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# **Hydrometallurgical recovery of precious metals using magnetic adsorbents**

A dissertation submitted in partial fulfillment  
of the requirements for the degree of  
Doctorate in Engineering

by

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## Chapter 1

### GENERAL INTRODUCTION

#### 1.1 STATEMENT OF THE PROBLEM AND OBJECTIVES OF THE STUDY

Precious metals, such as gold (Au), silver (Ag), platinum (Pt), palladium (Pd), rhodium (Rh) and other platinum group metals (PGMs), are widely used in various manufacturing fields including jewelry, electronics, catalysts, dental, medicine, glass and other chemical industries. These metals exhibit distinctive properties, such as high resistance to chemical attack, excellent high-temperature characteristics, stable electrical properties, workability and outstanding catalytic properties which make most of them highly in demand and thus, expensive. Some of the precious metals, specifically gold, has been used as a symbol of wealth since ancient times and a measure of economic status of nations around the world (Hunt et.al., 1969; Crundwell et al., 2011; Rao and Reddi, 2000; Fujiwara et l., 2007; Ramesh et al., 2008).

The precious metals are scarce materials. In the case of platinum group metals (PGMs), annual primary production is small with an estimated value of about 500 tonnes per year. Considering the rising demand coupled with the declining resources available, efficient recovery of these precious metals from secondary sources has become inevitable and has been considered as an important technology and research interest. Amongst the secondary materials being studied and developed as sources of precious metals include electronic wastes, scrap jewelry, spent catalysts and waste effluents from precious metal processing plants (Jimenez de Aberasturi et al., 2011; Jha et al., 2013; Raju et al., 2012; Kononova et al., 2010; Nowotny et al., 1997; Acacia de Sa Pinheiro et al., 2004; Shams and Goodarzi, 2006; Chand et al., 2009; Wojnicki et al., 2015; Macaskie et al., 2006).

Hydrometallurgical techniques play an important role in the processing of precious metals from both primary and secondary sources, due to their simple operation, lower cost requirement, and relatively well-purified products with minimal loss of target metals (Lam et al., 2007; Wiraseranee et al., 2008). The process is generally comprise of two major stages. The first stage is the leaching of ores, concentrates or waste materials containing

precious metals, using various lixiviants. The most common ones are cyanide, chloride and other halide-based solutions, *aqua-regia*, ammonium thiosulfate, thiourea and other alternative reagents. The second stage is the separation and recovery of the dissolved precious metal ions from the solution.

Separation and recovery of the dissolved precious metals in solution still remain a problem and pose a real challenge. Several methods were proposed to recover the extracted metals from the solution phase and these include precipitation, solvent extraction, cementation, ion-exchange and solid phase extraction (SPE) including adsorption (Benguerel et al., 1996; Wolowicz and Hubicki, 2009; Lam et al., 2007; Aktas and Morcali, 2011; Kononova et al., 2010; Kononova et al., 2011; Raju et al., 2012; Nikoloski et al., 2015; Wojnicki et al., 2013; Sun et al., 2012; Nowotny et al., 1997; Mulwanda and Dorfling, 2015; Ramesh et al., 2008). Among these methods, adsorption offers a number of advantages, such as easy operation, low energy consumption, simple maintenance, possibility of adsorbent regeneration, and large capacity (Lam et al., 2007; Aktas and Morcali, 2011; Ramesh et al., 2008).

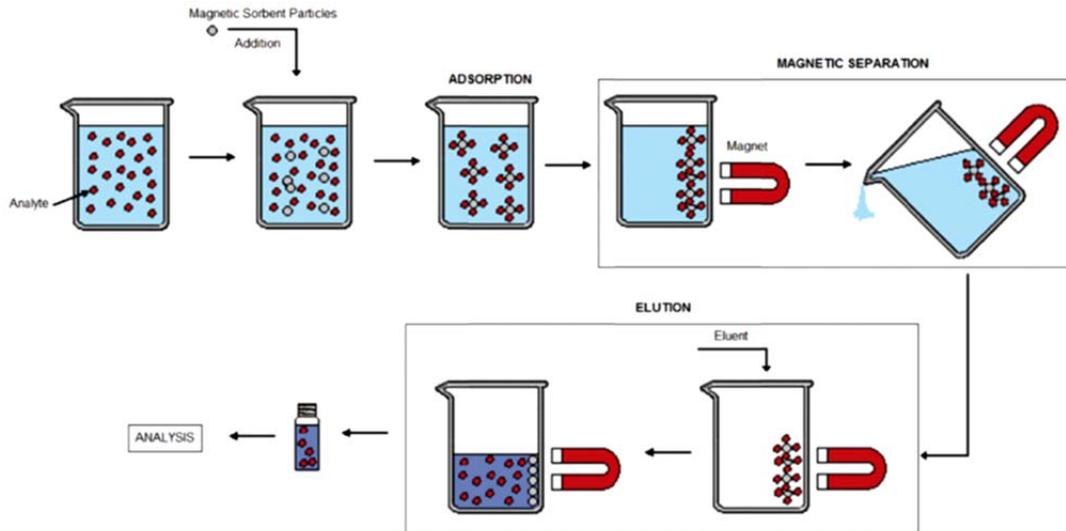
In the hydrometallurgy of precious metals, leaching solutions usually contain low concentrations of precious metal ions together with high concentrations of impurity metal ions. Separation of precious metals from these solutions can be complicated and may lead to losses of valuable metals (Kononova et al., 2010). The complex chemistry and the overlapping properties of precious metals pose a real challenge in the recovery of these metals from aqueous solutions. Therefore, adsorbents that are highly selective towards precious metals are desirable.

One of the emerging technologies that demonstrate potential application in the recovery and separation of precious metal ions from hydrometallurgical processes is the magnetic solid-phase extraction (MSPE). MSPE is a procedure based on the use of magnetic sorbents for the separation and pre-concentration of different organic and inorganic analytes from large sample volumes. Figure 1-1 illustrates the procedure. The magnetic sorbent is added to the sample solution and the target analyte is adsorbed onto the surface of the magnetic sorbent particles (Giakisikli and Anthemidis, 2013; Herrero-Latorre et al., 2015). The use of magnetic materials in solid phase extraction has received considerable attention in recent years due to the many advantages arising from the inherent

characteristics of magnetic particles. By applying an external magnetic field, problems associated with filtration or phase separation in a conventional solid-liquid system can be easily performed with MSPE methodology (Giakisikli and Anthemidis, 2013; Herrero-Latorre et al., 2015).

Magnetic solid phase extraction (MSPE) is a relatively new technology. In a review reported by Giakisikli and Anthemidis (2013) and Herrero-Latorre et al. (2015), a brief history of the development of the technology is presented. The first report on magnetic separation was on biotechnological applications in 1973, followed by phase separation application in liquid-liquid extraction procedures using ferrofluids or iron oxide particles in 1987, and more recently, application on radium, lead and polonium recovery from seawater samples using manganese dioxide coated magnetite as a sorbent. However, the term of magnetic solid phase extraction (MSPE) was first introduced by Safariköva and Safarik in 1999 for analytical purposes (Giakisikli and Anthemidis, 2013; Herrero-Latorre et al., 2015).

Magnetic adsorbents generally consist of magnetic elements such as iron, nickel, cobalt or their oxides and alloys with ferromagnetic or superparamagnetic properties. Magnetic particles can be found naturally or can be synthesized in the laboratory (i.e.  $\text{Fe}_3\text{O}_4$ ). They are available in a wide range of sizes from nano to microparticles. The simplicity of producing magnetic particles in large quantity as well as the easiness of surface modification enable them to have a wide range of potential applications in environmental, biological, food analysis and more recently, metal recovery. Moreover, the magnetic particles can be reused or recycled. Among magnetic particles, iron oxides like magnetite ( $\text{Fe}_3\text{O}_4$ ) and maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ), as a new kind of magnetic adsorbent, have received considerable attention due to their small size and high surface area providing better kinetics and greater extraction capacity for analytes. In addition, their superparamagnetic property allows their easy manipulation under the influence of an external magnetic field (Giakisikli and Anthemidis, 2013; Herrero-Latorre et al., 2015).



**Figure 1-1. Magnetic solid-phase extraction method (Herrero-Latorre et al., 2015)**

The potential of magnetite as a selective sorbent for gold recovery from chloride solutions have been previously reported (Alorro et al., 2010a; Alorro et al., 2010b; Alorro et al., 2015). Magnetite ( $\text{Fe}_3\text{O}_4$  or  $[\text{Fe}^{2+}\text{Fe}_2^{3+}]\text{O}_4$ ) is a common iron oxide mineral in the Earth's crust and it oxidizes to maghemite ( $\gamma\text{Fe}_2\text{O}_3$  or  $\gamma[\text{Fe}_2^{3+}]\text{O}_3$ ), which is an Fe-deficient, metastable spinel polymorph of hematite, as follows (White et al., 1994):



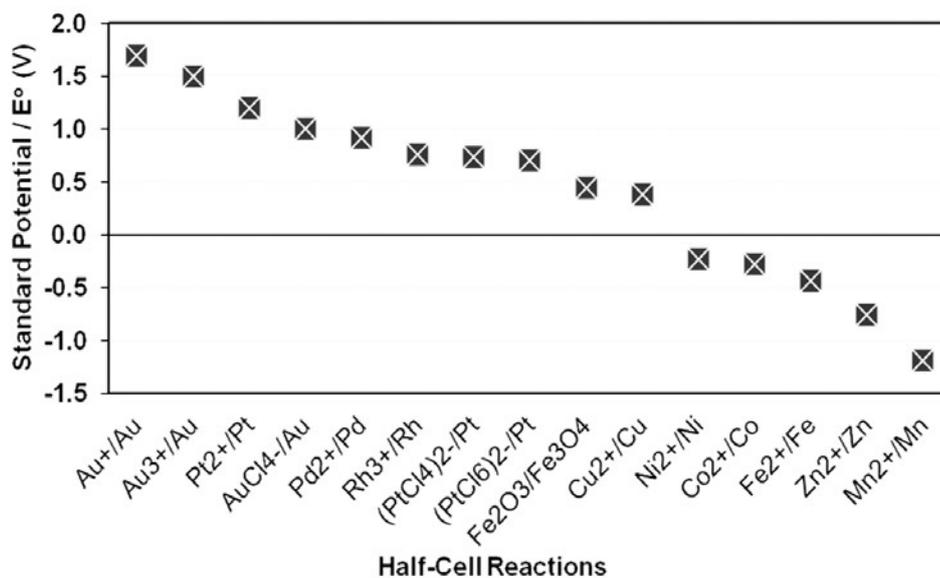
The standard redox potential of this half-cell reaction presented in Equation 2-1 is 0.444 V vs. Standard Hydrogen Electrode (SHE) and it is lower compared to the standard potential of  $\text{AuCl}_4^-/\text{Au}^0$  redox pair (1.002 V vs. SHE). Therefore,  $\text{AuCl}_4^-$  in chloride solutions is reduced on magnetite according to the following reactions:



On the other hand, the standard redox potentials of  $\text{Cu}^{2+}/\text{Cu}^0$ ,  $\text{Zn}^{2+}/\text{Zn}^0$ ,  $\text{Ni}^{2+}/\text{Ni}^0$  redox pairs are lower than that of magnetite/maghemite redox pair, so these common metal ions are not reduced on the surface of magnetite. Because of this, the selective recovery of gold on magnetite is realized even in the presence of the common metal ions (Alorro et al., 2010a; Alorro et al., 2010b). The electrochemical studies conducted by the authors (Alorro

et al., 2015) have confirmed that gold chloride complexes are reduced to metallic gold on the surface of magnetite.

Similar to gold, platinum group metals, such as Pt, Pd and Rh form chloride complexes in chloride solutions. At chloride concentrations of  $>100 \text{ mol/m}^3$ , the dominant Pt species are  $\text{PtCl}_4^{2-}$  and  $\text{PtCl}_6^{2-}$ , predominantly  $\text{PdCl}_4^{2-}$  for Pd, and  $\text{RhCl}_6^{3-}$ ,  $\text{RhCl}_5(\text{H}_2\text{O})^{2-}$  or  $\text{RhCl}_4(\text{H}_2\text{O})^{2-}$  as the main species for Rh (Colombo et al., 2008). It has also been reported that the solution pH and chloride ion concentration influence the adsorption of metal complexes (Uheida et al., 2006). The chloride complexes of PGMs have higher redox potentials than that of magnetite as shown in Figure 1-2 and can be regarded as redox sensitive species. From this premise, it can be expected that PGMs are selectively recovered by magnetite from chloride solutions.



**Figure 1-2. Standard reduction potentials of different metal half-cell reactions and  $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$  redox pair**

The primary objective of this dissertation, therefore, is to investigate the hydrometallurgical recovery of precious metals, specifically Au, Pt, Pd and Rh, from aqueous solutions using magnetic adsorbents. Specifically, this study aims to (i) examine the potential of magnetite derived from different sources as adsorbent for precious metals; (ii) investigate the effects of different process parameters, such as pH, treatment time, type

of base solution, reagent concentration, and amount of adsorbent, on the recovery of precious metals; (iii) establish or propose mechanisms of recovery. The target application of this study is the recovery and separation of precious metal ions from two most widely used alternative lixivants for precious metal leaching, chloride and ammoniacal thiosulfate. Batch adsorption experiments were conducted and the results are divided into different parts and are presented in several chapters.

## 1.2 OUTLINE OF THE DISSERTATION

This dissertation is composed of five chapters. The key contents of each chapter are outlined as follows:

Chapter 1: introduces the background, statement of the problem and objectives of the study. A brief literature review is presented.

Chapter 2: presents the study on the recovery of platinum group metals (Pt, Pd and Rh) from chloride solution using synthetic magnetite.

Chapter 3: reports the study on the recovery of platinum group metals (Pt, Pd and Rh) from chloride solution using magnetite particles derived from copper converting slag.

Chapter 4: details the study on the recovery of gold from thiosulfate solution using magnetite particles recovered from a copper converting slag.

Chapter 5: gives the summary and conclusion of the dissertation.

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## Chapter 2

# RECOVERY OF PLATINUM GROUP METALS FROM CHLORIDE SOLUTION USING MAGNETITE

## 2.1 INTRODUCTION

Platinum (Pt), palladium (Pd) and rhodium (Rh) belong to a group of metallic elements known as the platinum group metals (PGMs), which exhibit distinctive properties, such as high resistance to chemical attack, excellent high-temperature characteristics, stable electrical properties, and outstanding catalytic properties. Due to these very useful properties, PGMs find varied applications in many different fields. The major consumer of these metals is the automobile industry where they are used as catalysts to reduce levels of carbon monoxide, unburnt hydrocarbons and nitrogen. Other applications include chemical industry catalysts, electronics, glass manufacturing, and jewellery (Hunt et al., 1969; Crundwell et al., 2011; Rao and Reddi, 2000). The PGMs are scarce materials with a small annual primary production of about 500 tonnes per year and are also costly to produce, making them highly valuable and expensive (Crundwell et al., 2011). Considering the growing demand coupled with the declining resources available, efficient recovery of these precious metals from secondary sources, such as spent catalysts and electronic wastes (De Aberasturi et al., 2011; Jha et al., 2013; Raju et al., 2012; Kononova et al., 2010; Nowotny et al., 1997; De Sa Pinheiro et al., 2004; Shams and Goodarzi, 2006), has become an important technology and research interest.

Hydrometallurgical techniques play an important role in the processing of PGMs from both primary and secondary sources, due to its simpler operation, lower cost requirement, and relatively well-purified products with minimal loss of target metals (Lam et al., 2007; Wiraseranee et al., 2008). However, separation and recovery of the dissolved precious metals in solution still remain a problem and pose a real challenge. Several methods were proposed to recover the extracted metals from the solution phase and these include precipitation, solvent extraction, cementation, ion-exchange and adsorption (Benguereel et al., 1996; Wolowicz and Hubicki, 2009; Lam et al., 2007; Aktas and Morcali, 2011; Kononova et al., 2010; Kononova et al., 2011; Raju et al., 2012; Nikoloski et al., 2015; Wojnicki et al., 2013; Sun et al., 2012; Nowotny et al., 1997). Among these methods,

adsorption offers a number of advantages, such as easy operation, low energy consumption, simple maintenance, possibility of adsorbent regeneration, and large capacity (Lam et al., 2007; Aktas and Morcali, 2011). In the hydrometallurgy of PGMs, leaching solutions usually contain low concentrations of PGMs together with high concentrations of common metals. Sorption recovery of PGMs from these solutions can be complicated and may lead to losses of valuable metals (Kononova et al., 2010). Therefore, adsorbents that are highly selective towards PGMs are desirable.

In this chapter, the sorption of Pt, Pd, and Rh from chloride solution on magnetite powders was investigated by batch experiments. Different recovery parameters, such as, pH, contact time, chloride concentration, and PGMs concentration were examined.

## 2.2 MATERIALS AND METHODOLOGY

### 2.2.1 Materials

The synthesized magnetite powder used in the experiments was of commercial grade and purchased from Wako Chemicals Co. Ltd., Japan. The chemical composition of the magnetite as determined by X-ray Fluorescence Spectrometer (JEOL Element Analyzer, JSX-3201A, Japan) is shown in Table 1. The magnetite powder has a purity of 98.5% with Mn as the major impurity. The surface area of synthesized magnetite determined by N<sub>2</sub>-BET method using a Nova 2200e Surface Area and Pore Size Analyzer (Yuasa Ionics, Japan) was 116 m<sup>2</sup>/g.

Reagent grade platinum (H<sub>2</sub>PtCl<sub>6</sub> in 1 mol/dm<sup>3</sup> HCl), palladium (PdCl<sub>2</sub> in 1 mol/dm<sup>3</sup> HCl), and rhodium (Rh(NO<sub>3</sub>)<sub>3</sub> in 2 mol/dm<sup>3</sup> HNO<sub>3</sub>) standard solutions (Wako Chemicals, Japan) were used to prepare PGM solutions. The other chemicals used in this study such as sodium chloride (NaCl), hydrochloric acid (HCl), and sodium hydroxide (NaOH) were all of reagent grades.

### 2.2.2 Methodology

Batch sorption tests were conducted to determine the ability of magnetite to recover Pt, Pd, and Rh from chloride solutions. The experiments were carried out by adding 0.1 gram of  $\text{Fe}_3\text{O}_4$  powder into a 50  $\text{cm}^3$  Erlenmeyer flask containing 10  $\text{cm}^3$  of NaCl solution (0.01 - 1.0  $\text{mol/dm}^3$ ) with varied concentrations of  $\text{H}_2\text{PtCl}_6$ ,  $\text{PdCl}_2$ , and  $\text{Rh}(\text{NO}_3)_3$ . The pH of the solution was adjusted by adding HCl or NaOH solutions. The mixture was shaken for 0.5-72 h in a water bath shaker (ML-10F, Taitec, Japan) at 120 strokes per minute and 298 K. After shaking, the mixture was centrifuged and filtered using a nitro-cellulose membrane filter (pore size; 0.20  $\mu\text{m}$ ). The PGM content and the iron concentration in the filtrate were determined using Inductively Coupled Plasma-Atomic Emission Spectrometer (SPS 7800, Seiko Instruments, Japan). The magnetite particles after the treatment were examined using the Scanning Electron Microscope (SEM) equipped with an Electron Dispersive X-ray Spectrometer (EDX) (SSX-550, Shimadzu, Japan) to check the presence of PGMs on the surface of the particles.

The PGM uptake was calculated according to the mass balance shown in Equation 3:

$$\text{PGMs uptake } [\mu\text{mol/g}] = (C_i - C_f) \times \frac{V}{W} \quad (3)$$

where  $C_i$  is the initial metal concentration,  $C_f$  is the remaining metal concentration in the aqueous phase,  $V$  is the volume of the aqueous solution, and  $W$  is the weight of the magnetite.

## 2.3 RESULTS AND DISCUSSION

Synthesized magnetite powder was used as adsorbent to recover platinum, palladium and rhodium from chloride solution. The effects of pH, contact time, chloride concentration, and initial PGM concentrations were investigated. The results are presented in succeeding sections.

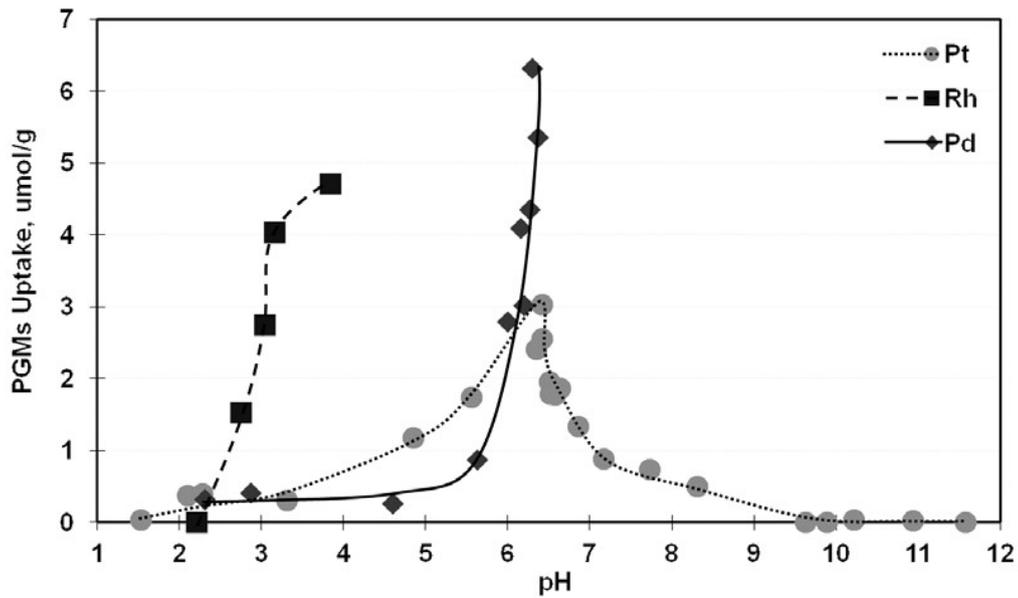
### 2.3.1 Effects of solution pH

The pH of the solution plays an important role in the sorption of metal ions onto the surface of oxides, such as magnetite. Control experiments were conducted without the addition of magnetite to determine the PGM precipitation windows at different pH ranges. It was confirmed that no Pt precipitation occurred at a pH range of 1-12, Rh and Pd precipitated at pH greater than 4 and 6.5, respectively. Considering the results of these control experiments, the succeeding PGM uptake experiments using magnetite were designed at pH 1-12 for Pt, pH 2-4 for Rh, and pH 2-6.5 for Pd.

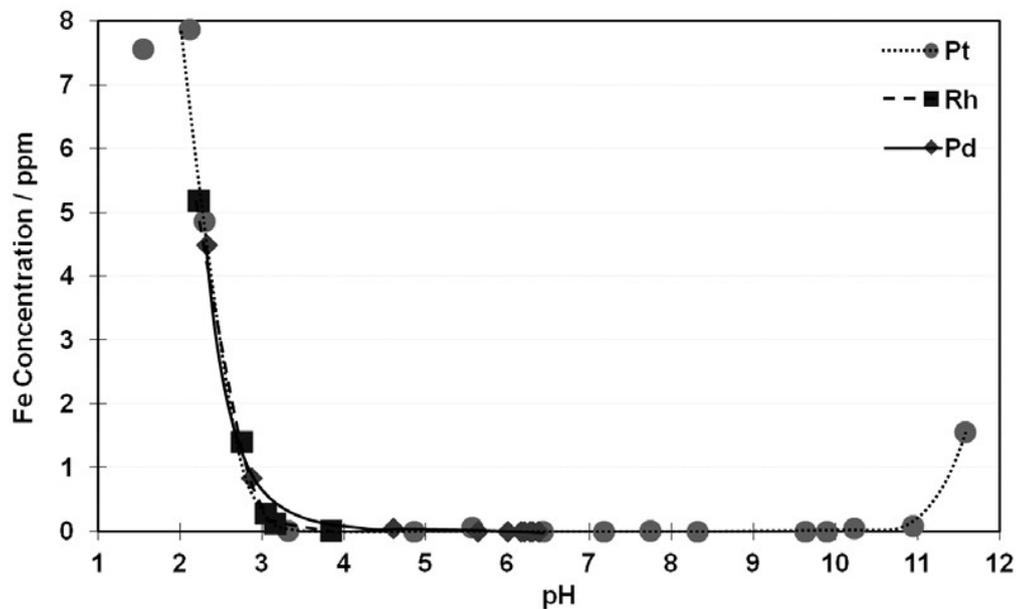
Figure 2 shows the effect of pH on Pt, Rh and Pd uptake by magnetite for 24 h from 0.1 mol/dm<sup>3</sup> NaCl solution containing 0.05 mol/m<sup>3</sup> PGM concentrations. In the case of Pd and Rh, the amount of the metals recovered by magnetite increased with increasing pH. The Pt uptake amount peaked with a value of 3.0 μmol/g at pH 6-7. At pH greater than or less than 6.5, the uptake amounts decreased gradually.

The concentration of Fe in the solution after the adsorption experiments was measured. Figures 3 and 4 show the effects of pH on the amount of Fe extracted from magnetite and the redox potential of the solutions measured by Pt electrode after 24h adsorption tests. At acidic pH region, significant amounts of Fe were detected in the solution, and the Fe concentration increased with decreasing pH. At around pH 2, the Fe concentration was about 0.1 mol/m<sup>3</sup>. The redox potential of the solutions was over the formula potential of the Fe<sup>3+</sup>/Fe<sup>2+</sup> redox pair (0.64 V vs. SHE in 5 mol/dm<sup>3</sup> HCl solution), indicating that the Fe<sup>3+</sup> concentration is higher than that of Fe<sup>2+</sup>. These results could be explained by assuming acid dissolution of magnetite, according to Equation 4.

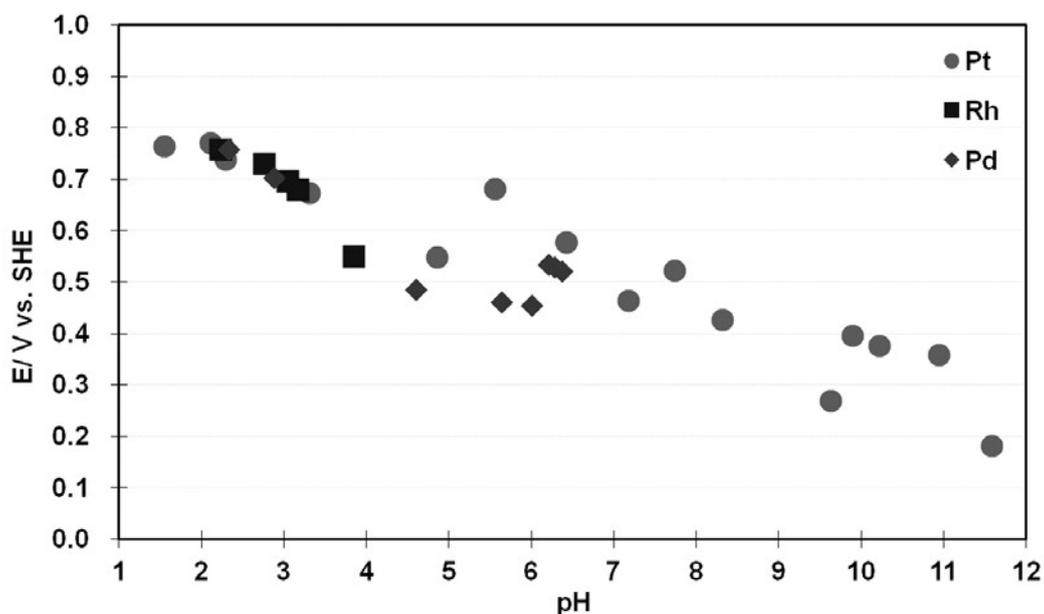




**Figure 2-2. Effect of final solution pH on Pt, Rh and Pd uptake by magnetite. Initial Pt, Rh and Pd concentrations:  $0.05 \text{ mol/m}^3$ ; contact time: 24 h; NaCl concentration:  $0.1 \text{ mol/dm}^3$ ;  $\text{Fe}_3\text{O}_4$  amount: 0.1 g; temperature: 298 K.**



**Figure 2-3 Effect of final solution pH on the amount of Fe extracted from magnetite. Initial Pt, Rh and Pd concentrations:  $0.05 \text{ mol/m}^3$ ; contact time: 24 h; NaCl concentration:  $0.1 \text{ mol/dm}^3$ ;  $\text{Fe}_3\text{O}_4$  amount: 0.1 g; temperature: 298 K.**

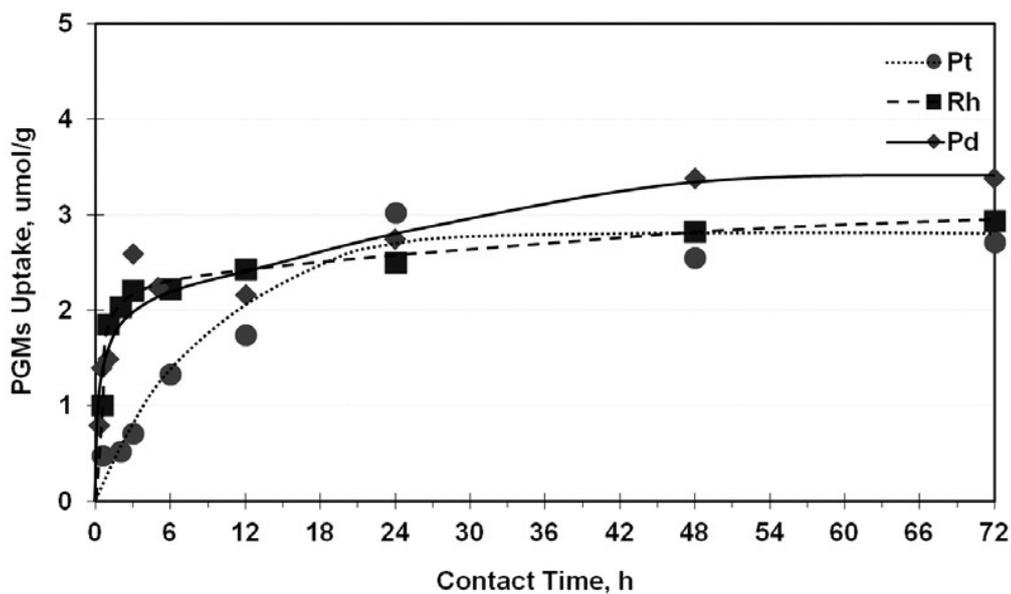


**Figure 2-4 The redox potential of the solution measured by platinum electrode at 24 h.**

### 2.3.2 Effects of contact time and platinum group metals concentrations

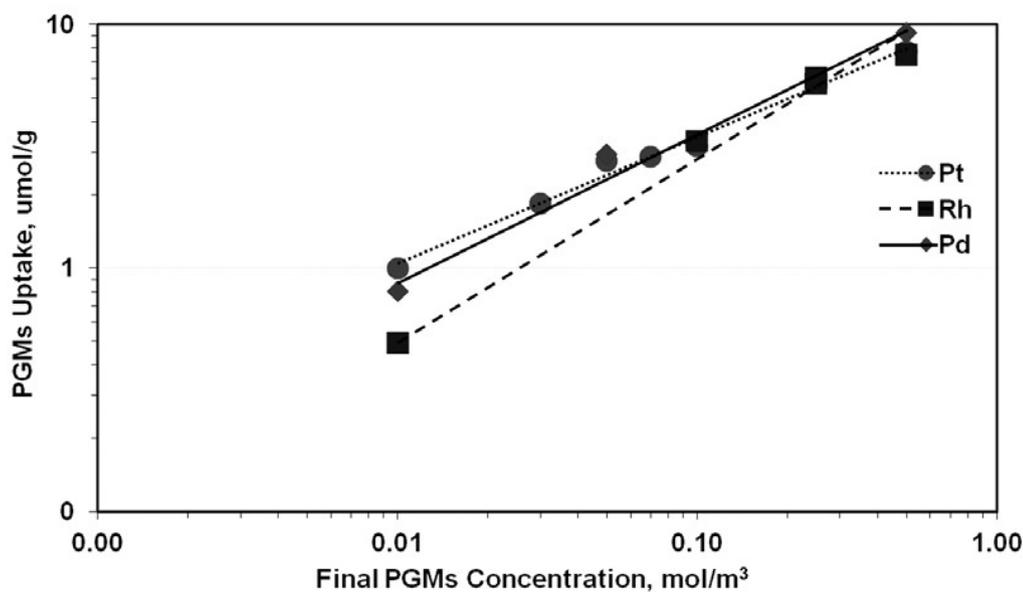
The effects of contact time and PGMs concentration on metal uptake were investigated using the optimum pH values described in 3.1. These pH values were 6-7 for Pt and Pd, and pH 3 for Rh.

Figure 5 shows the effect of contact time on the PGMs uptake on the magnetite from  $0.1 \text{ mol/dm}^3$  NaCl solutions containing  $0.05 \text{ mol/m}^3$  PGMs. It was observed that PGMs uptake by magnetite increased with time and became constant after 24 h. As can be seen in the figure, PGMs uptake kinetics is slow: about 24 hours are needed to reach maximum uptake ( $3.0 \text{ } \mu\text{mol Pt /g Fe}_3\text{O}_4$ ,  $2.8 \text{ } \mu\text{mol Pd /g Fe}_3\text{O}_4$  and  $4.2 \text{ } \mu\text{mol Rh /g Fe}_3\text{O}_4$ ).



**Figure 2-5. Effect of contact time on PGMs uptake by synthetic magnetite. Initial PGMs concentration:  $0.05 \text{ mol/m}^3$ ; pH: 3 for Rh and pH 6-7 for Pt and Pd; NaCl concentration:  $0.1 \text{ mol/dm}^3$ ;  $\text{Fe}_3\text{O}_4$  amount: 0.1 g; temperature: 298 K.**

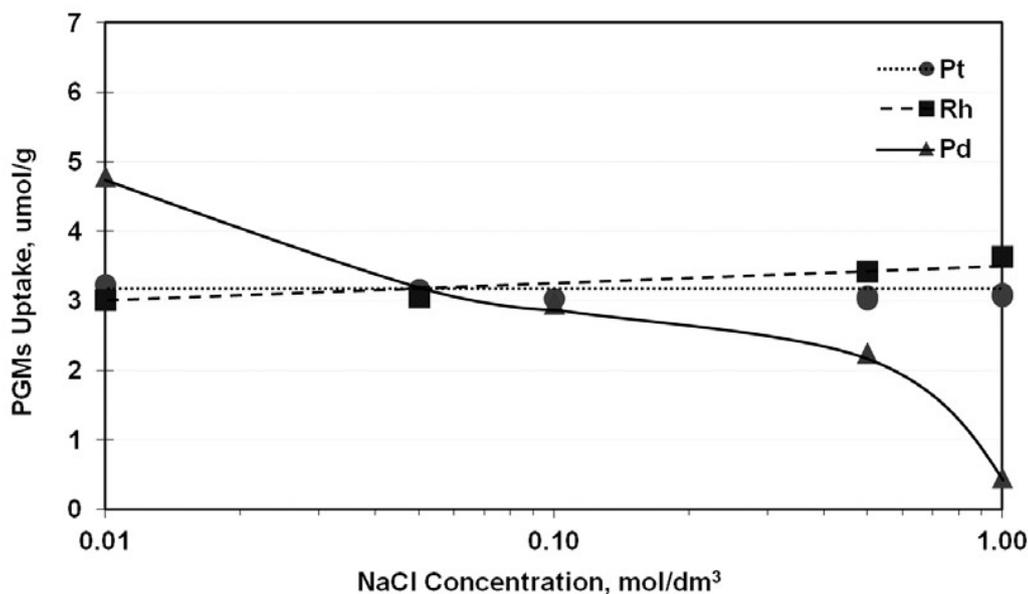
Figure 6 shows the effect of the PGMs concentration on the PGMs uptake on the magnetite. In the experiments, initial Pt, Rh and Pd concentration were varied from  $0.01$  to  $0.50 \text{ mol/m}^3$ . These working PGM concentrations are within a similar range with the solutions used by Sun et al. (2012), Kononova et al. (2011), and Aktas and Morcali (2011) in their studies. The PGMs uptake after 24 h increased with increasing the final PGMs concentration.



**Figure 2-6. Effect of residual PGMs concentration on PGMs uptake by synthetic magnetite. NaCl concentration: 0.1 mol/dm<sup>3</sup>; pH: 3 for Rh and pH 6-7 for Pt and Pd; contact time: 24 h; Fe<sub>3</sub>O<sub>4</sub> amount: 0.1 g; temperature: 298 K.**

### 2.3.3 Effects of chloride concentrations

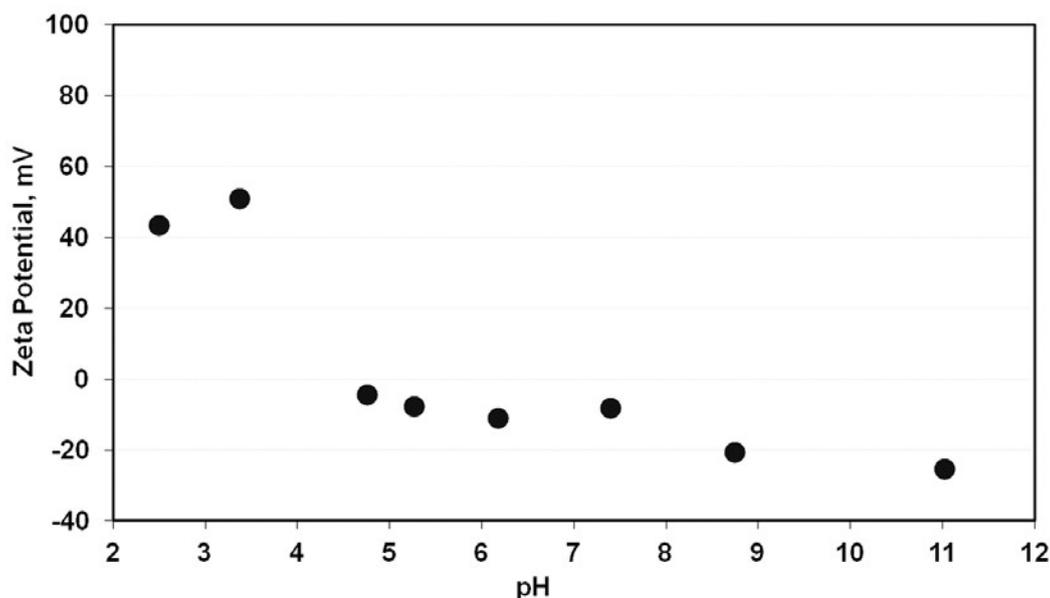
Figure 7 illustrates the effect of chloride concentration on the uptake of Pt, Rh and Pd by synthesized magnetite particles. As a source of chloride ions, NaCl was used and the concentration was varied from 0.01 to 1.0 mol/dm<sup>3</sup>. The Pt, Rh and Pd concentration, Fe<sub>3</sub>O<sub>4</sub> amount, contact time and pH were fixed at 0.05 mol/m<sup>3</sup>, 0.1 g, 24 h, and pH 3 for Rh, pH 6-7 for Pt and Pd, respectively. The increase in the NaCl concentration from 0.01-1.0 mol/dm<sup>3</sup> did not affect the Rh and Pt recovery, and more than 3.0 μmol Rh /g Fe<sub>3</sub>O<sub>4</sub> and 3.0 μmol Pt /g Fe<sub>3</sub>O<sub>4</sub> were recovered. On the other hand, the Pd uptake is markedly affected by the NaCl concentration; the uptake decreases with increasing the NaCl concentration.



**Figure 2-7. Effect of NaCl concentration on PGMs uptake by synthetic magnetite. Initial PGMs concentration: 0.05 mol/m<sup>3</sup>; pH: 3 for Rh and pH 6-7 for Pt and Pd; contact time: 24 h; Fe<sub>3</sub>O<sub>4</sub> amount: 0.1 g; temperature: 298 K.**

### 2.3.4 Zeta potential of magnetite

The zeta potential of solid surface is an important factor to determine the electrostatic adsorption of metal ions onto the surface. Figure 8 shows the zeta potentials of the magnetite in 0.1 mol/dm<sup>3</sup> NaCl solution at different pH values measured using a Zeta Potential Analyzer (Brookhaven Instruments Corporation, USA). Figure 8 shows that the surface charge of the magnetite is positive at pH < 4 and negative at pH > 5. From this figure, the iso-electric point of synthesized magnetite in 0.1 mol/dm<sup>3</sup> NaCl solution is evaluated as around 4.5.



**Figure 2-8. Zeta potential of the synthetic magnetite at 0.1 mol/dm<sup>3</sup> NaCl concentration.**

### 2.3.5 SEM-EDX analyses

The magnetite particles treated in 0.1 mol/dm<sup>3</sup> NaCl solutions containing 0.5 mol/m<sup>3</sup> Pt, Rh or Pd for 24 h at pH 6-7 were collected, washed with distilled water and dried in a vacuum oven for one day. The dried magnetite powders were examined under Scanning Electron Microscopy-Energy Dispersive X-ray Spectrometer (SEM-EDX) and Back Scattering Electron (BSE) analyses. The results of the spectrometric analyses are displayed in Figures 9 and 10 for synthesized magnetite treated in Rh and Pd solutions, respectively. The presence of rhodium and palladium on the surface of synthesized magnetite was detected by SEM-EDX and BSE as shown in the figures. Rhodium was observed as the glittering white part and palladium in a lighter grey part in the midst of synthesized magnetite particles in the BSE image. The elemental mapping and point analysis by EDX confirmed that the shiny component in Figure 9 was rhodium and the lighter component in Figure 10 was palladium. The EDX spectra identified the highest peak of Rh which was Rh-L $\alpha$  and Pd which was Pd-L $\alpha$ . SEM-EDX could not detect Pt from the synthesized magnetite containing Pt.

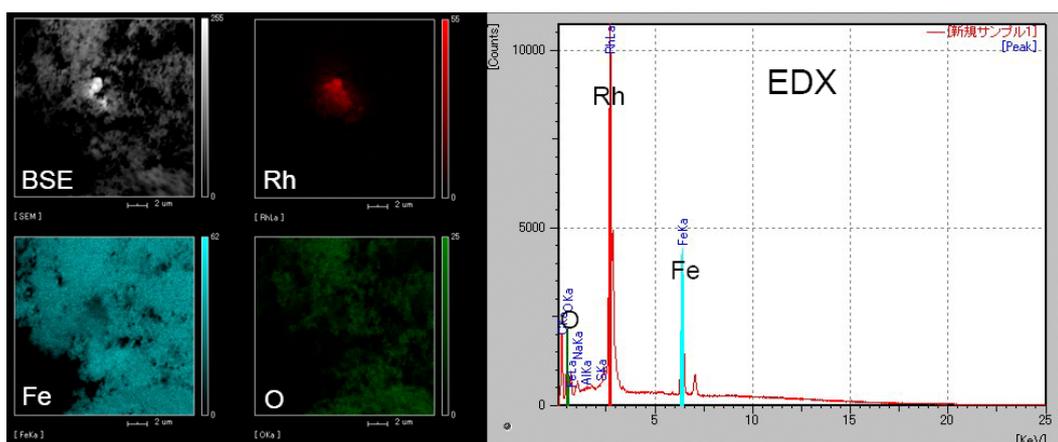


Figure 2-9. SEM-EDX and BSE image, mapping and spectra of magnetite containing Rh (magnification, 6000x).

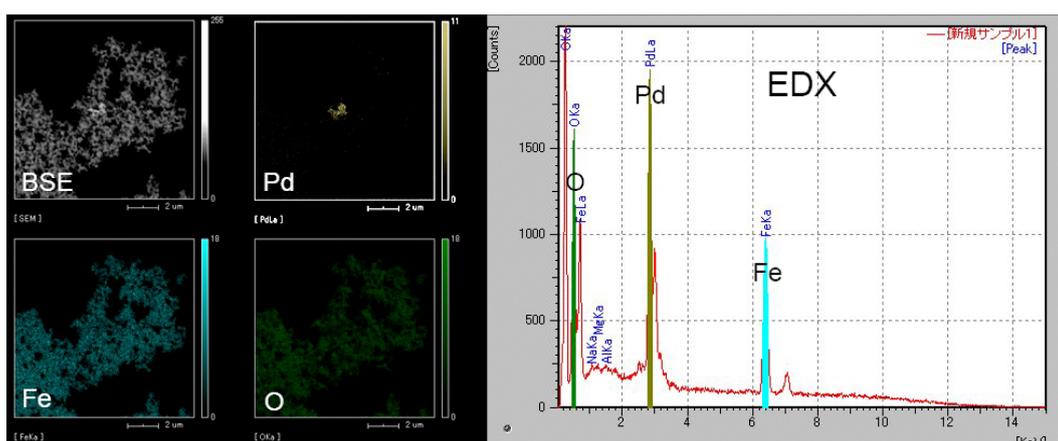
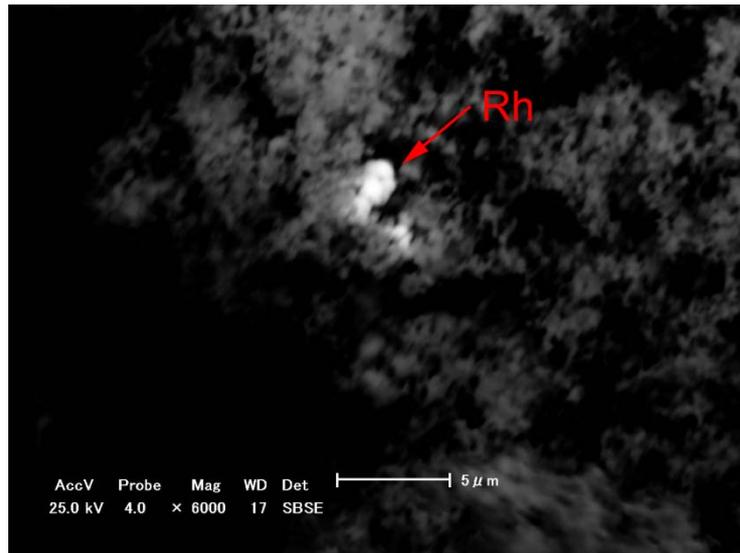
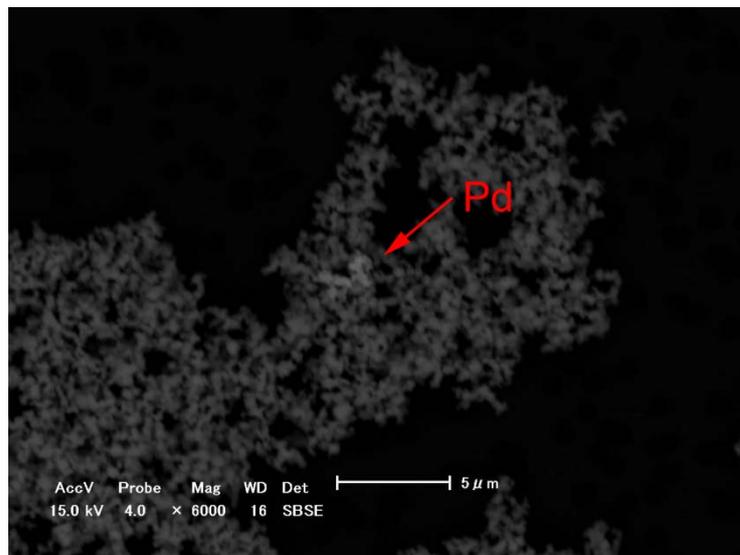


Figure 2-10. SEM-EDX and BSE image, mapping and spectra of magnetite containing Pd (magnification, 6000x).

Figures 11 and 12 show the high magnification BSE images for the magnetite samples treated in Rh and Pd solutions, respectively. Rh and Pd are present as the brighter section at the center of the images. The images indicated that Rh and Pd are not uniformly distributed on the surface of the magnetite.



**Figure 2-11. SEM SEM image of magnetite showing clusters of rhodium cements/precipitates (white part) on magnetite surface (magnification, x 6000).**



**Figure 2-12. SEM image of magnetite showing clusters of palladium cements/precipitates (lighter grey part) on magnetite surface (magnification, x 6000).**

## 2.4 DISCUSSION

The experimental results presented in the previous section are summarized as follows:

- 1) The PGMs uptake was strongly affected by pH: Pd and Rh uptake increases with increasing pH, and Pt uptake peaked at around pH 6.5.
- 2) The kinetics of PGMs uptake by magnetite is slow: over 24 h are required to reach steady state (Figure 2).
- 3) The PGMs uptake was not saturated in the PGMs concentration range between 0.01-0.5 mol/m<sup>3</sup> (Figure 3).
- 4) The Pt and Rh uptake was not affected by the NaCl concentration, while the Pd uptake decreased with increasing the NaCl concentration.

The simplest assumption to interpret the PGMs uptake by magnetite may be the electrostatic adsorption model. In this model, there are two adsorption scenarios: 1) positively charged metal ions are attracted to negatively-charged solid surface, and 2) negatively charged metal complexes (i.e., PtCl<sub>6</sub><sup>2-</sup>) are attracted to positively-charged solid surface. Because of this, speciations of PGMs in solution phase and the zeta potential of magnetite in chloride solution are important to discuss the PGM uptake based on the electrostatic adsorption model.

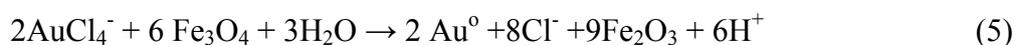
Colombo et al. (2008) studied the complexation of platinum, palladium and rhodium with inorganic ligands and discussed the PGM-Cl system. The authors reported that the concentration of the chloride ions determines which Pt, Pd or Rh species occurs and chloride complexes form when the chloride concentration is greater than 0.4 mol/m<sup>3</sup> for Pt-Cl system, 0.1 mol/m<sup>3</sup> for Pd-Cl system, and 4 mol/m<sup>3</sup> for Rh-Cl system. At high chloride concentrations (>100 mol/m<sup>3</sup>), the dominant Pt species are PtCl<sub>4</sub><sup>2-</sup> and PtCl<sub>6</sub><sup>2-</sup>, predominantly PdCl<sub>4</sub><sup>2-</sup> for Pd, and RhCl<sub>6</sub><sup>3-</sup>, RhCl<sub>5</sub>(H<sub>2</sub>O)<sup>2-</sup> or RhCl<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub><sup>-</sup> as the main species for Rh (Colombo et al., 2008). This speciation study confirmed the results of Levitin and Schmuckler (2003) and the review conducted by Benguerel et al. (1996) which suggested that PdCl<sub>4</sub><sup>2-</sup>, and Rh(H<sub>2</sub>O)Cl<sub>5</sub><sup>2-</sup> are the dominant species in the presence of 0.1 mol/dm<sup>3</sup> Cl<sup>-</sup> in acidic region, or at high chloride concentrations.

If we assume that the dominant PGMs species in chloride solution are anionic metal chloro-complexes as discussed above, such as PtCl<sub>6</sub><sup>2-</sup>, PdCl<sub>4</sub><sup>2-</sup> and Rh(H<sub>2</sub>O)Cl<sub>5</sub><sup>2-</sup>, a large

PGMs uptake would be observed in acidic region, because the zeta potential of magnetite is positive below pH 4.5 (Figure 8). This is inconsistent with the observed result: the Pt and Pd uptake was very small below pH 4.5, implying that the Pt and Pd uptake by magnetite is not due to the electrostatic adsorption. In the case of Rh, a significant amount of Rh was adsorbed at pH below 4.5, but the amount decreases with decreasing pH. This pH dependence of Rh adsorption on magnetite is difficult to interpret based on the electrostatic adsorption model, because zeta potential of magnetite becomes more positive when pH decreases. Considering the above, simple electrostatic adsorption model alone is not adequate to interpret PGM adsorption onto magnetite.

The slow kinetics observed in PGM uptake by magnetite also suggests that the uptake mechanism may not be due to electrostatic adsorption. Simple physical processes like electrostatic adsorption usually exhibit a fast reaction kinetics. The slow kinetics of PGM uptake implies that the uptake process involves chemical reactions.

The authors previously studied the mechanism of gold uptake by magnetite from chloride solutions based on the adsorption experiments, surface analysis and electrochemical experiments using magnetite electrode (Alorro et al., 2010a; Alorro et al., 2010b; Alorro et al., 2015). The presence of elemental gold, Au<sup>0</sup>, on magnetite surface was confirmed by electrochemical studies and the mechanism for Au uptake by magnetite was proposed. In the proposed model, magnetite supply electron and the gold chloride complex (AuCl<sub>4</sub><sup>-</sup>) is reduced on the surface of magnetite according to the combination of the reaction in Equations 1 and 2. The overall reaction can be represented by



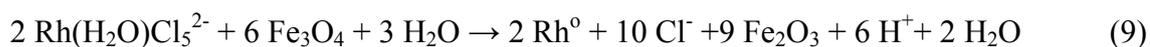
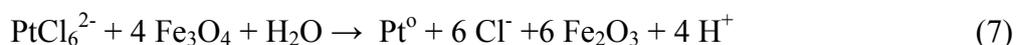
This model involves chemical reactions, and is in line with the observed slow uptake kinetics. The pH dependence of Au uptake is similar to that observed for Pt in the present study (Figure 5), i.e. the uptake was maximum at a certain pH and decreases in both acidic and alkaline region.

The authors reported that the small Au uptake in alkaline region is caused by the electrostatic repulsion between negatively charged magnetite surface and gold chloride complex (AuCl<sub>4</sub><sup>-</sup>): gold chloride complex cannot approach to the magnetite surface and

this suppresses the Au uptake in alkaline region. The small Au uptake in acidic region was confirmed to be due to the presence of  $\text{Fe}^{3+}$  dissolved from magnetite. The dissolved  $\text{Fe}^{3+}$  is an oxidizer and the following reaction competes with gold reduction in Equation 2 on the surface of magnetite:



The same interpretation may be applied for the pH dependence of the PGMs uptake observed in this study, if we assume the electrochemical model for PGMs uptake by magnetite, according to the following reactions:



In these reactions, the presence of  $\text{Cl}^-$  may cause the back-reaction to suppress the PGM uptake. This may interpret the effect of NaCl concentration on Pd uptake (Fig.7), but not for Pt and Rh. The effect of chloride concentrations on the adsorption of Pd (II) complexes has been reported by Wolowicz and Hubicki (2009) and they confirmed a similar trend, i.e., Pd adsorption efficiency decreases with increasing chloride concentration. The authors further discussed that the efficiency of adsorption is smaller at higher chloride concentrations than in the case of low concentrations ( $< 1.0 \text{ M}$ ). Further investigation is required in this regard to establish the relationship between Pt and Rh uptake and chloride concentration. In addition, there is still no evidence to confirm the presence of elemental PGMs on magnetite surface, which could indicate the reduction of the PGM complexes. Therefore, further study is needed to establish the mechanism of the PGMs uptake on magnetite.

## 2.5 CONCLUSION

The recovery of Pt, Rd, and Pd from chloride solutions on magnetite was studied. Batch sorption experiments were performed using synthesized magnetite at 298 K, and the

effects of different parameters, such as pH, contact time, the NaCl concentration and the PGMs concentrations were investigated. The uptake amounts of Pt, Pd, and Rh increased with time and reached a constant value over 24 h. This slow sorption kinetics indicates that the uptake is not due to a simple physical adsorption, and involves chemical reactions. The uptake amounts of Pt, Pd, and Rh were strongly affected by pH. The SEM-EDX and BSE analyses confirmed the presence of rhodium and palladium concentrated on some areas of the magnetite surface. These results indicate that  $\text{Fe}_3\text{O}_4$  can uptake platinum group metals and can be used as a potential selective sorbent to recover the metals from chloride solution or chloride leach liquors.

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## Chapter 3

### RECOVERY OF PLATINUM GROUP METALS FROM CHLORIDE SOLUTION USING MAGNETITE FROM COPPER CONVERTING SLAG

#### 3.1 INTRODUCTION

In Chapter 2, the utilization of magnetite as an adsorbent for the recovery of platinum group metals (PGMs) from chloride solution was presented. Adsorption experiments using synthetic and natural magnetite powders confirmed that magnetite can uptake PGMs from chloride solution. Results of the investigations revealed the great potential of  $\text{Fe}_3\text{O}_4$  as a selective adsorbent to recover PGMs from chloride solution.

Another potential source of magnetite that can be used for a similar purpose as described above is the converting slag generated during the pyrometallurgical processing of copper sulfide minerals. Converting (Figure 3-1) is the final stage in the smelting process of copper sulfide ores or concentrates and it generates a relatively pure copper metal product (blister copper) and a slag containing oxidized components mostly Fe and S.

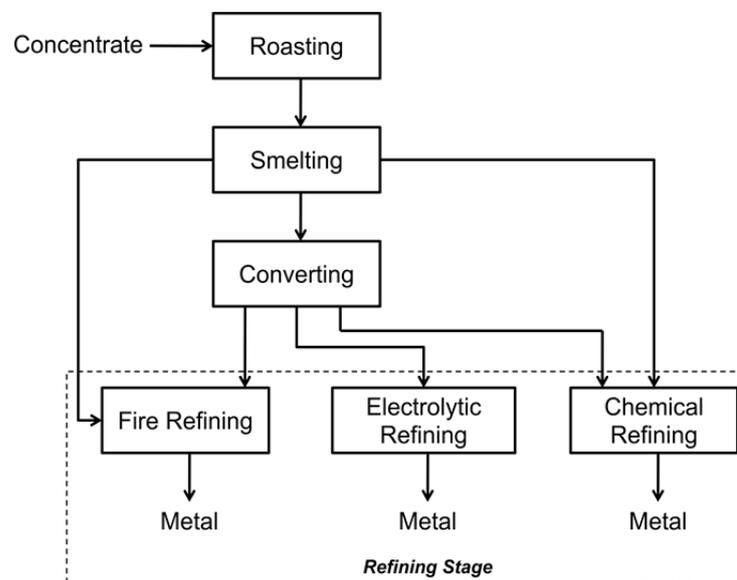
A typical converting process produces around 400 tons/day of converter slag (USEPA, 1993). Converting slag usually contains 4-8% Cu, 20-25%  $\text{Fe}_3\text{O}_4$  and 15-30%  $\text{SiO}_2$  (Table 3-1). The converting slag containing some amounts of copper and magnetite are usually returned, while still liquid, to smelting furnace to recover copper (Gill, 1980). However, the recycling of converting slag to smelting furnace may generate some problem due to the tendency of  $\text{Fe}_3\text{O}_4$  in the slag to settle down at the bottom of the furnace and if not checked, the build-up may cause the shutdown of the furnace due to the limited space for proper fuel combustion, and less available room for matte-slag layer formation and separation. Owing to this difficulty, an alternative method was considered. Instead of returning the converter slag to the smelting furnace, the slag can be cooled, crushed, ground and then the copper content can be recovered by froth flotation (Gill, 1980). The tailings which contain mostly  $\text{Fe}_3\text{O}_4$  and  $\text{SiO}_2$  are usually discarded.

**Table 3-1. Representative analysis of converter slag, mass% (Davenport et al, 2002).**

Cu	Total Fe	SiO <sub>2</sub>	Fe <sub>3</sub> O <sub>4</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO	ZnO
4-8	35-50	15-30	20-25	0-5	0-5	0-1	0-5

As mentioned above, copper converting slag contains appreciable amounts of magnetite which usually ends up in dump sites or disposal areas after recovering the copper values. The Fe<sub>3</sub>O<sub>4</sub> can be separated by crushing or grinding the converter slag and can then be concentrated using magnetic separation. The concentrated Fe<sub>3</sub>O<sub>4</sub> can be used as an adsorbent to recover PGMs from aqueous solution.

This chapter investigated the use of magnetite recovered from a converting slag of a copper smelting company for the recovery of PGMs from chloride solution. The converting slag magnetite provided by the company was characterized and was evaluated as a candidate carrier (adsorbent) for PGMs in batch sorption experiments. The effects of different parameters, such as pH, contact time, PGMs concentration, and chloride concentration, on the uptake of PGMs from chloride solution were studied.



**Figure 3-1. Principal processes of extracting metals from sulfide ores by pyrometallurgical technique (Gill, 1980).**

## 3.2 MATERIALS AND METHODOLOGY

### 3.2.1 Materials

The slag magnetite sample used in the experiments was provided by a copper smelting company in Japan. It was prepared by magnetic separation after crushing and grinding the converting slag. The chemical composition of the slag magnetite was determined using an X-ray Fluorescence Spectrometer (JEOL Element Analyzer, JSX-3201A, Japan) and is shown in Table 3-2. The slag magnetite used has a purity of 71.0 % and the major impurities include Si, Cu and Mg. Heavy metals, such as Zn and Pb, were also detected. The surface area of the sample determined by N<sub>2</sub>-BET method using a Nova 2200e Surface Area and Pore Size Analyzer (Yuasa Ionics, Japan) was 2.2 m<sup>2</sup>/g.

**Table 3-2. Composition (mole %) of copper converter slag magnetite as determined by X-ray Fluorescence Spectrometer (XRF).**

Components	Mole %							
	Fe <sub>3</sub> O <sub>4</sub>	SiO <sub>2</sub>	CuO	MgO	ZnO	SO <sub>3</sub>	CaO	PbO
Copper converter slag Magnetite	71.0	15.8	5.7	2.6	1.7	1.5	0.9	0.7

Reagent grade platinum (H<sub>2</sub>PtCl<sub>6</sub> in 1 mol/dm<sup>3</sup> HCl), palladium (PdCl<sub>2</sub> in 1 mol/dm<sup>3</sup> HCl), and rhodium (Rh(NO<sub>3</sub>)<sub>3</sub> in 2 mol/dm<sup>3</sup> HNO<sub>3</sub>) standard solutions (Wako Chemicals, Japan) were used to prepare PGM solutions. The other chemicals used in this study such as sodium chloride (NaCl), hydrochloric acid (HCl), and sodium hydroxide (NaOH) were all of reagent grades.

### 3.2.2 Methodology

Batch sorption experiments were performed to demonstrate the ability of Fe<sub>3</sub>O<sub>4</sub> to recover Pt, Pd, and Rh from chloride solutions. The experiments were carried out by adding 0.1 gram of Fe<sub>3</sub>O<sub>4</sub> powder into a 50 cm<sup>3</sup> Erlenmeyer flask containing 10 cm<sup>3</sup> of NaCl solution (0.01 - 1.0 mol/dm<sup>3</sup>) with varied concentrations of H<sub>2</sub>PtCl<sub>6</sub>, PdCl<sub>2</sub>, and

$\text{Rh}(\text{NO}_3)_3$ . The pH of the solution was adjusted by HCl or NaOH. The mixture was shaken for 0.5 - 72 h in a water bath shaker (ML-10F, Taitec, Japan) at 120 strokes per minute and 298 K. After shaking, the mixture was centrifuged and filtered using a nitro-cellulose membrane filter (pore size; 0.20  $\mu\text{m}$ ). The PGMs content and the iron concentration in the filtrate were determined using Inductively Coupled Plasma-Atomic Emission Spectrometer (SPS 7800, Seiko Instruments, Japan). The magnetite particles after the treatment were examined using the Scanning Electron Microscope (SEM) equipped with an Electron Dispersive X-ray Spectrometer (EDX) (SSX-550, Shimadzu, Japan) to check the presence of PGMs on the surface of the particles.

The PGMs uptake was calculated according to the mass balance in Equation 3-1:

$$\text{PGMs uptake } [\mu\text{mol/g}] = (C_i - C_f) \times V/W \quad (3-1)$$

where  $C_i$  is the initial metal concentration,  $C_f$  is the remaining metal concentration in the aqueous phase,  $V$  is the volume of the aqueous solution, and  $W$  is the weight of the magnetite.

### 3.3 RESULTS AND DISCUSSION

#### 3.3.1 Characterization of slag magnetite

Figure 3-2 shows the X-ray Diffraction (XRD) pattern for the slag magnetite. The magnetite peaks were easily identified. XRD did not detect the presence of copper or any copper compound in slag magnetite. Considering that about 5.7 mole% of Cu is present in the slag, this result seems unusual. A probable reason for this observation is the use of copper as a target metal to generate Cu-K $\alpha$  radiation. The target metal is essential as it determines the elements present in the sample based on the unique wavelengths produced by each element. Another possibility is the sensitivity of XRD to scan components from an amorphous material, like slag. The other metal components such as Zn and Pb were also not detected.

The SEM-EDX maps, Back Scattering Electron (BSE) image and EDX spectrum of the slag magnetite are presented in Figure 3-3 and Figure 3-4. In the BSE image, the

dark gray and shiny bright areas in the sample suggest that the slag magnetite is a composite material. A comparison of BSE image and SEM-EDX maps indicate that Fe is present in the dark gray areas, and Cu and S in the shiny bright areas of the image. This implies that the dark gray areas correspond to magnetite and the shiny bright areas to copper sulfides or matte (CuS and/or Cu<sub>2</sub>S), a major product of copper converting process. Optical microscope observations also confirmed the inclusions of metallic copper in the matrix of slag magnetite.

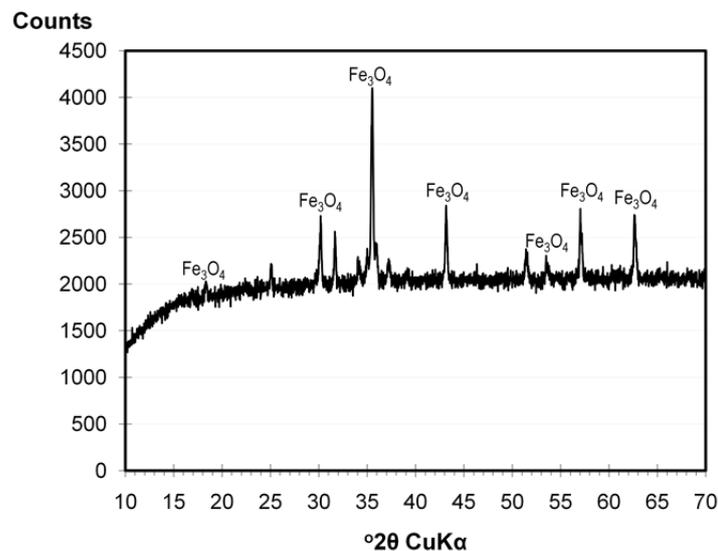


Figure 3-2. X-Ray Diffraction pattern of the magnetite from copper converter slag.

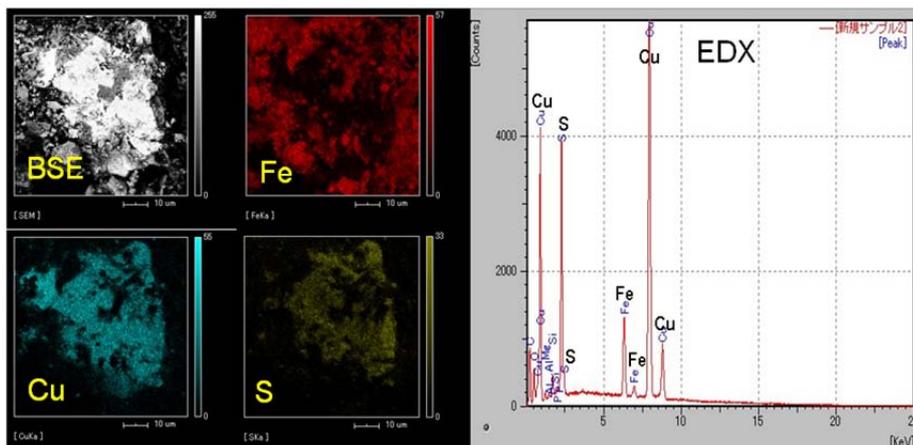
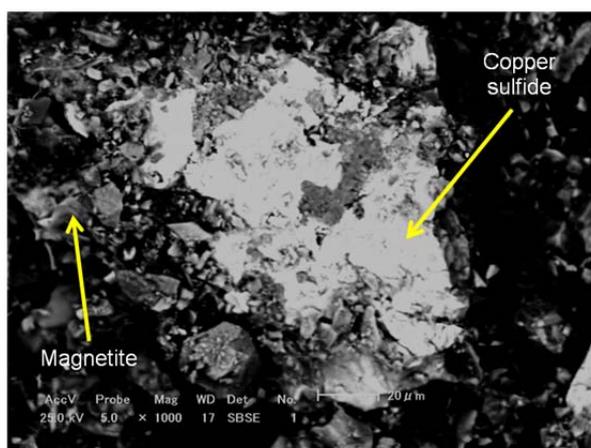


Figure 3-3. Scanning Electron Microscope-Energy Dispersive X-ray (SEM-EDX) and Back Scattering Electron (BSE) image, maps, and spectra of the copper converter slag magnetite.

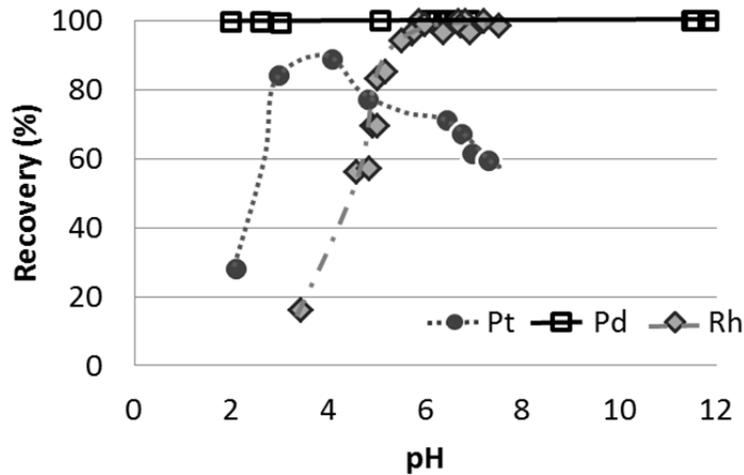


**Figure 3-4. Back Scattering Electron (BSE) image of a copper sulfide component (white part) present in the copper converter slag magnetite.**

### 3.3.2 Effects of pH

Preliminary or control experiments were carried out without the addition of magnetite to check the pH ranges where PGMs start to precipitate out of the solution. The base solutions used for control were  $0.1 \text{ kmol/m}^3$  NaCl solution containing  $0.05 \text{ mol/m}^3$  Pt, Pd or Rh. It was confirmed that no precipitation occurred for Pt at pH 1-12, while Rh and Pd precipitated at pH greater than 4.0 and 6.5, respectively. Considering these results, the PGM adsorption experiments using magnetite were designed at pH 1-12 for Pt, pH 2-6.5 for Pd, and pH 2-4 for Rh.

The effect of pH on PGM recovery by slag magnetite was investigated using  $0.1 \text{ kmol/m}^3$  NaCl solution containing  $0.05 \text{ mol/m}^3$  Pt, Pd or Rh and 3 h contact time. The results are shown in Figure 3-5. The Pt recovery increased with increasing pH, reached a maximum (about 90%) at pH 4, and then decreased with increasing pH values. The Pd uptake was more than 99% over a wide pH range (pH 2 to 12). The recovery of Rh increased with increasing pH and more than 95% was achieved over pH 6.

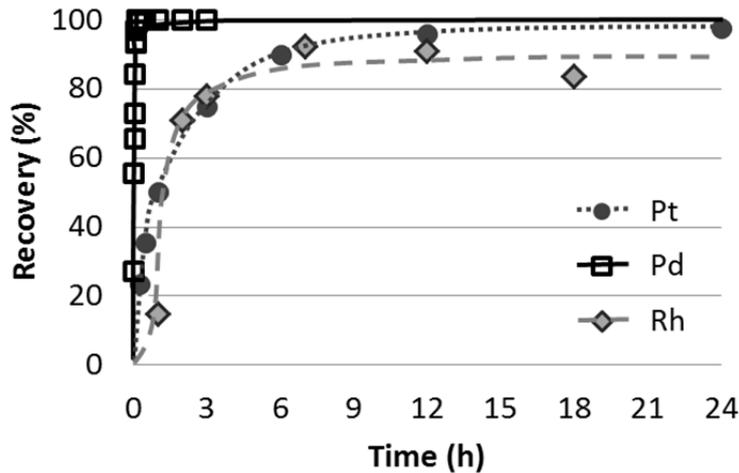


**Figure 3-5. Effect of solution pH on PGMs recovery. Initial PGMs concentration: 0.05 mol/m<sup>3</sup>; pH: 3 for Rh and pH 6-7 for Pt and Pd; NaCl concentration: 0.1 mol/dm<sup>3</sup>; Fe<sub>3</sub>O<sub>4</sub> amount: 0.1 g; temperature: 298 K.**

### 3.3.3 Effect of contact time

The effect of contact time on the recovery of Pt, Pd and Rh was investigated. The solutions used in the experiments were 0.1 kmol/m<sup>3</sup> NaCl containing 0.05 mol/m<sup>3</sup> PGMs. The initial pH of Pt, Pd, and Rh solutions were adjusted to 6.0, 2.2, and 2.5, respectively. The results are shown in Figure 3-6.

High recoveries were obtained for Pt, Pd and Rh. The results showed that the kinetics of Pd uptake was fast, reaching 99% at 8 minutes. In the case of Pt and Rh, 99% and 92% recovery values were achieved at 48 hours and 7 hours, respectively. These results present the superior performance of slag magnetite as an adsorbent as compared to the synthetic magnetite powder reported in Chapter 2. Higher PGM recoveries were obtained for slag magnetite even at shorter contact time. In the case of synthetic magnetite described previously, only less than 70% of PGMs were recovered from aqueous solution.

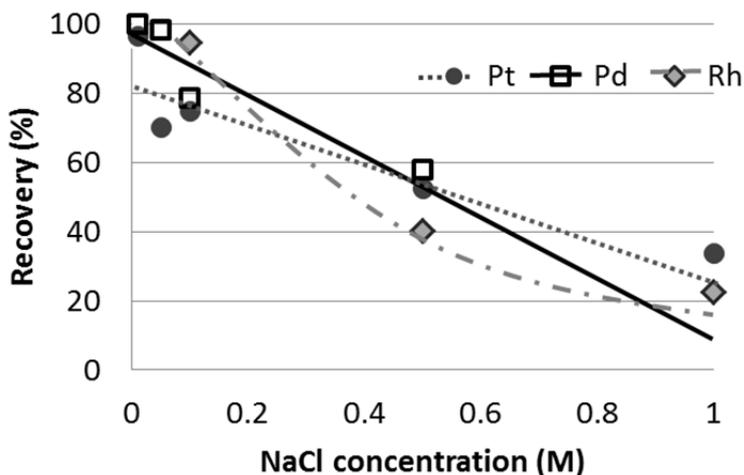


**Figure 3-6. Effect of contact time on PGM recovery by slag magnetite. NaCl concentration: 0.1 mol/dm<sup>3</sup>; pH: 3 for Rh and pH 6-7 for Pt and Pd; contact time: 24 h; Fe<sub>3</sub>O<sub>4</sub> amount: 0.1 g; temperature: 298 K.**

### 3.3.4 Effect of chloride concentration

The effect of chloride concentration on the uptake of Pt, Rh and Pd by slag magnetite was studied by varying NaCl concentration from 0.05 to 1.0 mol/dm<sup>3</sup>. The initial pH and contact time were 6.0 and 3 h for Pt, 2.2 and 0.05 h for Pd, and 2.5 and 3 h for Rh, respectively. Figure 3-7 illustrates the results. The PGMs recovery by slag magnetite increased with decreasing chloride concentration. From over 95% recovery at 0.05 mol/dm<sup>3</sup>, the values decreased to less than 40% when NaCl was 1.0 mol/dm<sup>3</sup>.

The results presented above signify that high chloride concentrations are unfavorable to Pt, Rh, and Pd uptakes by slag magnetite. Excess amount of chloride ions may affect the surface property of the slag magnetite by altering the surface charge and subsequently affect the diffusion and adsorption of gold chloride ions.

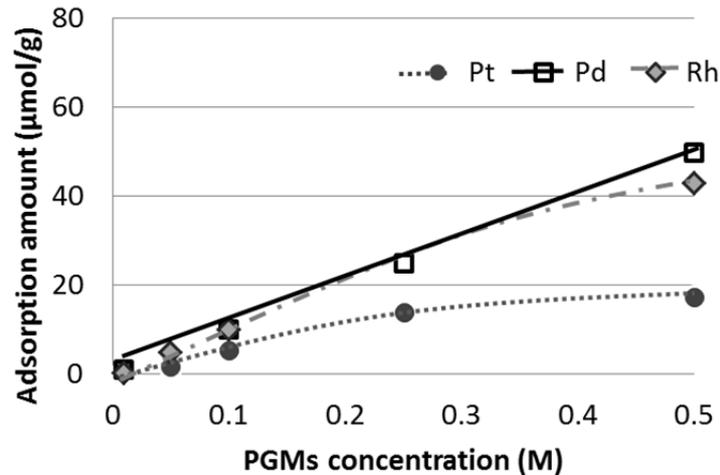


**Figure 3-7. Effect of NaCl concentration on PGMs uptake by slag magnetite. Initial PGMs concentration:  $0.05 \text{ mol/m}^3$ ; pH: 3 for Rh and pH 6-7 for Pt and Pd; contact time: 24 h;  $\text{Fe}_3\text{O}_4$  amount: 0.1 g; temperature: 298 K.**

### 3.3.5 Effect of PGM concentration

The effect of Pt, Rh and Pd concentrations on adsorption was examined by varying the initial PGM concentrations from  $0.01$  to  $0.50 \text{ mol/m}^3$  in the presence of  $0.1 \text{ mol/dm}^3$  NaCl. The initial pH and contact time were 6.0 and 3 h for Pt, 2.2 and 0.05 h for Pd, and 2.5 and 3 h for Rh, respectively.

Figure 3-8 shows the relation between the PGM uptake for 1.0g of slag magnetite and the initial PGM concentrations for Pt, Pd and Rh. The PGM uptake increased with increasing initial PGM concentrations. At the initial PGM concentration of  $0.5 \text{ mol/m}^3$ ,  $17.4 \text{ }\mu\text{mol/g}$  Pt,  $49.6 \text{ }\mu\text{mol/g}$  Pd, and  $43.0 \text{ }\mu\text{mol/g}$  Rh were recovered by slag magnetite. The graph also indicates that the maximum amounts adsorbed for Pt, Rh and Pd have not been achieved yet and further increase seems possible with increasing PGM concentrations. PGM concentrations over 0.5M were not investigated in this study.

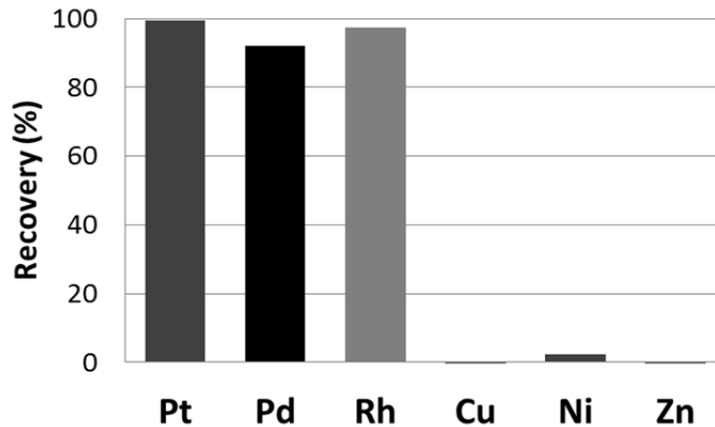


**Figure 3-8. Effect of PGMs concentration on PGMs recovery. Initial PGMs concentration: 0.05 mol/m<sup>3</sup>; contact time: 24 h; NaCl concentration: 0.1 mol/dm<sup>3</sup>; Fe<sub>3</sub>O<sub>4</sub> amount: 0.1 g; temperature: 298 K.**

### 3.3.6 Sorption of different metal ions on slag magnetite

Adsorption experiments involving Pt, Pd, Rh, Cu, Ni and Zn were conducted to evaluate the selectivity of the slag magnetite towards PGM ions. Solutions of 0.01 mol/dm<sup>3</sup> NaCl solution containing 0.05 mol/m<sup>3</sup> of the metal ions were used. The contact time and initial pH of the solution were fixed at 24 h and 3.3, respectively. The results as shown in Figure 3-9 revealed that the slag magnetite can recover over 90% of Pt, Pd, and Rh and negligible amounts (less than 5%) of base metal ions (Cu, Ni, Zn). This indicates that slag magnetite can be used to recover PGMs selectively from the solution containing both PGMs and common base metals like Cu, Ni, and Zn.

This study demonstrated that slag magnetite can uptake PGMs and can be used as a potential selective sorbent to recover PGMs from chloride solution or chloride leach liquors. Since magnetite is a magnetic material, the problem of phase separation associated with conventional separation techniques can be resolved.



**Figure 3-9. Selective recovery of PGMs by slag magnetite.**

### 3.4 CONCLUSION

The recovery of PGMs from chloride solution on slag magnetite was studied under different conditions. Characterization studies conducted on the slag magnetite revealed that it is a composite material with some amounts of metallic copper and copper sulfides (matte). Single-component batch sorption experiments confirmed that PGMs were recovered by slag magnetite. Higher recoveries at shorter contact time were observed with slag magnetite. It was found that the slag magnetite is a more superior adsorbent than the synthetic magnetite in terms of loading capacity and kinetics. It was also found that slag magnetite can recover Pt, Pd, and Rh selectively from the solution containing a mixture of PGM ions and base metal ions, such as Cu, Ni, and Zn. The presence of copper impurities in the slag magnetite matrix may have contributed significantly to the observed results.

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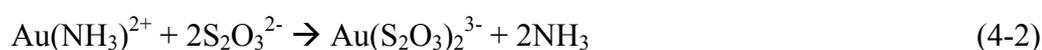
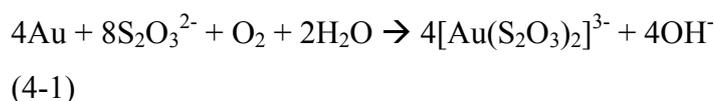
## Chapter 4

### GOLD RECOVERY FROM AMMONIUM THIOSULFATE SOLUTION USING MAGNETITE FROM COPPER CONVERTER SLAG

#### 4.1 INTRODUCTION

Thiosulfate can be considered as a promising alternative to cyanide to leach gold from primary and secondary sources. A study on thiosulfate leaching for gold hydrometallurgy by Abbruzzese et al. (1995) and the review articles published by Aylmore and Muir (2001), and Grosse et al. (2003) reported several advantages of thiosulfate process over cyanide. Among the cited advantages are: (1) non-toxicity, (2) faster gold dissolution rates compared to conventional cyanidation, (3) less sensitivity in the presence of metal ion impurities, (4) high gold recoveries obtained in the leaching of refractory and complex ores, and (5) can be cheaper than cyanide.

Gold leaching by thiosulfate solutions is an electrochemical-catalytic process and has evolved throughout the years. Significant improvement in the rate of dissolution of gold was achieved by the addition of ammonia and copper ion in the leaching system. Ammonia prevents the formation of a sulfur passivation layer, generated by the breakdown of thiosulfate to sulfur, on gold particles. Copper ion ( $\text{Cu}^{2+}$ ) serves as an oxidant and enhances the kinetics of gold dissolution (Aylmore and Muir, 2001). Proper control of appropriate concentrations of ammonia and thiosulfate solution with copper ions can result to efficient gold leaching from a range of gold ores (Aylmore and Muir, 2011; Grosse et al., 2003). Effective leaching is achieved by maintaining the appropriate concentrations of ammonia and thiosulfate in solution with copper ions. The different components in the ammoniacal thiosulfate leaching of gold can be represented by the following reactions:

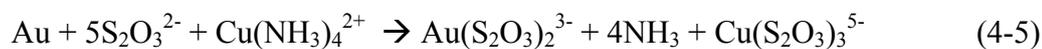




(4-3)



(4-4)



(4-6)

Whilst numerous studies and proposed applications of ammoniacal thiosulfate leaching systems are available in literature (Aylmore and Muir, 2001; Abbruzzese et al., 1995; Grosse et al., 2003; Ha et al., 2014; Feng and Deventer, 2006; Feng and Deventer, 2010; Feng and Deventer, 2011), the process has not been widely used on a commercial scale. The primary reasons include high consumption of reagents and the lack of a cheap and reliable technique for recovering gold from thiosulfate liquors (Aylmore and Muir, 2001).

Several methods have been studied and proposed to recover gold from ammoniacal thiosulfate leach liquors but none has justified commercial application so far. Techniques applied in the conventional cyanide leach liquors, such as precipitation, carbon adsorption, electrowinning, solvent extraction and ion-exchange resin, have been attempted but most of them suffered from poor efficiency due to chemical affinity to gold thiosulfate complexes, selectivity, operational and economic issues (Aylmore and Muir, 2001; Grosse et al., 2003). Among these methods, adsorption offers a number of advantages including ease of operation, low energy consumption, and large capacity (Lam et al., 2007; Aktas et al., 2009). However, the real challenge lies on finding a selective, efficient and cheap adsorbent. This presents an area of research importance.

In this chapter, a study on gold uptake from thiosulfate solution by the magnetic fraction of copper converter slag (slag magnetite) is presented. Investigations on the effects of various process parameters, such as pH, contact time, solid/liquid ratio, thiosulphate concentration, gold concentration, and oxic and anoxic environment are discussed.

## 4.2 MATERIALS AND METHODOLOGY

The slag magnetite sample used in this study was obtained from a copper smelting plant in Japan. Slag magnetite was produced by magnetic separation of crushed and ground converter slag. The slag magnetite sample was characterized using X-Ray Fluorescence Spectroscopy (XRF; JEOL Element Analyzer, JSX-3201A, Japan), Scanning Electron Microscopy–Energy Dispersive X-ray (SEM–EDX; SSX-550 Shimadzu, Japan), Nova 2200e Surface Area and Pore Size Analyzer (Yuasa Ionics, Japan), and Microtrac Size Analyzer (MT3300SX, USA) to determine the chemical composition, surface area, and particle size.

The ammonium thiosulfate solution containing gold was prepared with ion-exchange/distilled water and reagent grade chemicals consisting of 0.05mM  $\text{Na}_3\text{Au}(\text{S}_2\text{O}_3)_2$ , 0.1M  $\text{NH}_3$ , 0.05M  $(\text{NH}_4)_2\text{SO}_4$ , and 0.1M  $\text{Na}_2\text{S}_2\text{O}_3$ . Reagent grade  $\text{CuSO}_4$  was used as the source of copper ions and the concentrations were varied during the experiment. Reagent grade gold standard solution ( $\text{HAuCl}_4$  in 1 kmol/m<sup>3</sup> HCl, Wako Chemicals, Japan) was used as the source of gold ions.

Batch sorption experiments were performed to demonstrate the ability of slag magnetite to recover gold from ammonium thiosulfate solutions. The experiments were carried out by adding 0.1 gram of slag magnetite powder into a 50 cm<sup>3</sup> Erlenmeyer flask containing 10 cm<sup>3</sup> of 0.05 M ammonium thiosulfate solution purged with nitrogen gas (0.04 MPa) for 15 minutes and  $\text{Na}_3\text{Au}(\text{S}_2\text{O}_3)_2$ . After adding the slag magnetite, nitrogen purging for another 5 minutes was applied. The pH of the solution was adjusted by changing the ratio of  $\text{NH}_3$  and  $\text{NH}_4$ . The mixture was shaken for 0.5 - 48 h in a water bath shaker (ML-10F, Taitec, Japan) at 120 strokes per minute and 298 K. After shaking, the mixture was centrifuged and filtered using a nitro-cellulose membrane filter (pore size; 0.20  $\mu\text{m}$ ). The gold content in the filtrate was determined using an Inductively Coupled Plasma-Atomic Emission Spectrometer (SPS 7800, Seiko Instruments, Japan). The slag magnetite particles after the treatment were examined using the Scanning Electron Microscope (SEM) equipped with an Electron Dispersive X-ray Spectrometer (EDX) (SSX-550, Shimadzu, Japan) to check the presence of gold on the surface.

Gold uptake and recovery were calculated using to the following mass balance equations:

$$\text{Gold recovery, \%} = (C_i - C_f) / C_i \times 100 \quad \text{Equation (4-7)}$$

where  $C_i$  is the initial gold concentration,  $C_f$  is the remaining gold concentration in aqueous phase.

$$\text{Gold uptake } [\mu\text{mol/g}] = (C_i - C_f) \times V/W \quad \text{Equation (4-8)}$$

where  $C_i$  is the initial metal concentration,  $C_f$  is the remaining gold concentration in the aqueous phase,  $V$  is the volume of the aqueous solution, and  $W$  is the weight of the slag magnetite.

## 4.3 RESULTS AND DISCUSSION

### 4.3.1 Adsorption studies

Gold recovery experiments were performed to demonstrate the ability of slag magnetite to recover gold from ammonium thiosulfate solutions. The effect of pH on gold uptake was studied. The solution pH was adjusted by changing the ratio of  $\text{NH}_3$  and  $\text{NH}_4$ . Contact time was fixed at 24 h. The results are presented in Figure 4-1. High gold recovery was achieved in the alkaline pH range (pH 7 – 10). More than 93% of gold was recovered at this pH range.

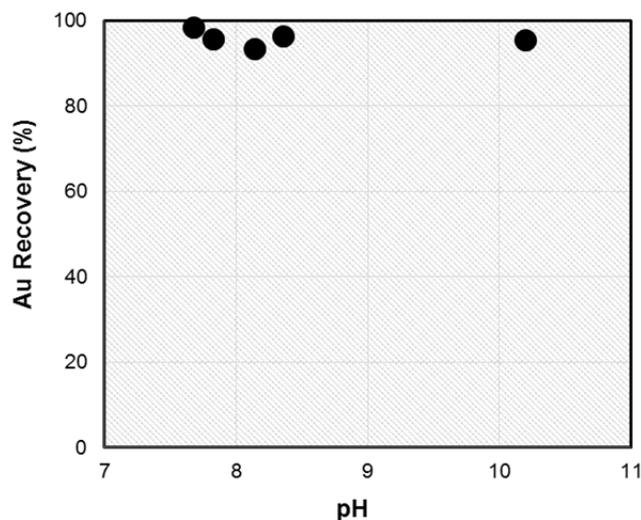


Figure 4-1. Effect of solution pH on Au recovery

The performance of the slag magnetite to recover gold from thiosulfate solution was compared to that of synthetic magnetite. The amount of magnetite added was varied from 0.1-0.3 g and contact time was fixed at 24 h. The results are presented in Figure 4-2. Slag magnetite recovered over 93% of gold from thiosulfate solution even with just 0.1 g addition. Increasing the slag magnetite amount did not affect significantly the gold recovery. The synthetic magnetite, on the other hand, did not recover gold from solution even at higher magnetite amounts.

The major difference between the two magnetites described above is the presence of metallic Cu and copper sulfides. Characterization studies conducted on the slag magnetite as discussed in Chapter 3 revealed that it is a composite material with some amounts of copper matte. The synthetic magnetite used was a reagent grade sample with minimal amount of impurities. The occurrence of copper impurities in slag magnetite may have contributed significantly to high gold recovery. The SEM-EDX maps, BSE image and EDX spectrum (Figure 4-3) of the slag magnetite from the experiment involving a solution containing 0.5 mM  $\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$  supported this premise. Gold was detected on the surface of slag magnetite and the EDX spectra strongly suggest that Au and Cu were present in same areas.

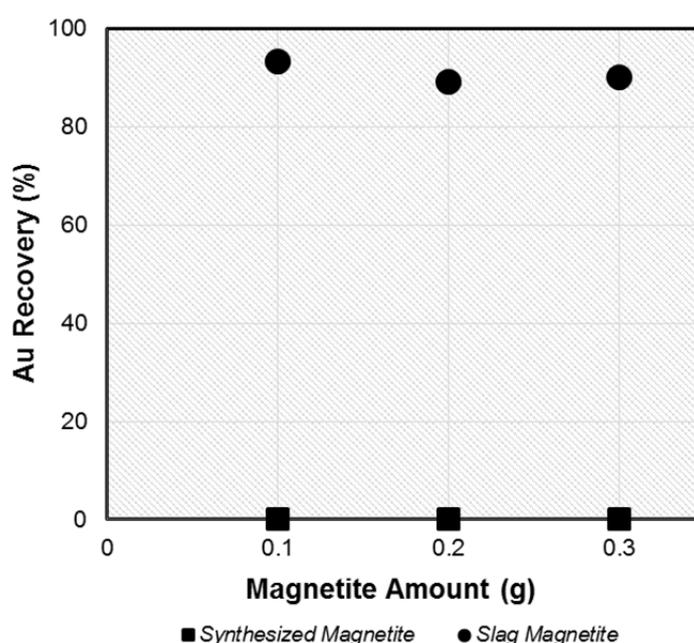
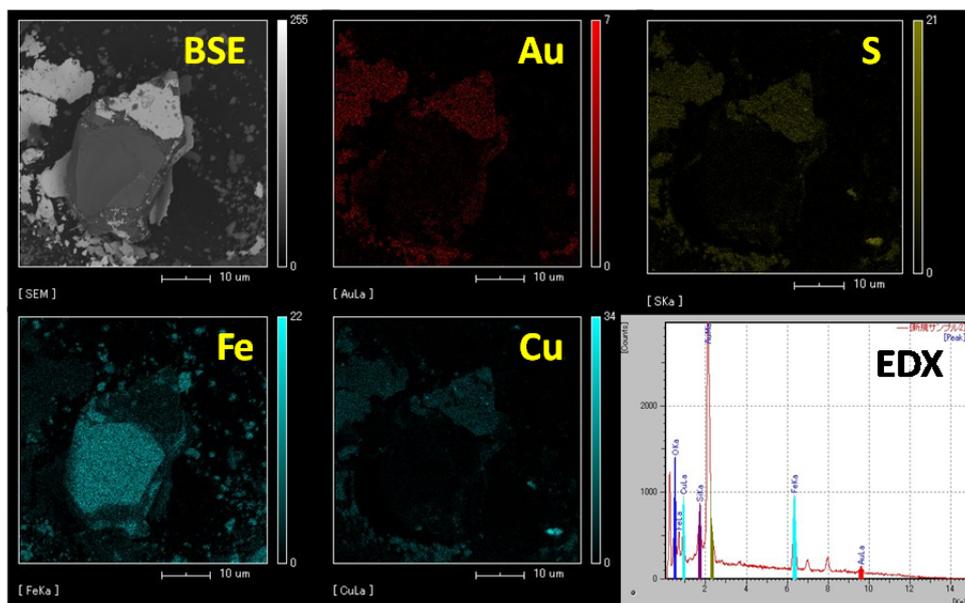
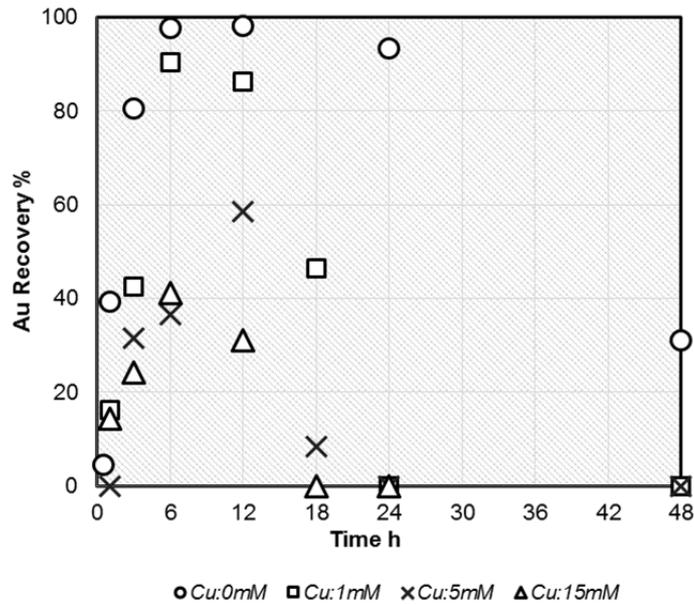


Figure 4-2. Effect of magnetite type on Au recovery



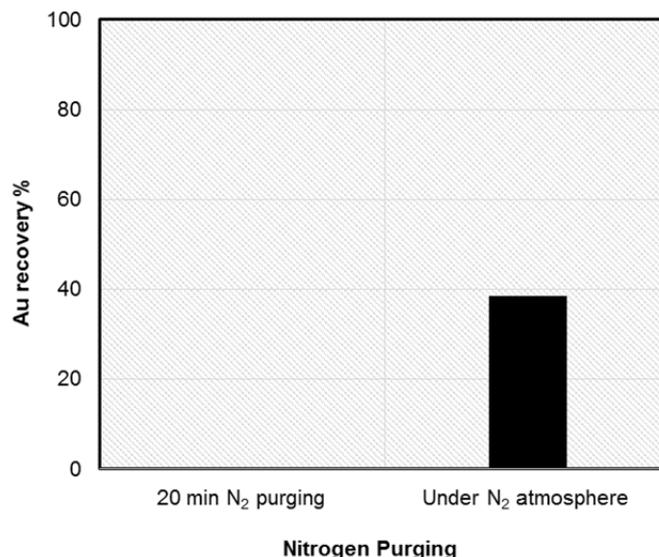
**Figure 4-3. SEM-EDX and BSE micrograph, mapping and spectra of the converter slag magnetite containing Au**

The effects of  $\text{CuSO}_4$  concentration and contact time on the recovery of gold using slag magnetite were studied. Copper is almost always present in real leach solutions since it is used as a catalyst for gold dissolution in thiosulfate leaching. The interactions between gold, copper and slag magnetite were studied by adding varied amounts of  $\text{CuSO}_4$  (0 mM, 1 mM, 5 mM, 15 mM). The results are presented in Figure 4-4. The results also suggest that the maximum gold recovery decreased with increasing concentration of  $\text{CuSO}_4$  added in the solution. Zhang and Dreisinger (2004) reported that copper is co-loaded with gold in ion exchange resins suggesting its significant role in gold recovery from thiosulfate solutions. In the case of slag magnetite, cupric ion can compete with gold ion as electron acceptor on the surface of magnetite. This can possibly explain the decrease in gold recovery with increasing  $\text{CuSO}_4$  concentration.



**Figure 4-4. Effect of contact time on Au recovery**

The results presented in Figure 4-4 also show that initially, gold recovery increased with increasing time, reached a maximum value and then started to decrease. It was assumed that the decrease in gold recovery on slag magnetite at longer contact period was due to the re-dissolution of adsorbed gold back into the solution due to oxygen contamination in the flask (Equation 4-1). To confirm this hypothesis, an experiment was carried out with 15 mM  $\text{CuSO}_4$  under  $\text{N}_2$  atmosphere. As shown in Figure 4-5, when the adsorption experiment was carried out in nitrogen environment (flask was placed in a  $\text{N}_2$  bag), 40% of gold was recovered after 24 h. No gold was recovered for the same experiment done at atmospheric condition. This result confirms that an aerobic environment causes a decrease in gold recovery.



**Figure 4-5. Effect of oxygen contamination on Au recovery**

The above results indicate that the presence of oxidants such as oxygen and cupric ion suppresses gold recovery by slag magnetite. In order to minimize the effect of the oxidants and subsequently increase gold recovery, increasing the amount of slag magnetite (electron donor) and adding a reductant which would consume the contaminant oxygen in the solution are deemed highly beneficial to the process. Experiments were conducted to confirm these propositions.

Figure 4-6 shows the effect of the amount of slag magnetite on gold recovery in the presence of 1mM CuSO<sub>4</sub> at 24h. There was no gold recovered when 0.1 g of slag magnetite was added but when the amount was doubled (0.2 g), gold recovery increased to more than 90%. The increase in slag magnetite amount provides more accessible active sites for gold adsorption and more electrons available for gold reduction. This balances off the hindering effect of copper ions on gold recovery.

Figure 4-7 shows the effect of the concentrations of S<sub>2</sub>O<sub>3</sub><sup>2-</sup> on gold recovery in the presence of 1mM CuSO<sub>4</sub> at 24 h. It can be seen that in the presence of thiosulfate ions in the solution influences the recovery of gold by slag magnetite. Gold recovery increased from 0% at 0.1mM S<sub>2</sub>O<sub>3</sub><sup>2-</sup> to more than 80% at 1.0mM S<sub>2</sub>O<sub>3</sub><sup>2-</sup>. This result suggests that increasing S<sub>2</sub>O<sub>3</sub><sup>2-</sup> concentrations is beneficial for gold recovery by slag magnetite. This can

be regarded as an advantage since in real gold thiosulfate systems, excess amounts of  $S_2O_3^{2-}$  are present.

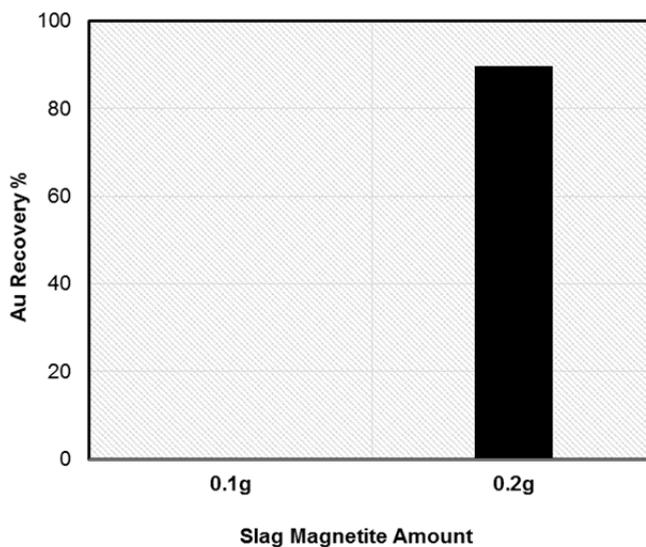


Figure 4-6. Effect of magnetite amount on Au recovery

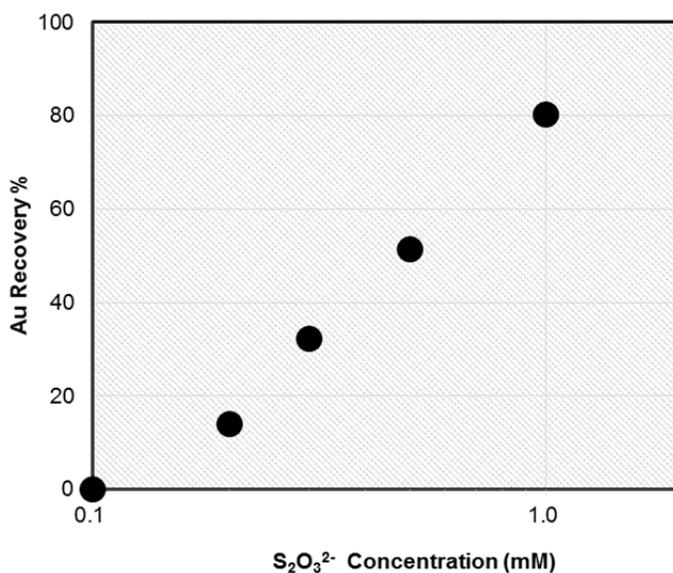
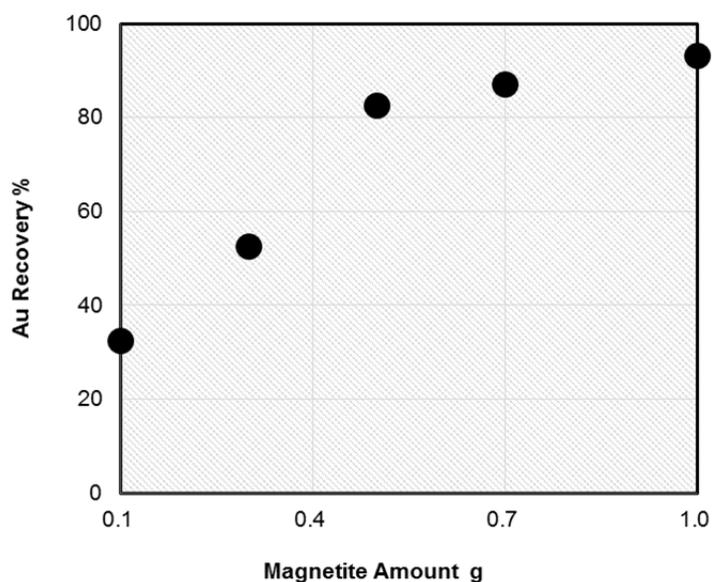


Figure 4-7. Effect of  $S_2O_3^{2-}$  concentration on Au recovery

The effect of larger amounts of slag magnetite on gold recovery was investigated in the presence of a higher concentration of  $S_2O_3^{2-}$  (1 M). The experiments were carried out with the addition of 15 mM  $CuSO_4$  at 24 h in  $N_2$  environment. The results are presented in

Figure 4-8. Gold recovery increased with increasing slag magnetite amounts. More than 93% of gold was recovered at 1 g slag magnetite addition.



**Figure 4-8. Effect of magnetite amount on Au recovery**

### 4.3.2 Gold concentration experiments

As discussed in section 4.3.1, oxygen is a key factor in the transport of gold between slag magnetite and ammonium thiosulfate solutions. In the absence of oxygen, gold from aqueous solution is loaded on slag magnetite, but is released from the magnetite back to the aqueous phase when oxygen is present. This suggests that the transportation of gold between solid/liquid phases can be controlled reversibly by regulating the oxygen content in the system. This was applied to concentrate gold from thin liquor or low concentration solution.

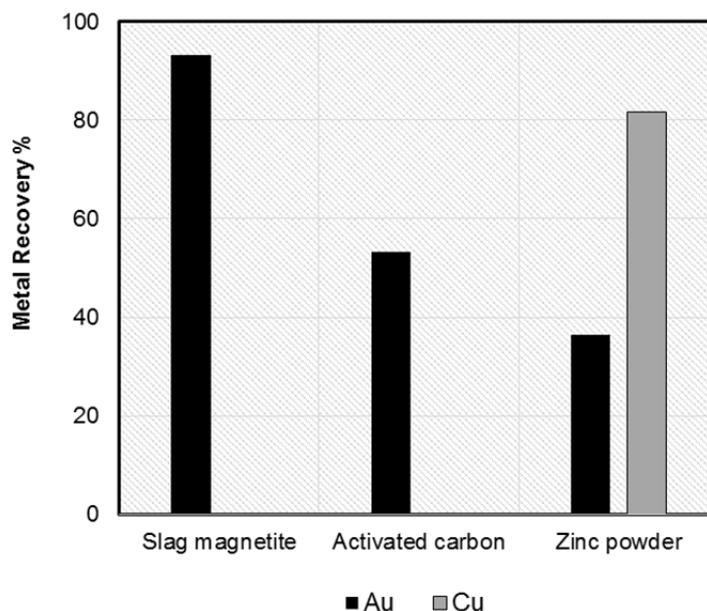
Experiments consisting of two steps were carried out to examine the concentration of gold from thin liquors. The first step consisted of gold adsorption on 0.1 g slag magnetite from 10 mL thin gold liquor of fixed concentration ( $0.05 \text{ mM Au(S}_2\text{O}_3)_2^{3-}$ ,  $0.1 \text{ M NH}_3$ ,  $0.1 \text{ M NH}_4^+$ , and  $1 \text{ M S}_2\text{O}_3^{2-}$ ) in  $\text{N}_2$  environment. After 24 h, the gold loaded slag magnetite was collected by centrifugal separation. The gold loaded slag magnetite was found to

contain 98  $\mu\text{g Au}$  /0.1 g slag magnetite. The second step entailed a gold desorption experiment using the gold loaded slag magnetite and 1mL leaching solution (0.1 M  $\text{NH}_3$ , 0.1 M  $\text{NH}_4^+$ , and 1 M  $\text{S}_2\text{O}_3^{2-}$ ) in an aerobic condition. After 24 h shaking, the leaching solution was recovered by filtration. The filtrate was analyzed for gold content and it was found to contain 0.49 mM of gold. This means that about 10 times gold concentration was achieved by the two-step procedure. This result confirmed the important role played by oxygen in gold recovery from thiosulfate solution by slag magnetite.

### 4.3.3 Comparison of adsorbents for gold recovery

The performance of slag magnetite was compared to that of zinc powder and activated carbon, known adsorbents to recover gold from aqueous solutions. Adsorption experiments were carried out 24 h in the absence of oxygen and involved the addition of 1.0 g of adsorbent to gold solution containing 15 mM  $\text{CuSO}_4$ . The adsorption of Cu was also investigated. The results are shown in Figure 4-9.

Zinc powder recovered not only gold but copper as well. More than 35% Au and more than 80% Cu recoveries were observed. Both slag magnetite and activated carbon selectively recovered gold from solution but slag magnetite registered a higher recovery value. About 93% Au was recovered against over 50% for activated carbon. This result reveals that slag magnetite could recover gold selectively from ammonium thiosulfate solutions in the presence of cupric ions.



**Figure 4-9. Comparison of adsorbents for gold recovery**

#### 4.4 CONCLUSION

A converter slag magnetite collected from a copper smelting company in Japan was utilized as an adsorbent to recover gold from ammonium thiosulfate solution. Batch sorption experiments were performed to evaluate the effects of pH, contact time, thiosulfate concentration, and initial copper concentration on Au uptake amount. The results showed that slag magnetite can effectively recover gold from ammonium thiosulfate solution. Parameter studies and spectrometric analyses suggested that chalcocite ( $\text{Cu}_2\text{S}$ ) and metallic Cu present in the slag magnetite reduced the gold thiosulfate complex. Gold was detected on the surface of the converter slag magnetite, and the EDX images strongly suggest the Au and Cu present in same areas. It was found that the presence of  $\text{O}_2$  in the system hinders gold uptake by slag magnetite and an anaerobic condition is much preferred. It is important to eliminate  $\text{O}_2$  in the system to increase gold recovery. Gold can also be concentrated to about 10 times the original concentration through a two-step adsorption-desorption scheme with  $\text{O}_2$  control. Converter slag magnetite can be used as a selective, economical, and effective adsorbent to recover gold from secondary sources.

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## Chapter 5

### GENERAL CONCLUSION

Precious metals, such as gold (Au), silver (Ag), platinum (Pt), palladium (Pd), rhodium (Rh) and other platinum group metals (PGMs), found wide applications in various manufacturing fields due to their superior chemical and physical properties. The increasing demand for these metals coupled with the declining resources available, prompted the development of recycling technologies to recover precious metals from secondary sources. Hydrometallurgical techniques play an important role in the processing of precious metals from secondary sources and have been the focus of numerous researches and studies for many years.

One of the challenges that is yet to be resolved in the hydrometallurgical processing of precious metals from secondary sources is the separation and recovery of the dissolved precious metals in solution, specifically from non-cyanide based leach liquors, such as chloride and thiosulfate. Magnetic solid-phase extraction (MSPE) using magnetic adsorbents has been reported to show great potential in the separation of precious metal ions from aqueous solutions. Magnetic adsorbents have gained significant attention recently due to their inherent magnetic property which can be exploited to overcome problems associated with phase separation. Among the magnetic adsorbents reported in literature, magnetite ( $\text{Fe}_3\text{O}_4$ ) seems the most promising due to its wide availability and ease of synthesis, ferromagnetic property and recyclability.

This dissertation investigated the use of magnetite derived from two different sources as adsorbent to recover precious metals (Pt, Au, Pd and Rh) from chloride and thiosulfate solutions. The effects of various process parameters were investigated and the mechanisms of adsorption were proposed. The results of the numerous experiments conducted for this research were presented and discussed in several chapters. The background and the objectives of the study, general literature review, and dissertation outline were the main themes of Chapter 1. This section summarizes the main findings and the general conclusions of this research.

In Chapter 2, the study on the recovery of Pt, Rh, and Pd from chloride solutions on synthetic magnetite powder was reported. The study involved batch adsorption experiments using synthetic magnetite at 298 K. The effects of different parameters, such as pH, contact time, the NaCl concentration and the PGMs concentrations were investigated. The uptake amounts of Pt, Pd, and Rh increased with time and reached a constant value over 24 h. This slow sorption kinetics indicates that the uptake is not due to a simple physical adsorption, and involves chemical reactions. The uptake amounts of Pt, Pd, and Rh were strongly affected by pH. The SEM-EDX and BSE analyses confirmed the presence of rhodium and palladium concentrated on some areas of the magnetite surface. These results signify that  $\text{Fe}_3\text{O}_4$  can uptake platinum group metals and can be used as a potential selective sorbent to recover the metals from chloride solution or chloride leach liquors.

In Chapter 3, the study on the recovery of Pt, Rh and Pd from chloride solution on magnetite derived from copper converting slag (slag magnetite) was detailed. The effects of various process parameters such as pH, contact time, NaCl concentration, and Pt, Rh and Pd concentrations, were investigated. Characterization studies conducted on the slag magnetite as revealed that it is a composite material with some amounts of metallic Cu and copper sulfide ( $\text{Cu}_2\text{S}$ ). Single-component batch adsorption experiments confirmed that Pt, Rh and Pd were recovered by slag magnetite. Higher recoveries at shorter contact time were observed. It was found that the slag magnetite is a more superior adsorbent than the synthetic magnetite in terms of loading capacity and kinetics. It was also found that slag magnetite can recover Pt, Pd, and Rh selectively from the solution containing a mixture of PGM ions and base metal ions, such as Cu, Ni, and Zn. The presence of copper impurities in the slag magnetite matrix may have contributed significantly to the observed results.

In Chapter 4, the utility of slag magnetite as adsorbent was extended to the recovery of gold from ammonium thiosulfate solution. Batch sorption experiments were performed to evaluate the effects of pH, contact time, thiosulfate concentration, and initial copper concentration on Au uptake amount. The results showed that slag magnetite can effectively recover gold from ammonium thiosulfate solution. Parameter studies and spectrometric analyses suggested that chalcocite ( $\text{Cu}_2\text{S}$ ) and metallic Cu present in the slag magnetite reduced the gold thiosulfate complex. Gold was detected on the surface of the converter slag magnetite, and the EDX images strongly suggest the Au and Cu present in

same areas. It was found that the presence of O<sub>2</sub> in the system hinders gold uptake by slag magnetite and an anaerobic condition is much preferred. It is important to eliminate O<sub>2</sub> in the system to increase gold recovery. Gold can also be concentrated to about 10 times the original concentration through a two-step adsorption-desorption scheme with O<sub>2</sub> control. The converting slag magnetite can be used as a selective, economical, and effective adsorbent to recover gold from secondary sources.

The experimental results presented in this research have demonstrated the potentials of synthetic magnetite and magnetite from waste material as adsorbents for the recovery of precious metals from chloride and thiosulfate solutions. Both types of magnetite exhibited selectivity towards precious metal ions. Selectivity is an important requirement in recycling where co-existence of precious metal ions with impurity metal ions is a common problem. It was also found that slag magnetite is more versatile as it can be applied in both chloride and thiosulfate-based liquors. There are still gaps that need to be filled in this research but the main findings already paved way to a promising technology worth considering.

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