)^-$, $AuCl_2(OH)_2^-$ and $AuCl(OH)_3^-$ with increasing pH. (Figure 5.1)

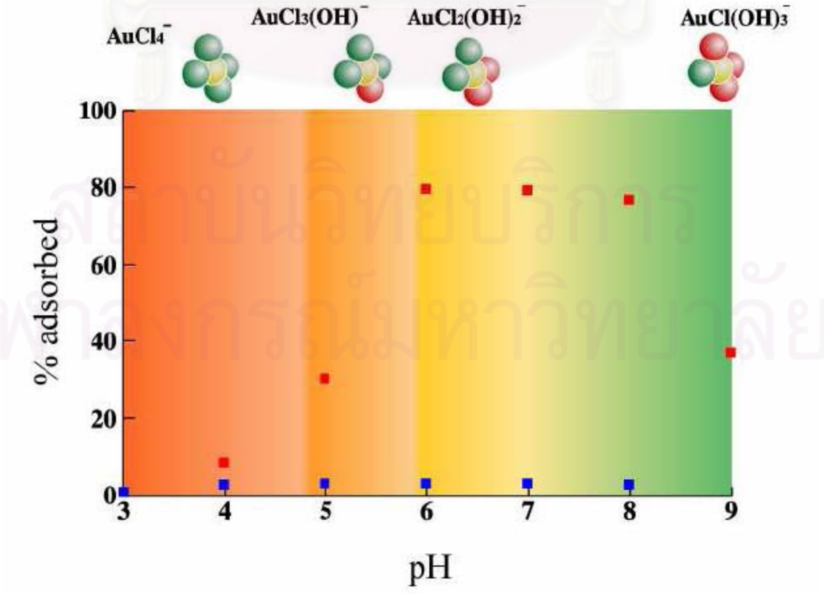
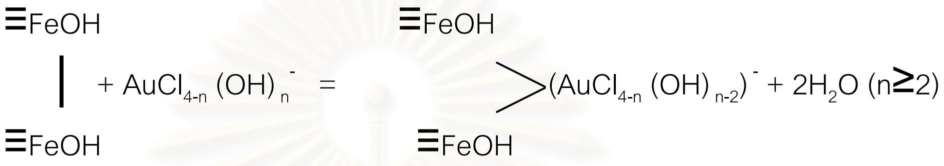


Figure 5.1 The effect of pH on adsorption of gold ions (below) and the pre-dominant gold species in each pH solution. *(Baes and Mesmer, 1976)*

The adsorption of Au (III) complexes is controlled by the balance between the degree of hydrolysis of $AuCl_4^-$ and the positive charge density on the surface of adsorbent such as iron and aluminum hydroxides. The stoichiometry of the adsorption process in case of iron hydroxide can be expressed as follows *(Uchida et al., 2002)*.



$$\begin{array}{l}\equiv FeOH \\ | \\ \equiv FeOH\end{array} + AuCl_{4-n}(OH)_n^- = \begin{array}{l}\equiv FeOH \\ \quad > \\ \equiv FeOH\end{array}(AuCl_{4-n}(OH)_{n-2})^- + 2H_2O\ (n \geq 2)$$

The surface of iron (III) hydroxide has positive charges below pH 8.0*(Uchida et al., 2002).*

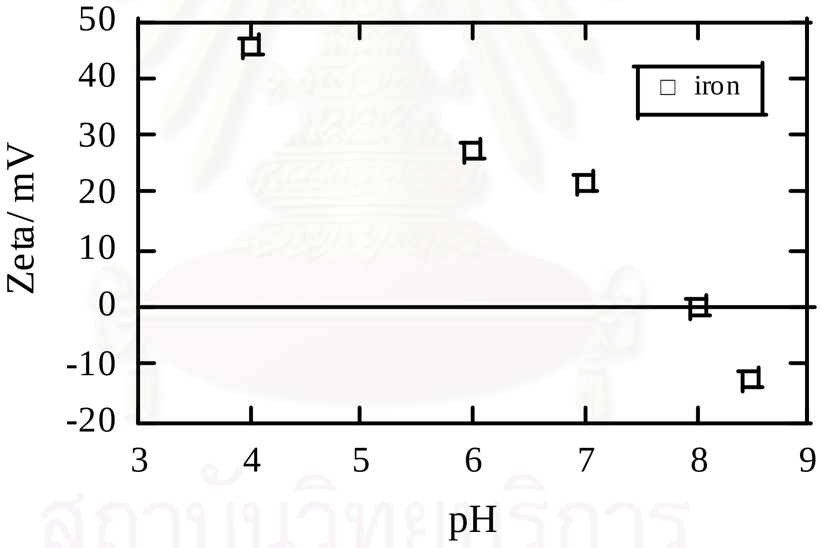


Figure 5.2 Zeta potential for iron (III) hydroxide as a function of pH in 0.12 mol dm^{-3} NaCl solution.(Uchida, 2002)

In short, $AuCl_{4-n}(OH)_n^-$ is electrostatically attracted to the surface of iron hydroxide with positive charge and then Fe-O-Au bond is formed by the condensation reaction between each OH group on the surface of iron hydroxide and $AuCl_{4-n}(OH)_n^-$.

The leachate after leaching by aqua regia (described in chapter IV) contains Au^{3+}, Ag^{+}, Fe^{3+}, Fe^{2+} and Cu^{2+}. The ratio of Au^{3+}: Ag^{+}: Fe^{3+}:Cu^{2+} is approximately estimated 1: 1: 5: 7. (From the result in chapter IV) As a result, the co-precipitation method by metal hydroxides can be applied to recover gold and silver.

Reaction equation;

$$Fe^{3+} + 3\ OH^{-} \Rightarrow Fe\ (OH)_3$$

$$Cu^{2+} + 2\ OH^{-} \Rightarrow Cu\ (OH)_2$$

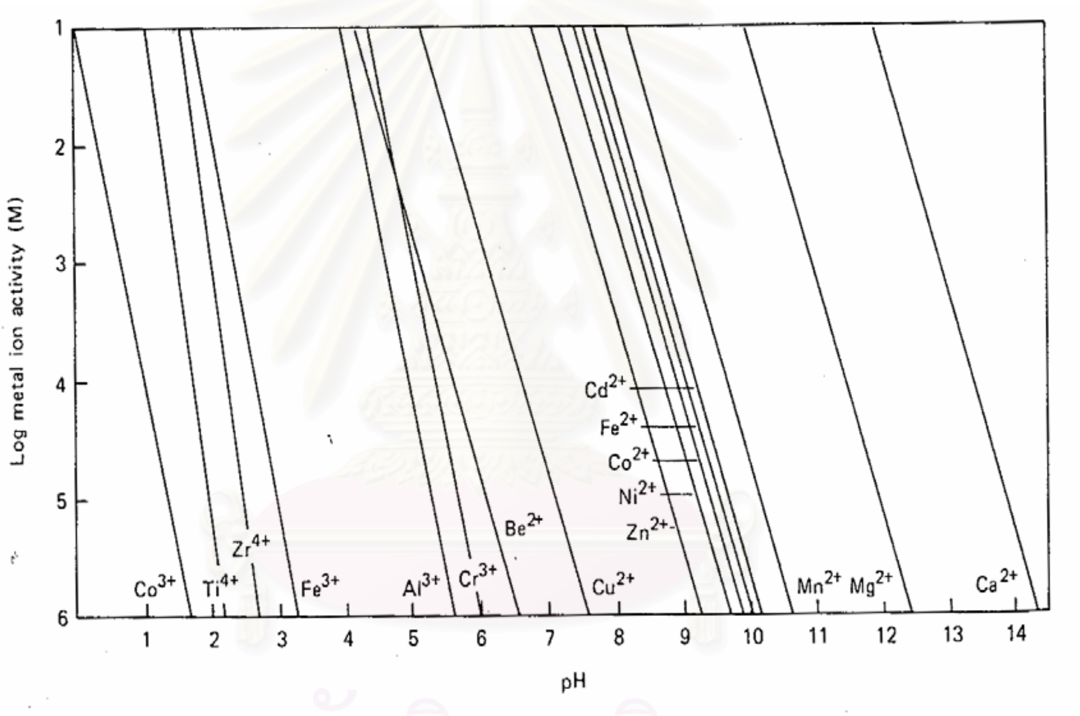


Figure 5.3 Precipitation diagram for metal hydroxides.

(Marden, J. & House, I, 1992)

Figure 5.3 shows the hydrolysis equilibrium of various metal hydroxides. For example, Fe^{3+} and Cu^{2+} precipitate in the pH range from 2 to 3, and from 5 to 7, respectively.

The metal hydroxide carrying gold and silver is produced by mixing an acidic aqueous solution containing base metal, gold and silver ions with NaOH solution. The co-precipitated gold and silver ions with the metal hydroxide are reduced by the metallic gold and silver with effect of H_2O attacking *(Uchida, 2002 Doctoral thesis)* or electron donors such as Fe^{2+} *(Greffie et al., 1996)* as follows:

$$AuCl_4^- + 3Fe^{2+} + 6H_2O \;=\; Au^0_{(s)} + 3FeO(OH)_{3(s)} + 4Cl^- + 9H^+$$

Then, the gold and silver co-precipitated with the metal hydroxide are separated from the metal hydroxides to recover the gold and silver.

The purpose of this chapter is to recover precious metals, especially gold and silver, from aqueous solution containing gold and silver (after leaching of concentrate with aqua regia) by co-precipitation method and purification process.

5.2 Experimental

5.2.1 Instruments

1. 500 ml Pyrex beaker
2. 100 ml Pyrex beaker
3. Magnetic Stirrer
4. pH meter (Horiba F-21 ToupH series)
5. Vacuum filter kit
6. 0.45 μm membrane filter
7. Glass pipettes
8. NIPPON Jarrel Ash AA-835 flame atomic absorption spectrophotometer (AAS)
9. Nikon polarization microscope E6TP-M61
10. Rigaku RIX 3100 X-ray fluorescence spectrometer (XRF)
11. Shimudsu Superscan SS-550 Scanning electron microscopy (SEM-EDX)

5.2.2 Chemicals and reagent

1. NaOH analytical grade (Wako Chemicals)
2. HNO_3 analytical grade (Wako Chemicals)
3. HCl analytical grade (Wako Chemicals)

5.2.3 Procedure of co-precipitation experiment

The co-precipitation method is applied for solution obtained from aqua regia leaching. All experiments were conducted in the batch method at room temperature. The pH of sample solutions was adjusted to 6.0 by adding NaOH solution to precipitate metal hydroxide with gold and silver. The pH was continuously monitored with a pH meter (Horiba F-21 ToupH series) and maintained within ±0.1 pH using HNO_3 and NaOH solutions. Suspensions were magnetically stirred. At adequate intervals, aliquots of the suspensions were taken out with a glass pipette and filtered with a 0.45 μm membrane filter. The gold, silver, copper and iron concentration in the filtrate was determined by AAS. Then, the amount of gold and silver co-precipitated with metal hydroxides was estimated from the decrease in gold concentration in the solution. After batch experiments, each co-precipitate on the filter (solid sample) was air-dried in a dark room at ambient temperature.

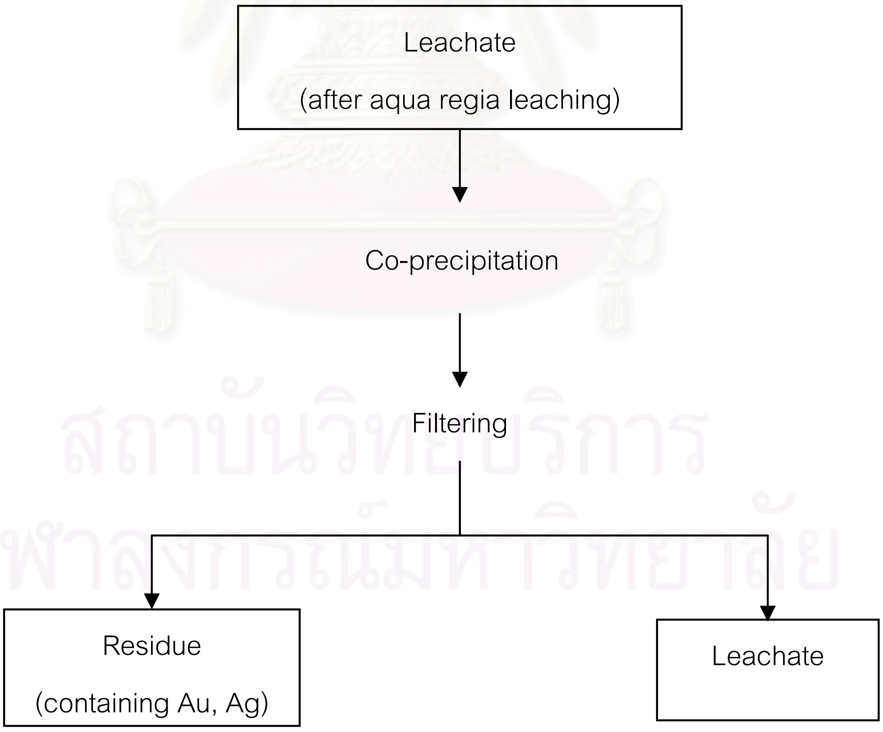


Figure 5.4 Co-precipitatiion experiment procedure used for leachate after aqua regia leaching.

5.2.4 Analytical method for solid and solution sample after co-precipitation experiments

The bulk chemical composition of the residue on the filter paper after aqua regia leaching was determined using Rigaku RIX 3100 X-ray fluorescence spectrometer (XRF) at the Department of Earth Resources Engineering, Kyushu University, Japan. Compressed powder pellets were used to analyze major and trace elements.

For solution samples were determined the concentration of gold, silver, copper and iron was measured by NIPPON Jarrel Ash AA-835 flame atomic absorption spectrophotometer (AAS) at the Department of Earth Resources Engineering, Kyushu University, Japan.

The particle sizes of gold that co-precipitate with metal hydroxides were observed by Nikon polarization microscope E6TP-M61. at the Department of Earth Resources Engineering, Kyushu University, Japan.

The distribution of elements and electron image were observed by Shimudsu Superscan SS-550 scanning electron microscopy (SEM-EDX) at the Analytical center, Kyushu University, Japan.

5.2.5 Procedure of purification solid residue (on the filter after co-precipitation) by HCl and HNO_3

To purification gold and silver from solid residue after co-precipitation experiment, HCl and HNO_3 were selected to dissolve base metals and compared the result of each data. All chemicals were analytical grade (Wako Chemicals). All experiments were conducted at room temperature and magnetically stirred during the experiments. The volume of 1M HCl and 1M HNO_3 used were 50 ml and reaction time is selected for 1 hour. After the prescribed settling time, the solid residue was filtered with a 0.45 μm membrane filter. The gold, silver, copper and iron concentration in the filtrate was determined by AAS. Then, the amount of gold and silver on the filter paper was estimated from the decrease in gold and silver concentration in the leachate. After batch experiments, each gold and silver on the filter (solid residue) was air-dried in a dark room at ambient temperature.

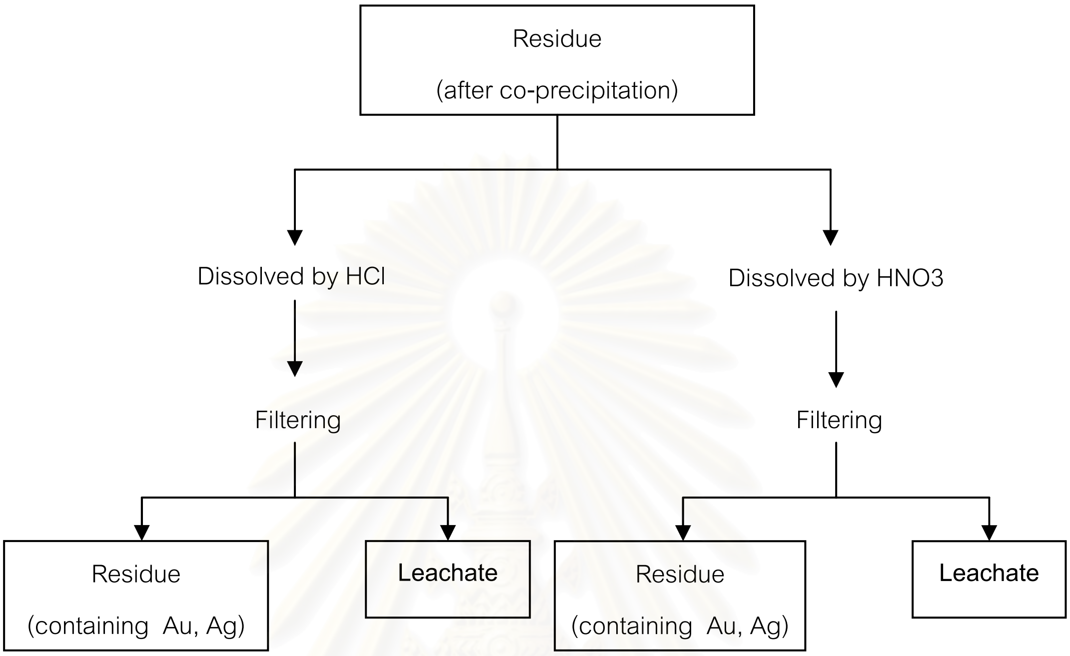


Figure 5.5 Purification experiment procedure used for residue after co-precipitation.

5.2.6 Analytical method for solid and solution sample after purification solid residue (on the filter after co-precipitation) by HCl and HNO_3 experiments

For solution samples were determined the concentration of gold, silver, copper and iron was measured by NIPPON Jarrel Ash AA-835 flame atomic absorption spectrophotometer (AAS) at the Department of Earth Resources Engineering, Kyushu University, Japan.

To identify the gold (after dissolved by HCl and HNO_3), solid sample on the filter was air dried in the dark room at ambient temperature. The particle sizes of gold were observed by optical microscopy (Nikon polarization microscope E6TP-M61) at the Department of Earth Resources Engineering, Kyushu University, Japan.

The distribution of elements and electron image were observed by Shimudsu Superscan SS-550 scanning electron microscopy (SEM-EDX) at the Analytical center, Kyushu University, Japan.

5.3 Results and Discussion

5.3.1 The effect of reaction time on metal co-precipitate

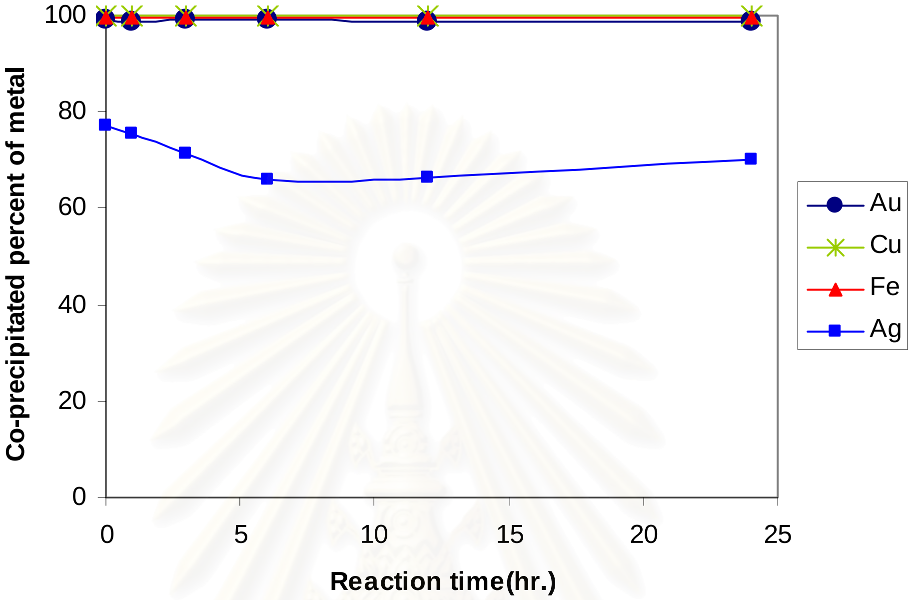


Figure.5.6 Percentage of metal co-precipitated with hydroxides as a function of reaction time. (pH 6, the amount of sample 5g, at room temperature).

Figure 5.6 illustrates the variation of percentage of metal co-precipitated with time at pH 6. The percentage of silver, copper and iron co-precipitated attained constant value near 100 % from the beginning. In case of silver, about 80 % of silver were co-precipitated and decreased gradually until 6 hours, and then became apparently constant until 24 hours. It is inferred that almost 100 % of gold and about 80 % of silver were co-precipitated with metal hydroxides within in only 1 hour from the beginning.

5.3.2 The characteristic of gold reduced on metal hydroxides

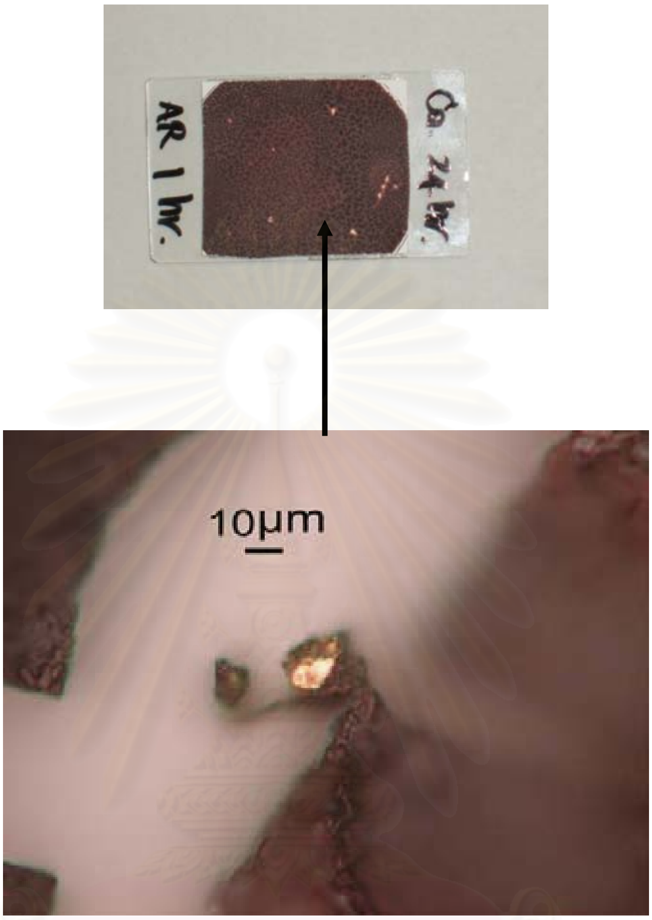


Figure 5.7 Photomicrograph of gold particle on metal hydroxide after co-precipitation at pH 6, reaction time 1 hour, at room temperature.

The solid samples obtained by filtration after co-precipitation showed red brown in color. Figure 5.7, shows the photomicrograph of gold co-precipitate. The particle bright yellow part indicates the presence of gold particle. It seems that the size of the unit gold particle was around 10 μm. This observation certainly suggests that chlorohydroxy Au (III) complexes adsorbed on metal hydroxides were reduced to elemental gold (Au (0)) without specific reducing reagent.

5.3.3 The distribution of elements and electron image on metal hydroxides

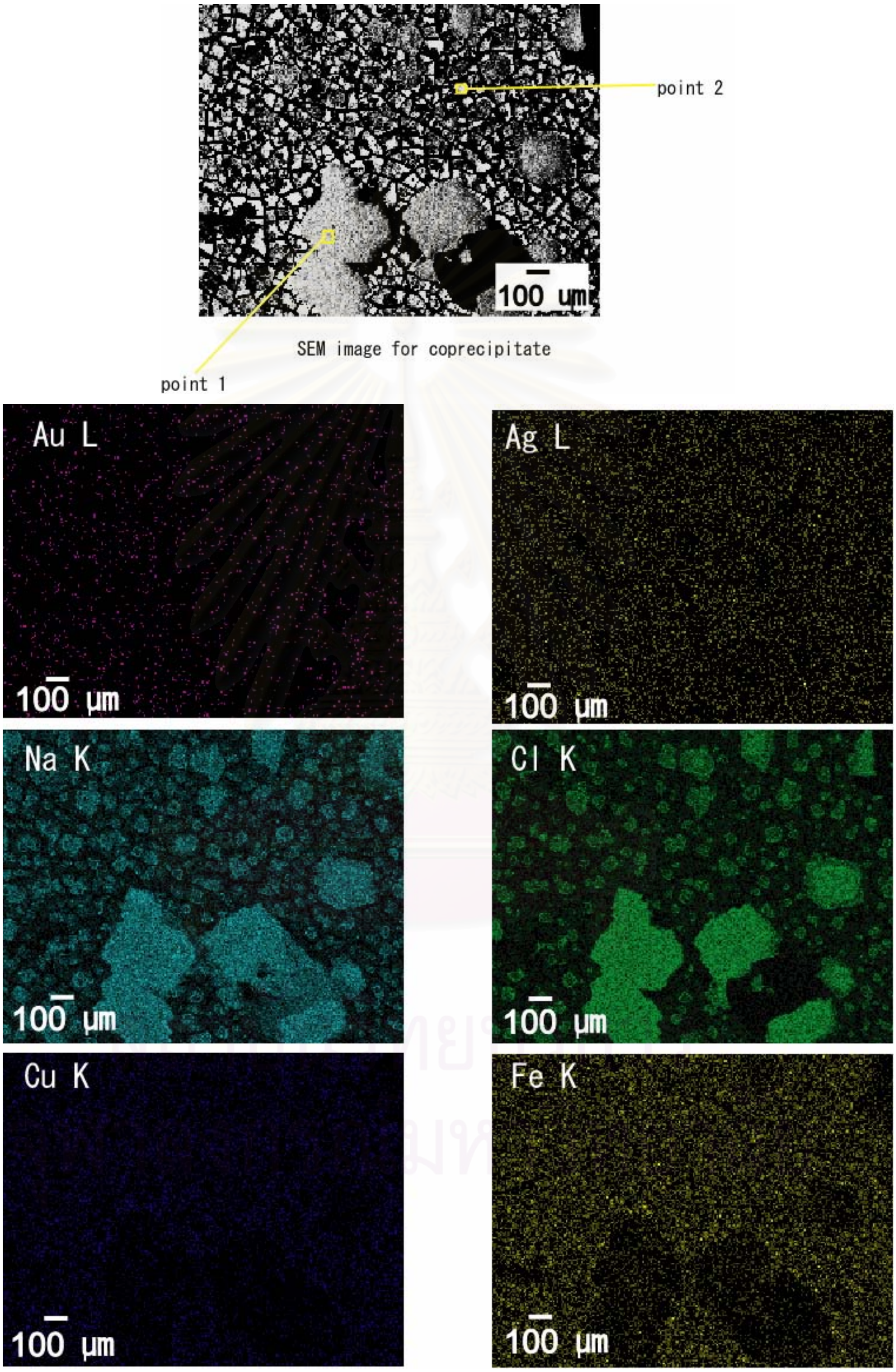
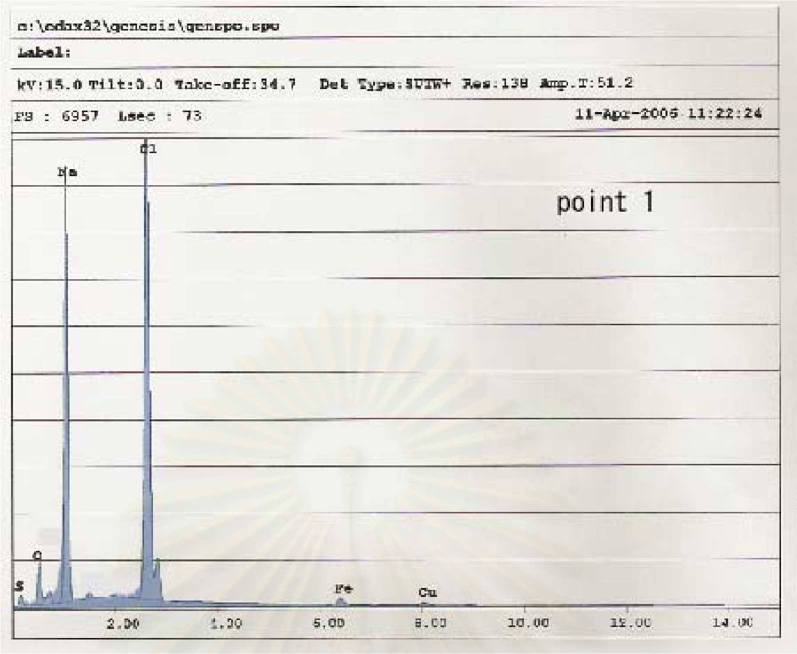


Figure 5.8 SEM image and distribution of metal hydroxide (on the filter paper) after co-precipitation at pH 6, reaction time 1 hour, room temperature.



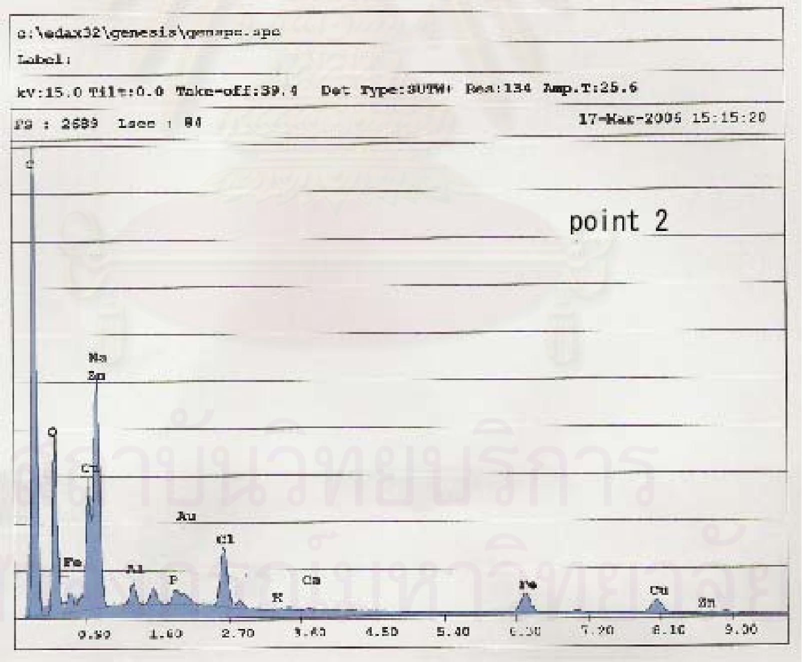


Figure 5.9 The spectrum showing the chemical composition of metal hydroxide (on the filter paper) after co-precipitation at pH 6, reaction time 1 hour, at room temperature.

The solid samples obtained by filtration were determined by SEM-EDX. Figure 5.8 shows the SEM image and the distribution of elements on metal hydroxides after co-precipitation and Figure 5.9 shows the spectrum of chemical composition of metal hydroxides after co-precipitation at point 1 and point 2 (from SEM image in Figure 5.8).The observation by SEM-EDX made clear that gold and silver were co-precipitated with metal hydroxide. Metals are contained in the same phase with NaCl and the NaCl in the solid samples were come from the reaction of Na^+ from NaOH for adjust pH and Cl^- from aqua regia solution, as the follow reaction;

$$Na^+ \quad + \quad Cl^- \longrightarrow NaCl$$

5.3.4 The effect of purification by HNO_3 and HCl

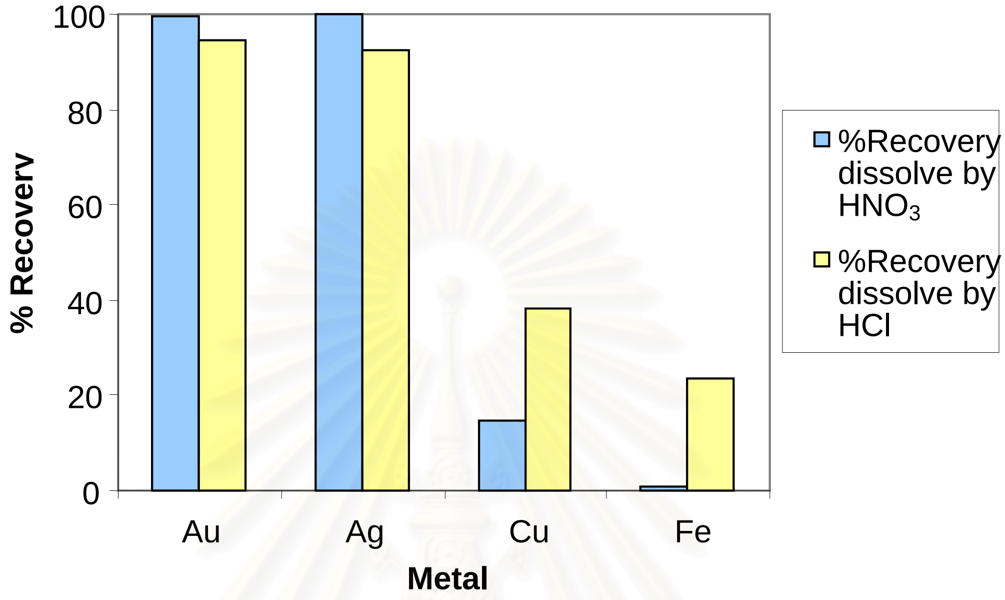


Figure 5.10 Percent of metal recovery after purified with 1M HNO_3 and 1M HCl. 50ml. reaction time 1 hour, at room temperature.

The efficiency of purification by 1M HNO_3 and 1M HCl is shown in Figure 5.10. The result was compared between before and after purification by 1M HNO_3 and 1M HCl. The gold and silver were not removed by purification with 1M HNO_3. In contrast, 85 % of copper and almost all iron were removed by this process. The 5-10 % of gold and silver were removed by purification with 1M HCl, whereas 60 % of copper and 78 % of iron were removed by this process.

As the result, it is proved that 1M HNO_3 is more effective than 1M HCl for purification gold and silver after co-precipitation by metal hydroxides. The HNO_3 has a property for removing copper and iron, and recovering gold and silver better than HCl. If the chemical state of gold is stayed in complex form, it should be dissolved by either acid. Therefore, this result emphasize that gold co-precipitated with metal hydroxides was almost reduced to elemental gold.

5.3.5 The characteristic of gold after purification

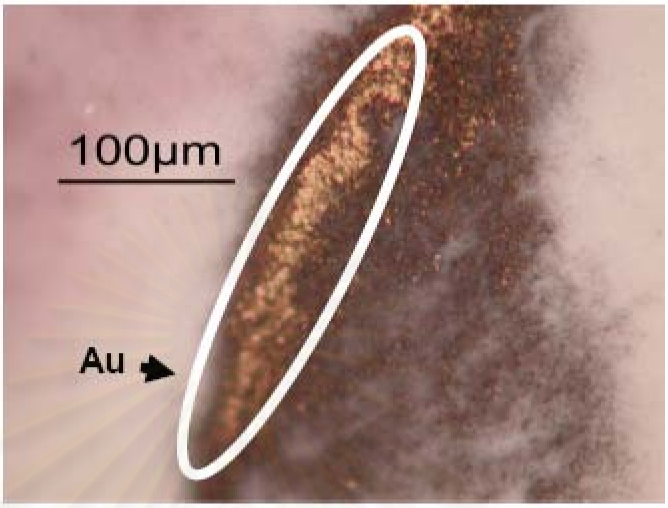


Figure 5.11 Photomicrograph of gold particle after purification by 1M HCl. 50 ml. reaction time 1 hour, at room temperature.

The solid samples obtained by filtration after purification were purple in color at a glance. The nano size of gold particle often shows the purple color, which is considered as gold. Figure 5.11, shows the photomicrograph of the sample collected after purification by HCl. The existence of aggregated particle showed bright yellow, indicating the presence of not only nano size of gold particle but also grown gold particle. The size of the unit gold particle was around 1-10 μm. This observation certainly indicates that chlorohydroxy Au (III) complexes adsorbed on metal hydroxides were reduced to elemental gold (Au (0)) without specific reducing reagent.

5.3.6 The distribution of elements and electron image of the residue after purification by 1M HCl

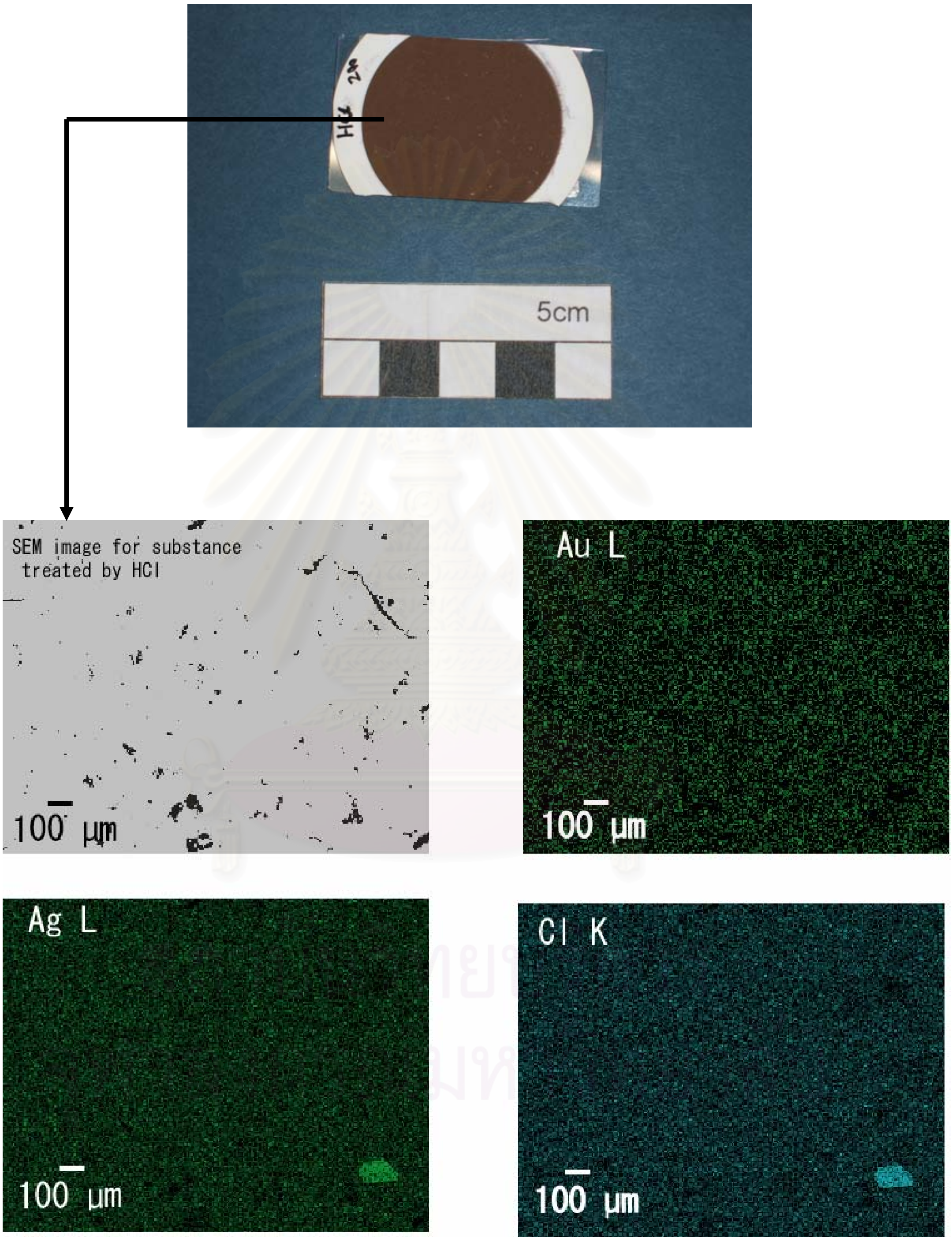


Figure 5.12 SEM image and distribution of the residue (on the filter paper) after purification by 1M HCl. 50 ml. reaction time 1 hour, at room temperature.

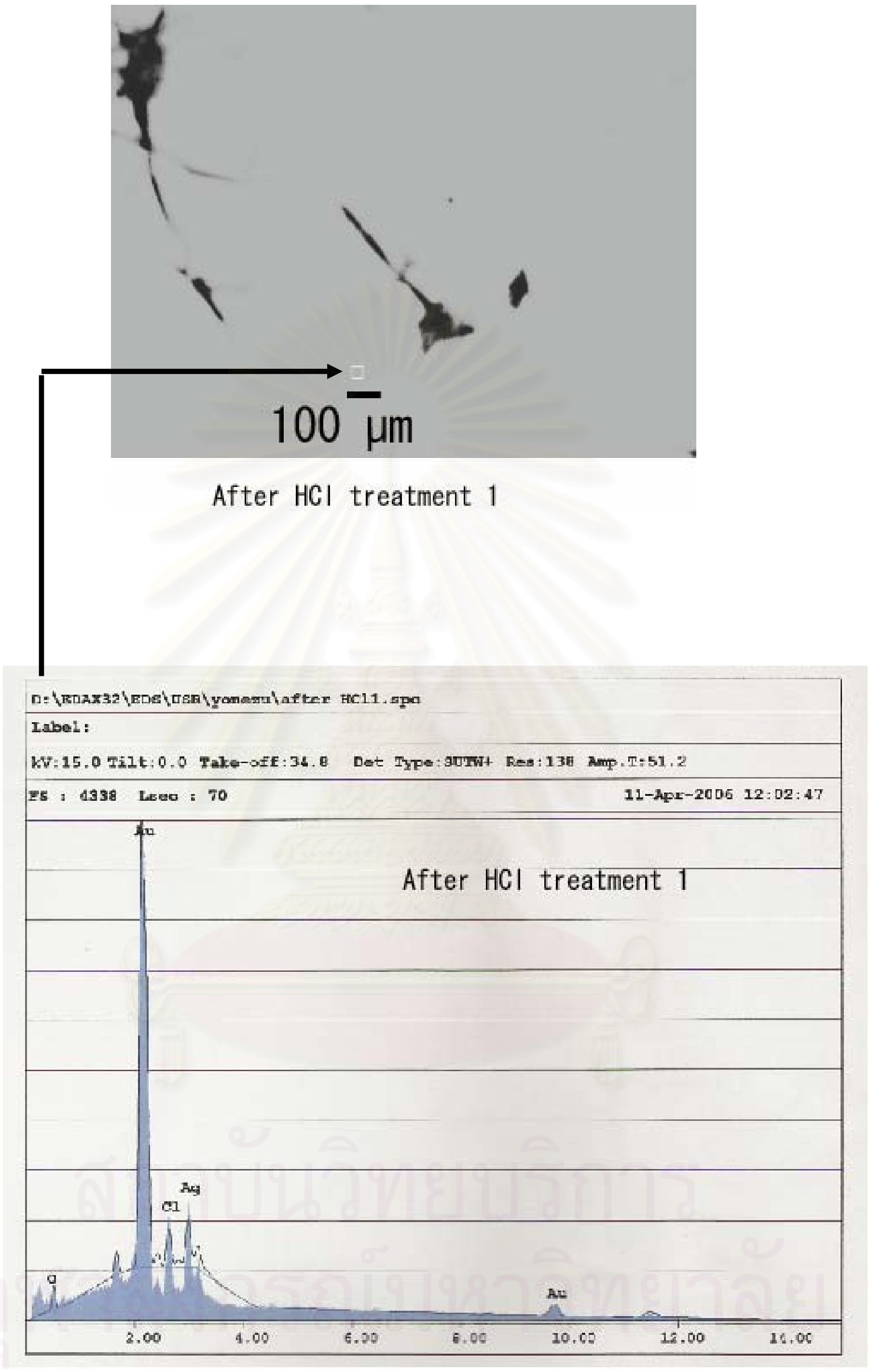


Figure 5.13 The spectrum showing the chemical composition of the residue (on the filter paper) after purification by 1M HCl 50 ml. reaction time 1 hour, at room temperature.

5.3.7 The distribution of elements and electron image of the residue after purification by 1M HNO_3

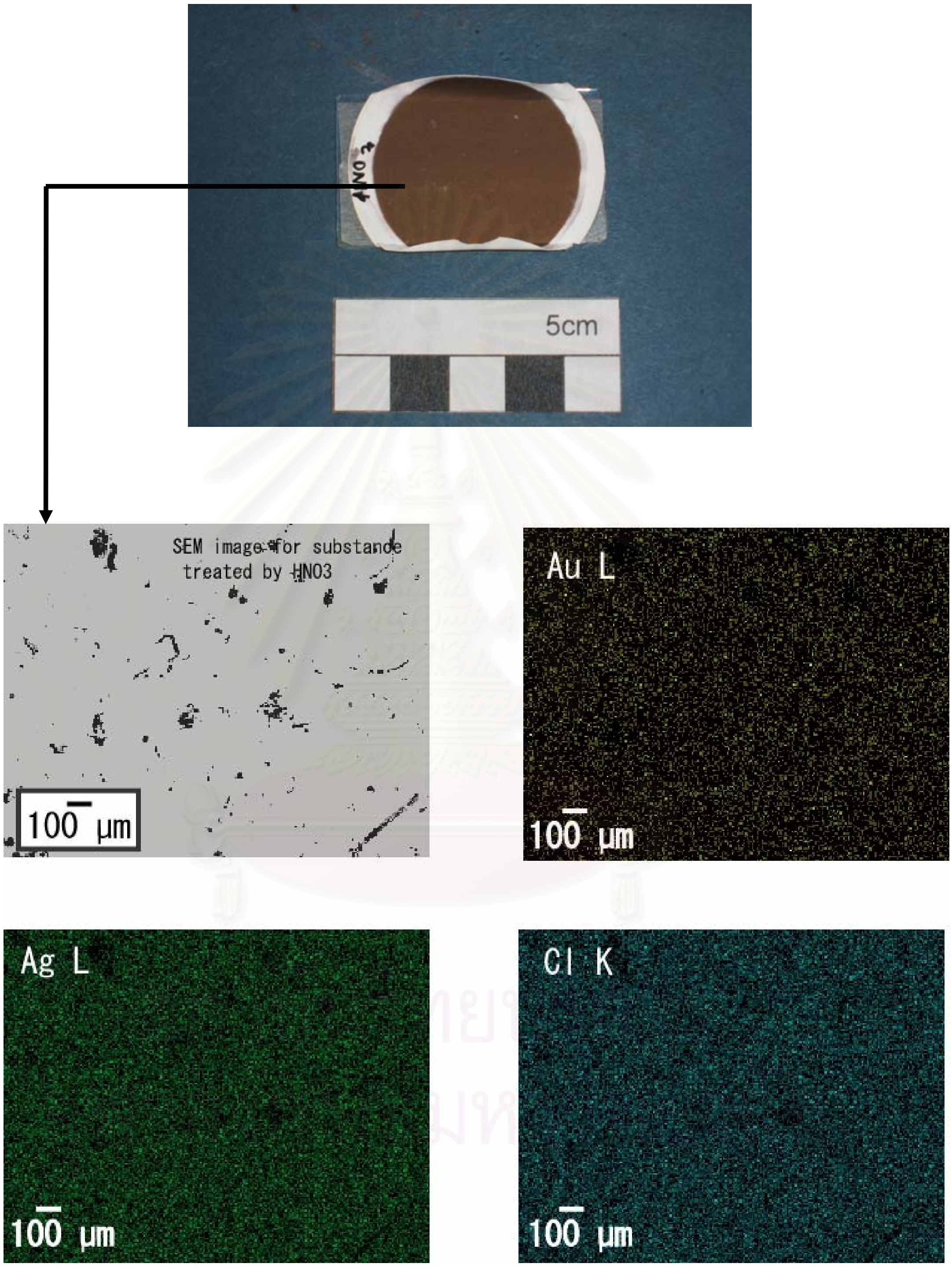


Figure 5.14 SEM image and distribution of the residue (on the filter paper) after purification by 1M HNO_3 50 ml. reaction time 1 hour, at room temperature.

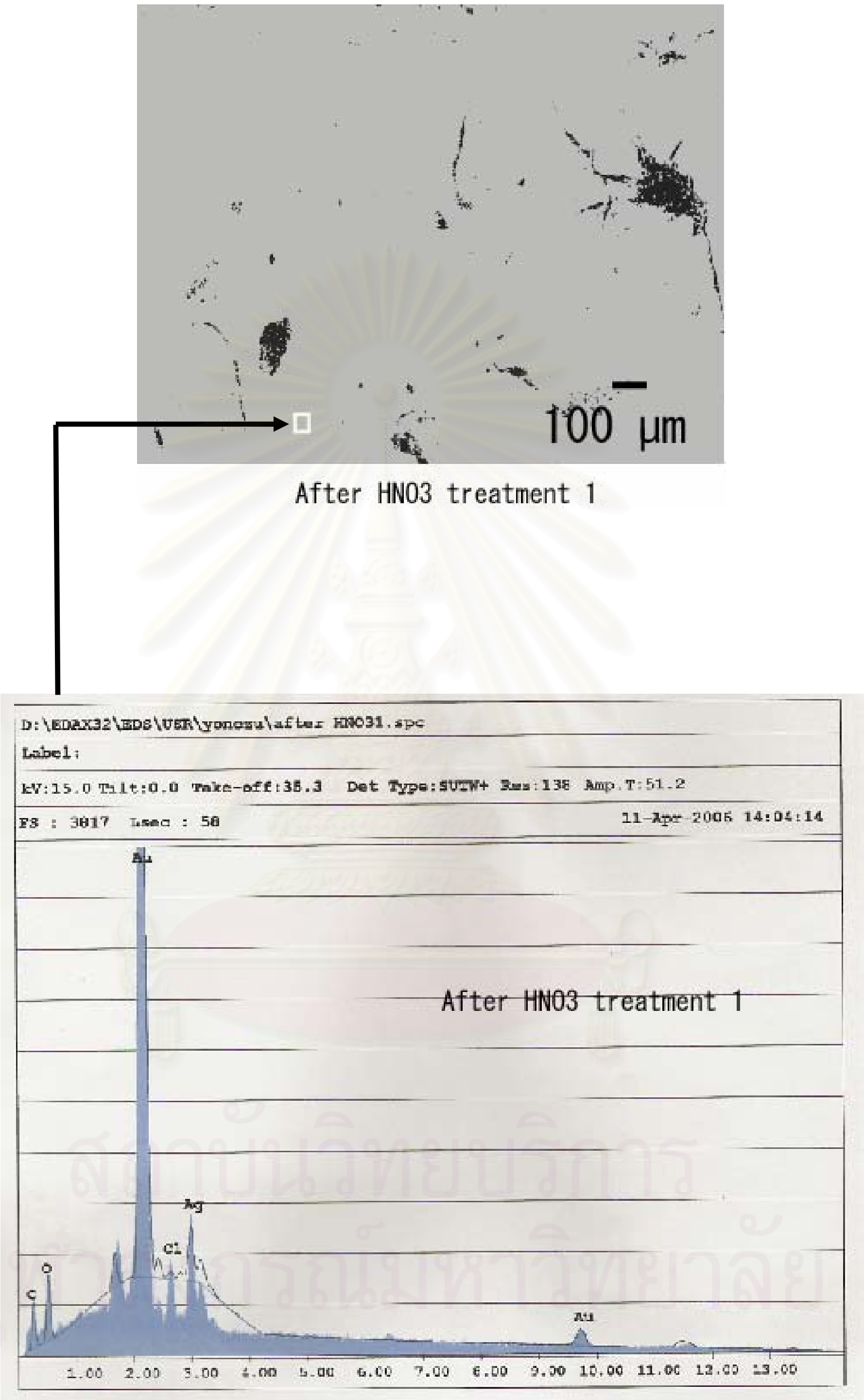


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Figure 5.15 The spectrum showing the chemical composition of the residue (on the filter paper) after purification by 1M HNO_3 50 ml. reaction time 1 hour, at room temperature.

The solid samples obtained by filtration after purification by 1M HCl and 1M HNO_3 were observation by SEM-EDX. Figure 5.12 and 5.13, shows the SEM image and distribution of chemical composition of the residue (on the filter paper) after purification by 1M HCl. Figures 5.14 and 5.15, show the SEM image and distribution of chemical composition of the residue (on the filter paper) after purification by 1M HCl. The results of both illustrated are very similar. The silver is in the form of AgCl. Although the gold and silver after purification by acid were clearly higher than before purification (Figure 5.8 and 5.9).This observation certainly indicates that chlorohydroxy Au (III) complexes adsorbed on metal hydroxides were reduced to elemental gold (Au^0) without specific reducing reagent.

5.4 Conclusions

1) The co-precipitation with metal hydroxides method at pH 6 shows effective recovery; e.g. almost 100 % recovery of gold and more than 70% recovery of silver from the leachate after leaching by aqua regia even within 1hour. The chlorohydroxy Au (III) complexes adsorbed on metal hydroxides were reduced to elemental gold (Au^0) without specific reducing reagent and could be seen as a gold particle.

2) The purification operation by using 1M HNO_3 is higher effective for gold and silver recovery than 1M HCl. Almost all of gold and silver is remained during the purification. After purification, both nano scale of gold and aggregated micron size of gold could be observed much more clearly.

CHAPTER VI

SUMMARY AND CONCLUSION

5.1 Summary

5.1.1 Recovery of gold

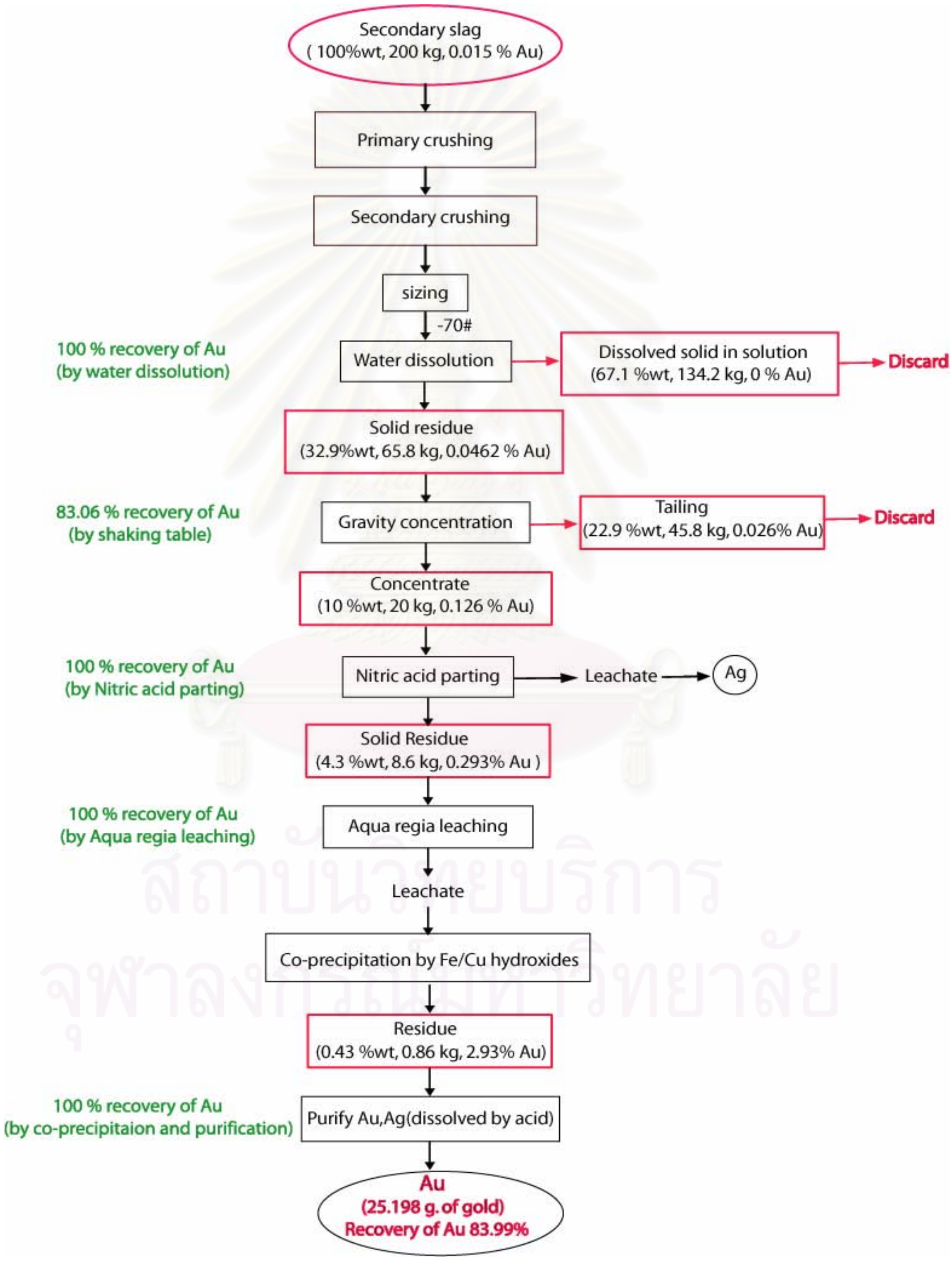

Figure 6.1 Variation of the total amount of secondary slag and gold concentration in all stages of the recovery process.

5.1.2 Recovery of silver

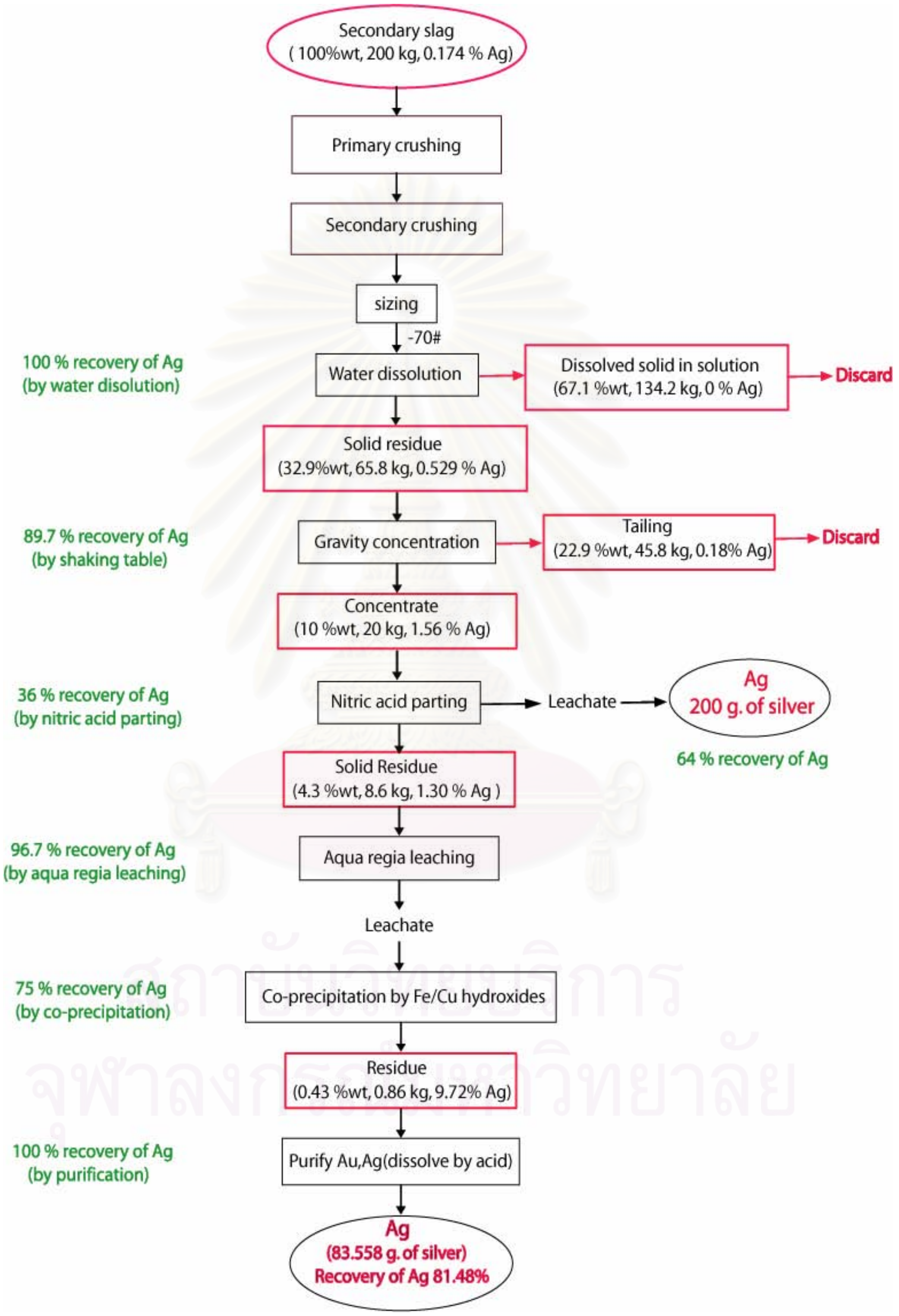

Figure 6.2 Variation of the total amount of secondary slag and silver concentration in all stages of the recovery process.

5.2 Conclusions

From all of process from physical concentration to purification treatments were conclusions as following;

1) The content of gold, silver and copper in the concentrate are significantly increased by performing of the shaking table process. The percent recovery of gold is 83% and silver is 90%.

2) The metallic particles in secondary slag are liberated from slag phase and can be determined in spherical shape due to the chemical composition. The metallic particles exist as Au, Ag, Cu alloys and show various colors depending on the content of Au, Ag and Cu.

3) Nitric acid parting can remove base metals and silver out of the sample, and then silver can be recovered from leachate after nitric acid parting by precipitation with sodium chloride and then reduced to metallic silver by heat with a reducing flux.

4) Most of gold and silver in the sample are completely leached within 1 hour by the aqua regia. For silver, the longer reaction time is, the more AgCl precipitate is formed in the residue.

5) Aqua regia is effective to extract gold, but not silver, especially under the high S/L ratio condition.

6) The co-precipitation with metal hydroxides method at pH 6 shows effective recovery; e.g. almost 100 % recovery of gold and more than 70% recovery of silver from the leachate after leaching by aqua regia even within 1hour. The chlorohydroxy Au (III) complexes adsorbed on metal hydroxides were reduced to elemental gold (Au^0) without specific reducing reagent and could be seen as a gold particle.

7) The purification operation by using 1M HNO_3 is higher effective for gold and silver recovery than 1M HCl. Almost all of gold and silver is remained during the purification. After purification, both nano scale of gold and aggregated micron size of gold could be observed much more clearly.

8) From all process concluded that 83.99% recovery of gold and 81.48% recovery of silver.

5.3 Recommendations

1) Percent recovery of silver less than percent recovery of gold from all chemical process, especially in the aqua regia leaching experiment. Silver is loss to the form of AgCl and contained in the residue for discard. From this result, the recovery of AgCl from the residue after aqua regia leaching should be considered the future work.

2) Other factors affecting purification efficiency such as the reaction time, the volume of acid (HCl and HNO_3) to samples ratio, the concentration of HCl and HNO_3 should be considered the future work.

3) The observation of the residue after co-precipitation and the residue after purification using EPMA and TEM recommended for the future study.

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APPENDICES

Appendix

Analytical machines for this study

X-Ray Fluorescence (XRF) Spectrometry

Basic theory

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.

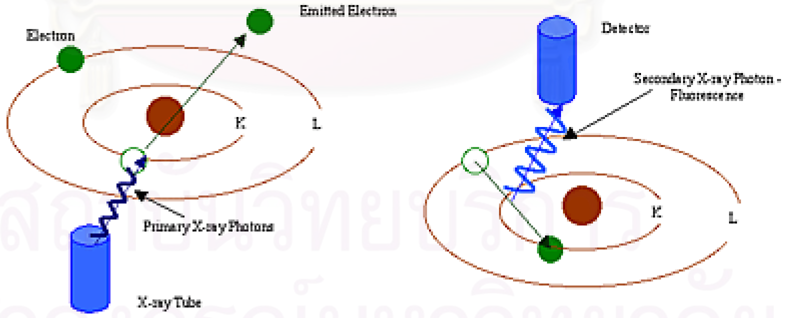


Figure A-1 Schematic of X-ray fluorescence spectrometry

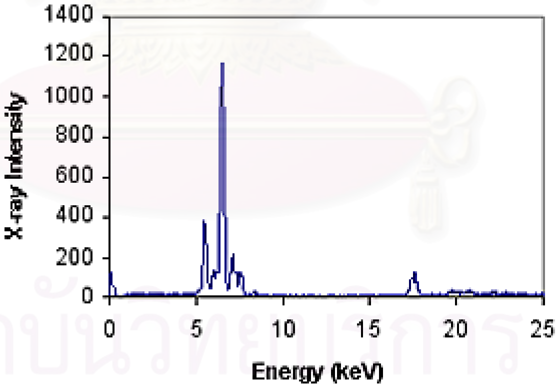
In XRF Spectrometry, high-energy primary X-ray photons are emitted from a source (X-ray tube) and strike the sample. The primary photons from the X-ray tube have enough energy to knock electrons out of the innermost, K or L, orbitals. When this occurs, the atoms become ions, which are unstable. An electron 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 Kα energy for Iron (Fe) is about 6.4keV. Typical spectra for EDXRF Spectrometry appear as a plot of Energy (E) versus the Intensity (I).



Elemental analysis

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.

Figure A-2 Rigaku RIX 3100 X-ray fluorescence spectrometer (XRF) at the Department of Earth Resources Engineering, Kyushu University, Japan

Figure A-3 Standard samples for analyze XRF

Figure A-4 Press machine

Figure A-5 Pellet samples for analyze XRF

Atomic-Absorption Spectroscopy (AAS)

Introduction

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.

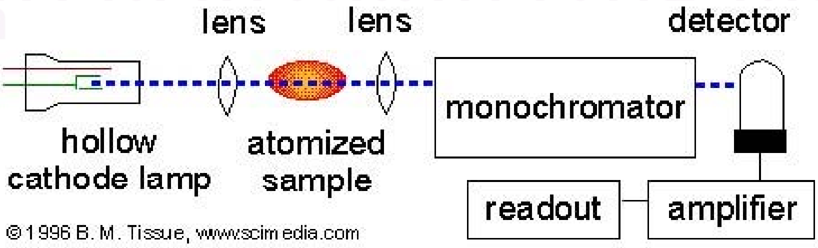


Figure A-6 Schematic of an atomic-absorption experiment

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 analyte 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.

Application

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.

Figure A-7 NIPPON Jarrel Ash AA-835 flame atomic absorption spectrophotometer (AAS) at the Department of Earth Resources Engineering, Kyushu University, Japan

Optical microscope

Basic theory

The optical microscope remains the fundamental tool for phase identification. The optical microscope magnifies an image by sending a beam of light through the object as seen in the schematic diagram of Figure 1. The condenser lens focuses the light on the sample and the objective lenses (10X, 40X, . . . 2000X) magnifies the beam, which contains the image, to the projector lens so the image can be viewed by the observer.

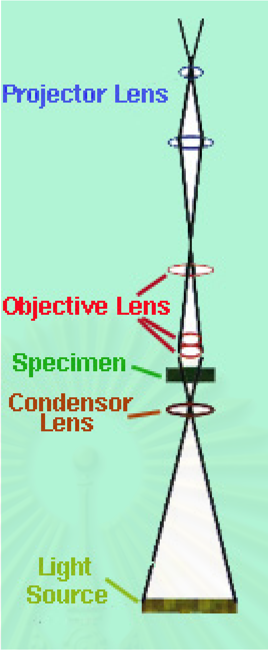


Figure A-8 Schematic diagram of the optical micrograph

In order for any specimen to be observed, the sample must first be ground using sandpaper of different grain sizes. Then the sample needs to polish into a mirror like image and then etched with a solution for a certain length. Careful technique is critical in sample preparation for without it, the optical microscope is useless.

Figure A-9 Nikon polarization microscope E6TP-M61

at the Department of Earth Resources Engineering, Kyushu University, Japan

Figure A-10 Thin section samples for observation by optical microscope.

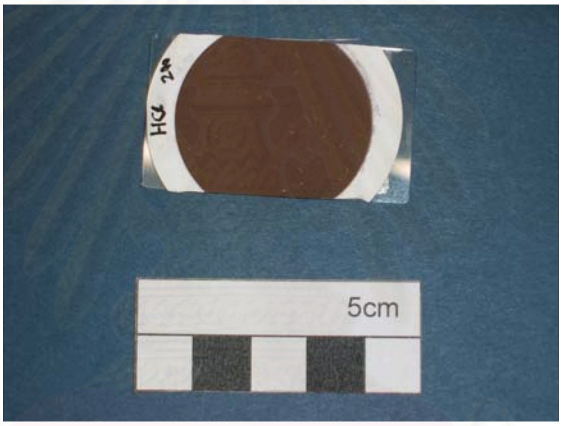


Figure A-11 The samples (on filter paper) fixed on the slide glass for observation by optical microscope.

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

EDX

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).

SEM

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)

Application

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

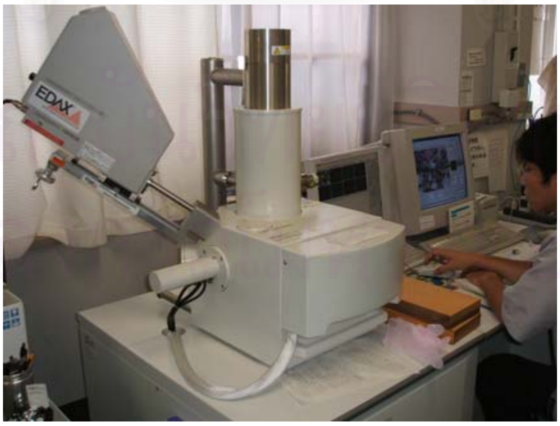


Figure A-12 Shimudsu Superscan SS-550 scanning electron microscopy (SEM-EDX) at the Analytical center, Kyushu University, Japan.

VITA

Miss Romchat Chairaksa was born on 15 February, 1980 in Chiang Mai, Thailand. She received a Bachelor's Degree of Material Science (Jewelry and Gemology) from the Faculty of Science, Srinarinwirot University in 2001. After then, she subsequently completed the requirements for a Master's Degree in Mining Engineering at the Department of Mining and Petroleum Engineering, Chulalongkorn University in 2006. During studying, she worked in the assistant production manager position at Gem plaza Co.,Ltd. After that, she worked in the sales engineer position at Leamthong syndicate Co.,Ltd.

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