



## LEACHING STUDY OF PRECIOUS METAL RECOVERY FROM FERRIC PERMANENT MAGNET WASTE

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### ABSTRACT

This paper describes the characterization and leaching behaviour of precious metal present from electronics scrap to obtain liquor which can be treated through hydrometallurgical techniques to purify the metals. The results of this study points out the technical feasibility of the recovery of the metals. The blank sample was characterized by X-ray florescence. This paper will also present the results of hydrometallurgical extraction experiments, which allow the recovery of rare earth element. Inductively Coupled Plasma–Mass Spectrometry (ICP-MS) was used in order to determine the element composition in the leaching process in term of molarity, temperature, and acid solvent. Two leachants were compared (sulfuric acid and hydrochloric acid) at different molarity (1 M, 2 M and 5 M) and different temperature (room temperature, 50 °C and 100 °C). It was found that sulfuric acid leaching was very promising as a leachant for recovery of Fe, Cu, Si, Ti and Nb metal at room temperature. At higher concentration, hydrochloric acid allowed the leaching up to almost 40% of Ti, 60% of Nb and impressively 200% of P more than H<sub>2</sub>SO<sub>4</sub>. The results shows that the hydrometallurgical recovery of precious metals present in permanent magnet is a technically feasible.

**Keywords:** precious metal, magnet waste, rare earth elements.

### INTRODUCTION

Permanent magnets are unique in their ability to deliver magnetic flux into the airgap of a magnetic circuit without any continuous expenditure of energy. Unlike temporary magnets such as electromagnets, permanent magnets do not lose their magnetic property unless they are heated above their Curie temperature. They are industrially manufactured through casting or sintering and are produced from magnetic metallic elements, composites and rare earth materials. Ferrite, neodymium-iron-boron (NdFeB), samarium cobalt (SmCo) and alnico are some of the examples of permanent magnets used in the industry.

Growth of the automotive industry due to several aspects such as technological advancement, rising population and increasing consumer demand is expected to be one of the primary factors driving the demand for permanent magnets over the next few years. In 2002, hard ferrites account for 55% by value, rare earth magnets are at 35%, and most of the remainder is alnico [1]. Ferrite magnet stand strongly and accounting for over 80% of the global demand, ten years later in 2012 [2]. According to report published by Transparency Market Research "Permanent Magnets (Ferrite, NdFeB, SmCo and Alnico) Market for Automotive, Electronics, Energy Generation and Other Applications - Global Forecast, Market Share, Size, Growth and Industry Analysis, 2013 - 2019," the global demand for permanent magnets was valued at USD 15.32 billion in 2012 and is expected to reach USD 28.70 billion in 2019. In terms of volume, the demand was 650.0 kilo tons in 2012 and is expected to be 1,168.7 kilo tons in 2019 [2].

Ferrite magnets can be found in variety of applications such as home appliance and computer. These magnets consist mostly of Fe metal and other precious metal such as titanium, niobium and rare earth. These magnets have been majorly used on account of several key

factors such as ease of availability, low price, significant performance properties, rapidly growing industrialization and extensively use of these materials in electronics and household appliances. The prices of commodities have risen sharply in recent years due to increase of demand from the consumers. Many metals that play a central role in the making of the permanent magnet are scarce. There are a number of reasons for potential supply restrictions. Natural ores can be exhausted or become too difficult to extract economically or in an environmentally acceptable way. For some minerals, reliance on supplies from a limited number of mines, mining companies or nations can carry added potential for restriction. Increases in mineral demand with new technology development can also alter mineral prices [3]. For these reasons recycling will have a key role to play in commodity supplies in future.

Based on report from the European Commission (EU) in 2014, EU listed 20 elements out of 41 elements that considered as critical and precious for the nation [4]. Raw materials with the highest criticality is position in cluster VI. These include germanium, rhenium and antimony. Cluster V, rated as "highly critical", includes tungsten, rare earth elements, gallium, palladium, silver, indium, tin, niobium, chromium and bismuth.

Hydrometallurgical route, which is defined as solvent extraction, separation and electrolytic, and a pyrometallurgical route, which is defined as direct melting in furnace, have already been established and applied industrially for the recycling of magnets, but there are problems of mass production on each. In hydrometallurgical route, although the results showed significantly low impurities in the recovered metals, there are notable drawbacks in the environment issues. At the end of the process, usually a large amount of acid solution discarded and leads to difficulties of business continuity [5]. As for a pyrometallurgical route, there are concerns



that the deterioration of alloy quality due to an impurity contained in scraps such as carbon, and its low operating efficiency due to an impurity contained in scraps such as oxygen. In order to improve recycling efficiency by direct melting recycling, the pre-treatment techniques to remove carbon and oxygen previously are required [6, 7].

Several recovery techniques in hydrometallurgical method including; leaching [8-10], cementation, solvent extraction [11], using magnesium [12] and biological method [13] for the precious metals from waste materials have been developed over the years. Leaching is the process of extracting minerals from a solid by dissolving them in a liquid. In leaching process, the liquid will act as diluents while solid used usually was a composite solid where it is quite difficult to separate the composite matter. The mechanism of leaching may involve simple physical solution or dissolution made possible by chemical reaction [14]. The recovery of the precious metals is much depended upon the type of acid used in the leaching system.

The objectives of this work was to recover the precious metals that contained in the ferric permanent waste magnet.

## EXPERIMENTAL PROCEDURES

### Chemicals and sample collection

Chemicals used was hydrochloric acid (HCl) with 32% purity, and sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) with 96% purity and diluted further in different concentration such as 1.0 mol/L, 3.0 mol/L and 5.0 mol/L. The entire chemicals were obtained from Sigma-Aldrich Malaysia. Sample were collected from electronic company in Kuantan, Pahang.

### Cutting and grinding

The obtained permanent magnet waste were already demagnetized and in the form of coil. Since the sample were too large to digest in the leaching reagent, the samples were cut and ground into powder form. The experiment were conducted with the desired particle size (<3mm) of magnetic waste to ensure the uniformity throughout the entire leaching process.

In a reaction between a solid and a liquid, the surface area of the solid will affect how fast the reaction occurs. Smaller particles have bigger surface areas than larger particles with the same mass. Therefore, if a reaction takes place on the surface of a substance, increasing the surface area, increase the quantity of substance available to react and thus increase the rate of the reaction.

### Batch leaching test

In order to recover the precious metal in the waste materials from the ground powder, a leaching method was adopted in this study with two leaching reagents such as hydrochloric acid and sulfuric acid. For each leaching test, a ratio of 1:50 of solid to liquid is used. About 1 g of rare earth element will be mixed with 50mL chemicals in a 200ml conical flask. The operating

parameters investigated in the leaching tests were the concentration of the leaching reagent and temperature. Triplicate setup with the same weight of sample and volume of leaching reagent were applied for each type of parameter. A gentle stirring using magnetic stirrer was continued during leaching process for 2 hours. Then the sample were filtered using Whatman No. 42 filter paper and the leachate were send to ICP-MS Agilent Model 7500 Series for composition analysis. Table-1 summarized the operating condition adopted in this study.

**Table-1.** Leaching operating condition of ferric permanent magnet waste.

Operating Condition	
Concentration (M)	1 M, 3 M, 5 M
Temperature (°C)	Room temperature (~37 °C), 50 °C, 100 °C
Reaction time (h)	2 hours
Solid:liquid ratio	1:50

## RESULT AND DISCUSSION

### Physical observation

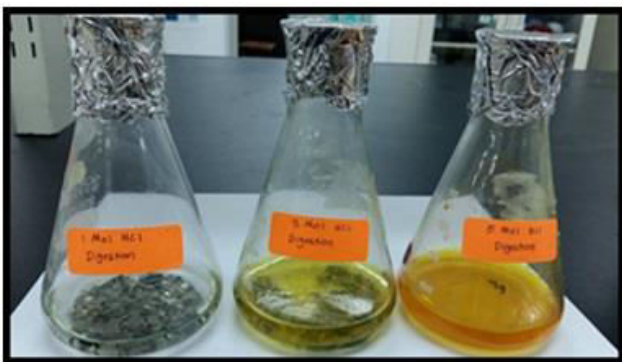
The sample containing precious metal were digested with two type of leaching reagent namely hydrochloric acid and sulfuric acid at different molarity. Figure-1 showed the reaction of the magnet sample as the leaching reagent poured in. For sulfuric acid, concentration of 1 M and 3 M were instantaneously dissolved the sample while it takes around 10 minutes for 5 M of H<sub>2</sub>SO<sub>4</sub>. In contrast, higher concentration of HCl dissolved the sample immediately and lower concentration have slower reaction towards the waste materials. The colour of the solution containing HCl as leaching reagent also changed to darker yellow as the concentration increased. It can be assumed that some of the metals interact with chloride ion and produced metal complex with yellow in color. It is differ with H<sub>2</sub>SO<sub>4</sub> as leaching reagent which the colour of solution remain colorless with different acid concentration.

### Batch leaching test

Leaching experiment were carried out in lab stirred flask, at room temperature for 2 hours of reaction time, with solid/ liquid ratio 1:50 using H<sub>2</sub>SO<sub>4</sub> and HCl as leaching reagent. The result as shown in Figure 2. Both reagent able to leach out Fe metal into the solution as Fe share almost 70% of common ferric permanent magnet waste composition. Recovery of Fe and Cu metal are depended on the concentration of the acid used. Generally, lower acid concentrations lead to incomplete dissolutions of the metals because of the insufficient supply of H<sup>+</sup> ions that is needed for the oxidation reaction. Additionally, the leachability of the trace precious metal in permanent magnet will depend more or less on the leachability of Fe [15].



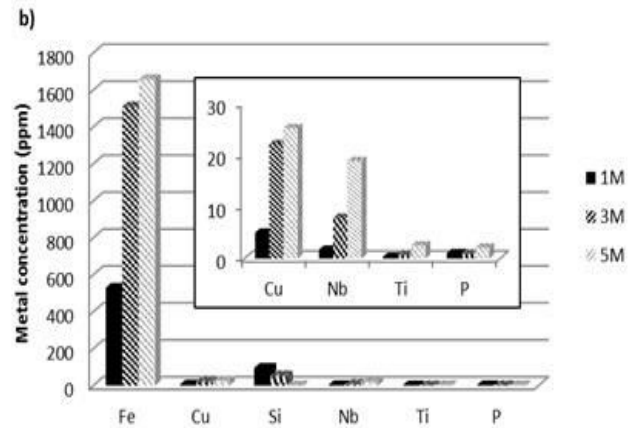
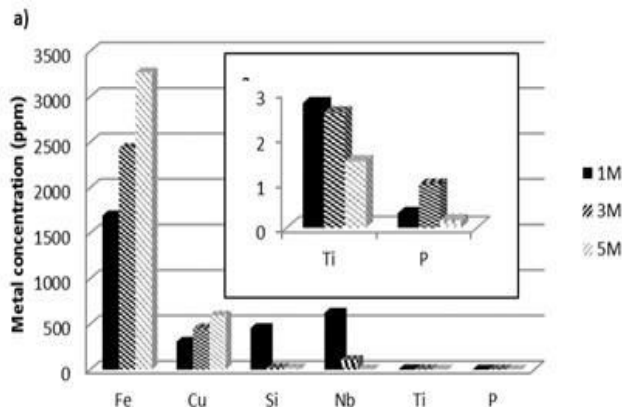
(a)



(b)

**Figure-1.** Comparison of leaching system of a)H<sub>2</sub>SO<sub>4</sub> and b)HCl as leaching reagent at different molarity; 1M, 3M and 5M.

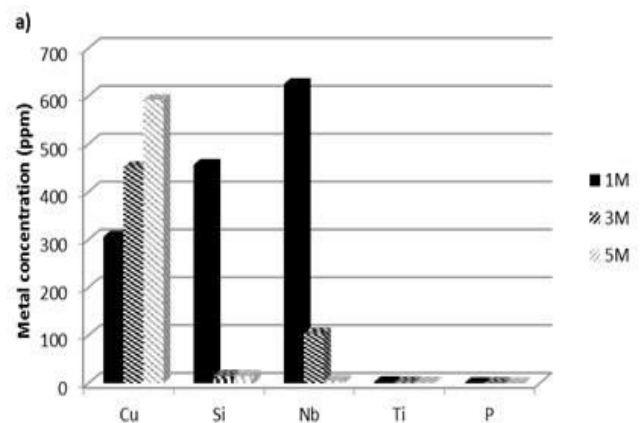
The results in Figure-2 indicate that except for phosphorus, other precious metal such as Fe, Cu, Nb and Ti favor sulfuric acid dissolution compared to hydrochloric acid. For Nb and Ti metal, highest metal recovery achieved at concentration of 1M for H<sub>2</sub>SO<sub>4</sub> at 625.4 ppm and 2.76 ppm, respectively. However, the metal recovery dropped to almost 70% for Nb and 20% for Ti when using H<sub>2</sub>SO<sub>4</sub> at concentration 3M. As for HCl as leachant, the leachability is greatly depended on the concentration of the acid. 5M concentration give highest metal recovery except for Si metal.

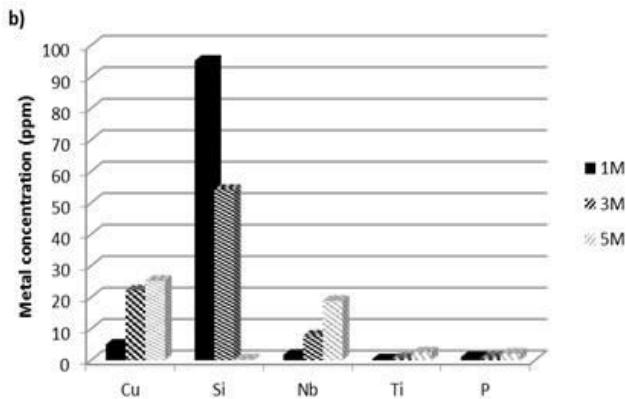


**Figure-2.** Comparison of a) H<sub>2</sub>SO<sub>4</sub> and b) HCl as leaching reagent for recovery of precious metals at room temperature with different molarity ; 1 M, 3 M and 5 M.

The effect of temperature in leaching process are carried out using following condition. Two types of acid, which is HCl and H<sub>2</sub>SO<sub>4</sub> with constant molarity of 1M. Figure 3 showed that most of the element the metal give positive effect as the temperature increase from room temperature to 100 °C. Generally, increasing temperature of a system increases the average kinetic energy of its constituent particles. As the average kinetic energy increases, the particles move faster and collide more frequently per unit time and possess greater energy when they collide. Both of these factors increase the reaction rate. Hence the reaction rate of virtually all reactions increases with increasing temperature.

In the leaching experiment using H<sub>2</sub>SO<sub>4</sub> as reagent, temperature parameter only have slight effect on the leaching of the permanent magnet waste except for Nb metal. Nb metal give around 650 ppm metal recovery at room temperature while sharply decrease to 142.5 ppm when temperature reach 100 °C. Fe, Si and Nb metal recovery increases as the temperature of leaching system using HCl increases. In contrary, Cu and Ti displayed 50 °C as the optimum temperature.





**Figure-3.** Comparison of different temperature of leaching process (room temperature, 50 °C and 100 °C) using 1M of a) H<sub>2</sub>SO<sub>4</sub> and b) HCl as leaching reagent for recovery of precious metals .

Comparing the effect of molarity and temperature towards the leaching process, it clearly demonstrated that temperature is a major contributor in controlling the process when HCl is used. Fe, Si and Nb metal leachability value increase as much as 100% of their value when the temperature at 100 °C. Contrary, for leaching system using H<sub>2</sub>SO<sub>4</sub> as leachant, concentration parameter give significant effect on improving the metal compared to temperature.

## CONCLUSIONS

On the basis of the study of the leaching of precious metals from permanent magnet waste, it can be conclude that although H<sub>2</sub>SO<sub>4</sub> and HCl were equally effective for scrap dissolution, H<sub>2</sub>SO<sub>4</sub> was used in the bulk of tests owing to better metal recovery and lower cost. H<sub>2</sub>SO<sub>4</sub> also works as better leachant in room temperature while HCl provide higher metal recovery at temperature of 100 °C. Further step dealing with the optimization of process parameters to form a separable precious metals need to be explored.

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