

**EFFECT OF PRESSURE ON THE PERFORMANCE
OF GAS-SOLID FLUIDIZED BED FOR THE
SEPARATION OF RARE EARTH ELEMENTS**

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ABSTRACT

This paper presents the effect of air pressure on the performance of gas-solid fluidized bed for the separation of rare earth elements (REEs) from printed circuit board. The printed circuit board (PCB) was cut using cutting tools into a size about 10 cm × 2.5 cm, then grind them successively until the sample become powder. The overall elements composition in PCB was analyzed using X-ray fluorescence (XRF). The result shows, only three elements of rare earth were found in the PCB; Erbium (Er), Ytterbium (Yb) and Scandium (Sc) with the composition of 0.10%, 0.0097% and 0.0057%. Then the samples were put into a cylindrical column and were fluidized under different air pressures; 15 psi, 20 psi, and 25 psi. During separation process, samples were taken at different heights; 11.5 cm, 32.0 cm, and 51.5 cm at 15 psi for 25 s, 20 psi for 30 s, and 25 psi for 35 s. All the collected samples with different air pressure and height were analyzed by using inductively coupled plasma mass spectrometry (ICP-MS) to know the concentration of the samples. The results showed that REEs do not exist at each of the sampling ports. However REEs still exist at the remaining samples content. This showed that the REEs were not segregated during separation as these elements were high density; Yb (6.965 g/cm³), Er (9.07 g/cm³), Sc (2.992 g/cm³). In order to overcome this problem, high pressures need to be used to segregate the samples successfully. The fabricated gas-solid fluidized bed column also multipurpose equipment where it can be used for other samples for separation processes.

ABSTRAK

Kertas kerja ini mengkaji kesan tekanan udara daripada alat ruangan gas-pepejal untuk memisahkan unsur-unsur nadir bumi daripada papan litur bercetak. Papan litur bercetak (PCB) telah dipotong menggunakan alat pemotong ke dalam saiz kira-kira $10 \text{ cm} \times 2.5 \text{ cm}$, kemudian mengisar mereka berturut-turut sehingga sampel menjadi serbuk. Keseluruhan komposisi unsur-unsur dalam PCB telah dianalisis dengan menggunakan X-ray pendarfluor (XRF). Hasil kajian menunjukkan hanya tiga unsur-unsur nadir bumi ditemui di PCB; Erbium (Er), Ytterbium (Yb) dan Scandium (Sc) dengan komposisi 0.10 %, 0,0097 % dan 0,0057 %. Kemudian sampel telah dimasukkan ke dalam lajur silinder dan berada di bawah tekanan udara yang berbeza, 15 psi, 20 psi, dan 25 psi. Semasa proses pemisahan, sampel telah diambil pada tahap yang berbeza; 11.5 cm, 32.0 cm, 51.5 cm dan pada 15 psi selama 25 s, 20 psi untuk 30 s, dan 25 psi selama 35 s. Semua sampel yang dikumpul dengan tekanan udara yang berbeza dan ketinggian telah dianalisis dengan menggunakan induksi plasma spektrometri jisim (ICP-MS) untuk mengetahui kepekatan sampel. Hasil kajian menunjukkan bahawa nadir tidak wujud di setiap injap lajur silinder. Walau bagaimanapun nadir masih wujud pada lebihan kandungan sampel. Ini menunjukkan bahawa nadir tidak diasingkan semasa pemisahan kerana elemen-elemen ini mempunyai ketumpatan yang tinggi; Yb ($6,965 \text{ g/cm}^3$), Er (9.07 g/cm^3), Sc ($2,992 \text{ g/cm}^3$). Untuk mengatasi masalah ini, tekanan tinggi perlu digunakan untuk mengasingkan sampel dengan jayanya. Alat ruangan gas-pepejal juga boleh digunakan pada sampel lain untuk proses pemisahan.

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LIST OF ABBREVIATIONS

EOL-EEEs	End-of-life electrical and electrical equipment
HREE	Heavy rare earth elements
ICP-MS	Inductively coupled plasma mass spectrometry
LREE	Light rare earth elements
NiMH	Nickel-metal hydride battery
PCB	Printed circuit board
PVA	Polyvinyl alcohol
PVC	Polyvinyl chloride
REEs	Rare earth elements
SFL	Spent Fluorescent lamp
SIR	Solvent impregnated resin
XRF	X-ray fluorescence

CHAPTER 1

INTRODUCTION

1.1 Background

Rare earths are a moderately abundant group of seventeen elements comprising the fifteen lanthanides, scandium (Sc), and yttrium (Y) (Chunsheng et al, 2013). The lanthanides comprise a group of fifteen elements with atomic numbers 57 through 71 that include the following in order of atomic number: lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), Terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), and lutetium (Lu) (Taylor & McClennan, 1985; Szumigala, 2011). These elements are located in the Periodical Table from low atomic number to higher atomic number as shown in Figure 1. According to the differences in chemical and physical properties of rare earth elements, rare earth are often described as being a “light-group rare-earth element” (LREE) and “heavy-group rare-earth element” (HREE) (Saraee Khadijeh et al, 2009; Gupta & Krishnamurthy, 1992; Zhanheng, 2011). LREEs are a group of eight elements on the periodic table between La with the atomic number 57 and Gd with the atomic number 64. While HREEs are a group of eight elements on the periodic table between Tb with the atomic number 65 and Lu with the atomic number 71. The group of HREEs also includes Y with atomic number 39.

1 H 1.00794																	2 He 4.00260																												
3 Li 6.941	4 Be 9.01218	REE														5 B 10.811	6 C 12.011	7 N 14.0064	8 O 15.9994	9 F 18.9984	10 Ne 20.1797																								
11 Na 22.989769	12 Mg 24.3047	21 Sc 44.955912	22 Ti 47.88	23 V 50.9415	24 Cr 51.9961	25 Mn 54.938045	26 Fe 55.845	27 Co 58.933195	28 Ni 58.6934	29 Cu 63.546	30 Zn 65.38	31 Ga 69.723	32 Ge 72.630	33 As 74.9216	34 Se 78.96	35 Br 79.904	36 Kr 83.80																												
37 Rb 85.4678	38 Sr 87.62	39 Y 88.905848	40 Zr 91.224	41 Nb 92.90638	42 Mo 95.94	43 Tc 98.9062	44 Ru 101.07	45 Rh 102.90550	46 Pd 106.3675	47 Ag 107.8682	48 Cd 112.411	49 In 114.818	50 Sn 118.710	51 Sb 121.757	52 Te 127.46	53 I 126.90545	54 Xe 131.29																												
55 Cs 132.905451	56 Ba 137.327	57 La 138.90547	72 Hf 178.49	73 Ta 180.94788	74 W 183.84	75 Re 186.207	76 Os 190.23	77 Ir 192.222	78 Pt 195.084	79 Au 196.96657	80 Hg 200.59	81 Tl 204.3833	82 Pb 207.2	83 Bi 208.9804	84 Po [209]	85 At [210]	86 Rn [222]																												
87 Fr [223]	88 Ra [226]	89 Ac [227]	104 Rf [261]	105 Db [262]	106 Sg [263]	107 Bh [264]	108 Hs [265]	109 Mt [266]	110 [267]	111 [268]	112 [269]	113 [270]	114 [271]																																
<table border="1"> <tr> <td>58 Ce 140.12</td> <td>59 Pr 140.90766</td> <td>60 Nd 144.24</td> <td>61 Pm [145]</td> <td>62 Sm 150.36</td> <td>63 Eu 151.964</td> <td>64 Gd 157.25</td> <td>65 Tb 158.92535</td> <td>66 Dy 162.5001</td> <td>67 Ho 164.93033</td> <td>68 Er 167.259</td> <td>69 Tm 168.93032</td> <td>70 Yb 173.0547</td> <td>71 Lu 174.967</td> </tr> <tr> <td>90 Th 232.0377</td> <td>91 Pa 231.03688</td> <td>92 U 238.02891</td> <td>93 Np [237]</td> <td>94 Pu [244]</td> <td>95 Am [243]</td> <td>96 Cm [247]</td> <td>97 Bk [247]</td> <td>98 Cf [251]</td> <td>99 Es [252]</td> <td>100 Fm [257]</td> <td>101 Md [258]</td> <td>102 No [259]</td> <td>103 Lr [262]</td> </tr> </table>																		58 Ce 140.12	59 Pr 140.90766	60 Nd 144.24	61 Pm [145]	62 Sm 150.36	63 Eu 151.964	64 Gd 157.25	65 Tb 158.92535	66 Dy 162.5001	67 Ho 164.93033	68 Er 167.259	69 Tm 168.93032	70 Yb 173.0547	71 Lu 174.967	90 Th 232.0377	91 Pa 231.03688	92 U 238.02891	93 Np [237]	94 Pu [244]	95 Am [243]	96 Cm [247]	97 Bk [247]	98 Cf [251]	99 Es [252]	100 Fm [257]	101 Md [258]	102 No [259]	103 Lr [262]
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Figure 1: Rare earth elements and their position in the periodic table

The common properties of rare earths are silvery-white metals that tarnish when exposed to air, forming oxides, relatively soft metals; hardness increases with higher atomic numbers and reacts with water to liberate hydrogen gas (Helmenstine & Marie, 1995). Besides that, rare earth elements (REEs) are slowly in cold or quickly upon heating and strongly paramagnetic. In addition, they also high melting and boiling points (Helmenstine & Marie, 1995). Now, REEs are found in most everyday applications because of their unique chemical and physical properties (Jordens et al., 2013). Their unique properties make them indispensable for a wide variety of emerging and critical technologies (Du & Graidel, 2011). Furthermore, REEs have widespread and unique applications in high technology, communications, power generation and defense industries (Hatefi et al., 2011). Instead of that, they become increasingly most important in the transition to a green, low-carbon economy due to their essential role in permanent magnets, rechargeable NiMH batteries and other applications as shown in Table 1 (Binnemans et al., 2013). According to Jordens et al (2013), REEs are required for many different applications for example, magnetic applications. REE is increasingly use in the permanent magnet. According to Castor and Hedrick (2006), neodymium-ion-boron magnets had been developed by the mid-1980s and have replaced samarium-cobalt magnets where neodymium-ion-boron magnets possess a magnetic energy of up to 2.5 times greater than the samarium-cobalt magnets. In addition, the wind turbines use neodymium magnets per megawatt in the range 0.6-1.0 tonne, of which

approximately 30 percent is REE (Avalon Rare Metals, 2010; Lifton, 2009). Furthermore, these REE are also used for hybrid cars such as the Toyota Prius where hybrid cars reduce fossil fuel by combining a petrol engine, battery-powered electric motors and brakes that capture energy during braking (Avalon Rare Metals, 2010). Besides, Dy and Tb are also used in magnets that will prevent the magnets from losing their magnetism at high temperature (Venter, 2009).

Second application is glass and polishing. According to Kingsnorth (2009), this application was accounted about 22 percent of total REE consumption by volume in 2008 and only six percent by value. The first commercial use of Ce was in 1896 when it was used as decolourising agent in glass. Small quantity of cerium will decolourise glass however one percent will turn it yellow and larger quantities brown (King, 2008). Otherwise, Nd colours glass red, Ho blue, Pr green, Er is used to colour glass pink and others colour are obtained by mixing with other elements among REE (Gupta & Krishnamurthy, 2005). In addition, La is an integral part of camera lenses as low silica glass that contains lanthanum oxide (King, 2008). Besides, according to Haxel et al., (2002), the most of polished glass products, for example television faceplates, mirrors and cathode ray tubes are finished using cerium oxide.

Meanwhile, REE also have major applications in metallurgical alloys. According to Venter (2009), the common use of this alloy is in the torches and in the flint ignition device of many lighters, although for this purpose it is blended with iron oxide and magnesium oxide since the REE alloy alone is too soft. REE also used in nickel metal hydride (NiMH) rechargeable batteries that power electronic products (King, 2008) where La is the main REE used in the NiMH battery (Australian Rare Earths, 2010). In addition, these batteries are also used in hybrid cars that use 10 to 15 kilograms of La (Lifton, 2009). Additionally REE also used in catalysts applications. Cerium carbonate and cerium oxide act as component of the converter's oxidizing catalyst system that used in the catalyst substrate (Castor & Hedrick, 2006). According to Lynas (2010), REEs play an important role where they increase the effectiveness and reduce the amount of platinum and other precious metals required, hence decreasing costs. Besides that, La and Ce also use in fluid cracking catalysts which are used in the process of refining crude oil that transform the heavy molecules into lighter compounds, finally make up petrol and other fuels such as gas, diesel and jet fuel (Lynas, 2010).

REEs that have ability to absorb neutrons and remain stable at high temperature also used in nuclear energy applications (Jackson & Christiansen, 1993). The other applications are Eu is used for control rods to regulate reactor operation (Gupta & Krishnamurthy, 2005) as well as Y also used as a coating to provide corrosion resistance and a lead-free surface primer for paints (Hedrick, 2001). Lastly, REE are used in defence applications. For examples optics, sonar transducers, surveillance and protection, microwave communication, laser and aircraft materials (Molycorp, 2009). However, in most cases the individual rare earth (RE) instead of their mixture shows unique intrinsic properties in electrics, optics, magnetism or catalysis, thus separation and purification of RE concentrates is necessary for their uses on functional materials (Hatefi et al., 2011).

Table 1: Rare earths usage by application, in % (Curtis, 2010; Long et al., 2010)

Application	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Y	Other
Magnets			23.4	69.4			2	0.2	5		
Battery alloys	50	33.4	3.3	10	3.3						
Metallurgy	26	52	5.5	16.5							
Auto catalysts	5	90	2	3							
FCC	90	10									
Polishing powders	31.5	65	3.5								
Glass additives	24	66	1	3						2	4
Phosphors	8.5	11				4.9	1.8	4.6		69.2	
Ceramics	17	12	6	12						53	
Others	19	39	4	15	2		1			19	

Quite different from their name, rare earth is really not that rare as they are relatively plentiful in the earth crust (Rudnick et al., 2005; Szumigala, 2011). There are about thirty four countries found to have rare earth reserves (Zhanheng, 2011). In addition, there are currently about 110 million tons of global REE reserves, with valuable deposits distributed over the world (Wubbeke, 2013). According to Wubbeke (2013), half of these reserves are located in China, while Russia accounts for 17.3 percent of global reserves and the United States for 11.8 percent (Figure 2). This condition leads China as the great manufacturer, exporter and even one of the great consumers of rare earth (RE) and provided most of the RE demand in the world since 1980 (Xu, 1995; Zhanheng, 2011). Besides, one fifth of REE being mined is currently

used for permanent magnets, 20% for alloys, 19% for chemical catalyst, 13% for polishing and 8% for glass and phosphors (Kingsnorth, 2012). These facts show that rare earth elements are widely distributed in the earth and are not really rare.

The principal sources of REEs are the minerals bastnasite, loparite and the lateritic ion-adsorption clays, and monazite (Szumigala, 2011). Although REEs are relatively abundant in the earth's crust (Zhanheng, 2011), however discovered minable concentration are less common than for most other ores (Szumigala, 2011). Figure 3 shows the location of some of the most main REE occurrences and deposits. According to the United States Geological Survey (2011), the most percentage of the world's rare – earth economic resources are bastnasite deposits in China and the United States, while monazite deposits in Australia, China, Brazil, Malaysia, India, South Africa, Sri Lanka, Thailand and the United States constitute the second largest segment. Kamitani and Kanazawa (2006) stated that, the major deposits are categorized genetically into igneous, sedimentary, and secondary types. Furthermore, figure 4 shows the world mine reserves and 2010 mine production based on different country.

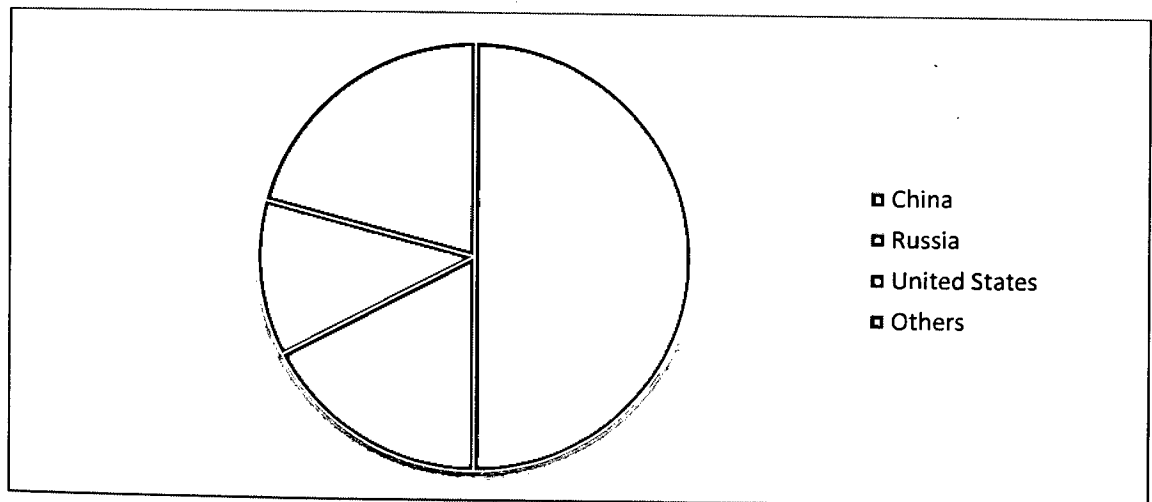


Figure 2: Global REEs Reserves 2013

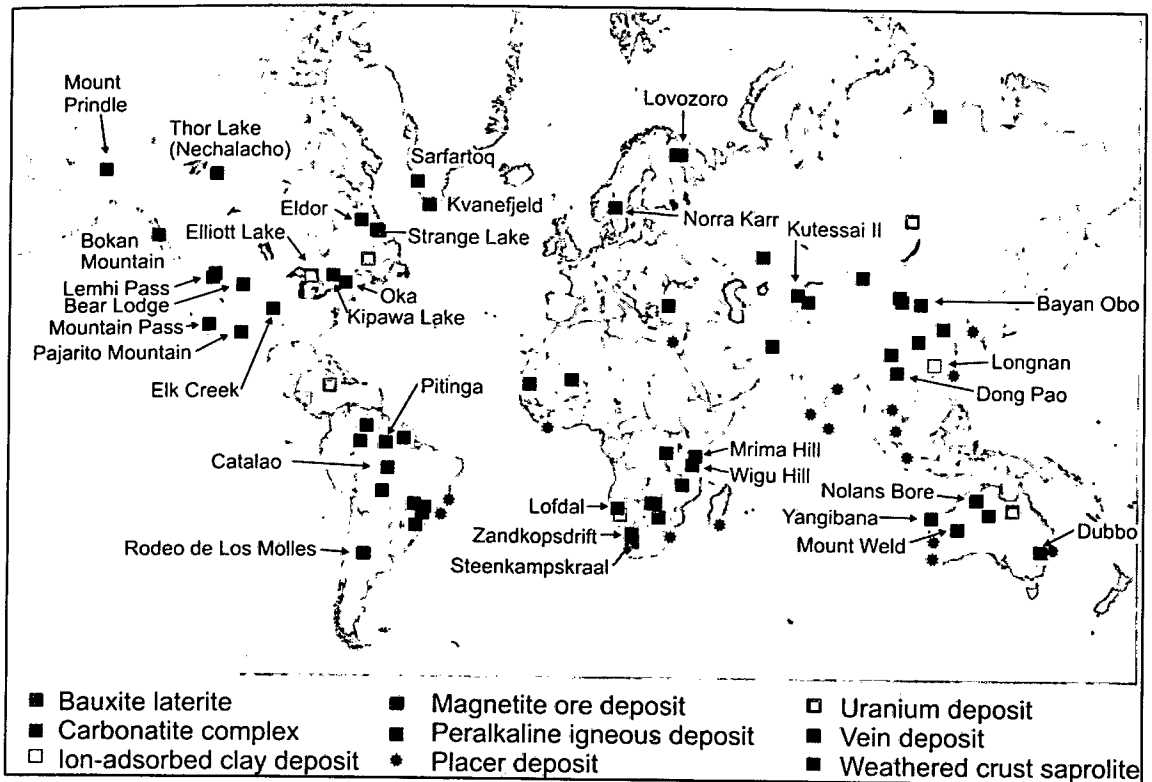


Figure 3: Global distribution of known rare earth element resources (Mariano et al., 2010)

World Mine Reserves and 2010 Mine Production		
Country	Reserves^a (tons of REE oxide)	Production (tons of REE oxide)
United States	14,300,000	0
Australia	180,000	0
Brazil	53,000	600
China	60,600,000	140,000
Commonwealth of Independent States (CIS)^b	20,900,000	NA ^c
India	3,400,000	2,900
Malaysia	33,000	385
Other Countries	24,000,000	NA ^c
World Total (rounded)	121,000,000	143,000

Figure 4: World Mine Reserves and 2010 Mine Production (USGS Mineral Commodity Summaries, 2011).

Due to REEs's increasing usage in numerous high-technology applications, such as high strength permanent magnets, phosphors for electronic displays, applications in a variety of renewable energy technologies, and as alloying agents in metals, the demand for rare earth elements has been rising in recent years (Crow, 2011; Meyer & Bras, 2011; Preinfalk & Morteani, 1986). According to Kingsnorth (2011), the current value of the REE market is about \$2-3 billion which is small compared with other minerals. The market of REEs has changed substantially from a position of oversupply to demand shortages where the rare earth oxide (REO) demand in 2008 was 124 000 tons, an increase of 45 percent compared to 2003 when demand was only 85 000 tons (Avalon Rare Metals Inc., 2009). Kingsnorth (2011) stated that the total demand is predicted to reach 190 000-210 000 tons by 2015 where magnets and metal alloys have a predicted consumption of up to 50 000 tons and 55 000 tons respectively (Table 2). According to UN Comtrade (2011), the largest importer of REE compounds in 2009 was USA at nearly 16 500 tons whereas Japan was the second largest with imports of just under 13 500 tons followed by Germany importing 8200 tons, France (7000 tons) and Austria (4500 tonnes). Moreover, the largest importer of REE metals is Japan with 4800 tons followed by France with 400 tons.

Table 2: Global demand for REE in 2008 and 2015 (Kingsnorth, 2011)

Application	Consumption REO (tonnes)		Market share 2015 %
	2008 actual	2015 forecast	
Catalysts	25 000	30–34 000	16
Glass	12 000	20–22 000	6.5
Polishing	15 000	50–55 000	11
Metal alloys	22 250	45–50 000	26
Magnets	26 250	39–43 000	23
Phosphors and pigments	9000	12–14 000	6.5
Ceramics	7000	8–10 000	5
Other	7500	10–12 000	6
Total/range	124 000	190–210 000	

According to IMCOA (2011), world demand for REEs is estimated at 13 600 tons per year, with global production around 133 600 tons in 2010 where it will rise to at least 18 500 tons annually by 2015. Other estimations point that the global demand for REEs may reach 210 000 tons per year by 2015 (Bloomberg News, 2010). This increasing demand is due to the dominant uses of REEs in our daily life such as automotive catalytic converters, metallurgical additives and alloys, petroleum refining catalyst, phosphors in color television and flat panel displays (cell phones, portable DVDs, and laptop), glass polishing and ceramics: permanent magnets and rechargeable batteries for hybrid and electric vehicles, and numerous medical devices (Panayotova & Panayotov, 2012; Binnemans et al., 2013). In addition, the increasing of these applications may increase the price of REEs (Binnemans et al., 2013). To address this issue, recycling is one of the main ways to ensure a supply of these critical raw materials (Panayotova & Panayotov, 2012). There are two major field of recycling of metals: pre consumer recycling, which means the recycling of production scrap of manufacturing processes ('new scrap') and the post-consumer recycling (Panayotova &

Panayotov, 2012). In this paper, I will focus on the REEs that will be recycling from electronic device by using gas-solid fluidized bed column.

1.1 Motivation and statements of problem

One of the most common uses of REEs is in hybrid cars, whereby a typical hybrid car battery needs around 10 – 15 kg of lanthanum (Szumigala, 2011). Though this is expected to increase to a region of around double that in the near future as technology evolves, and engineers push the boundaries to increase fuel consumption. Besides that, the increasing of electric and hybrid cars, compact fluorescent lamps and wind turbines is causing an increase in the demand and price of REEs (Binnemans et al., 2013). But now, rare earth elements become critical raw materials group, with the highest supply risk (European Commission, 2010). This problem makes rare earths availability has also increasing (Binnemans et al., 2013). China, the 97% of the global supply of rare earth metals has recently done copious cuts of its exports, in order to protect its environment, has greatly increased the rare earth prices and causing tension among the world hi-tech markets (Massari & Ruberti, 2013).

The high demand and the expected supply shortages, additionally triggered by Chinese export restrictions, lead to a significant increase in rare earth element prices (Szumigala, 2011). This steep increase is not only giving a burden for manufacturers and consumers, it also offers the chance to address the problem of today's rare earth supply in more depth and to build up a sustainable rare earth economy in all relevant sectors. Besides, the low prices in the past lead to a significant waste of resources. Until now, there has been almost no recycling of rare earths and maybe the higher prices might be a starting point to building up recycling systems for rare earth compounds (Darmstadt, 2011). So, a drastic improvement in the recycling of REEs is absolute necessary (Binnemans et al., 2013). To perceive at these problems, recycling is the best option to do as the demand for rare earth element is increasing. From these problems, this research will recover rare earth elements from electronic waste device using separation unit for recycling process.

1.2 Objective

The following is the objective of this research:

- To study the effect of pressure on the performance of gas-solid fluidized bed for the separation of rare earth elements

1.3 Scope of this research

The main purpose is to study the effect of air pressure. This study focus on how the air pressure will affect the performance of gas-solid fluidized bed for the separation of rare earth elements. Besides that, this study will overcome the limitation of material by using the unwanted waste of electronic device.

1.4 Organisation of this thesis

The structure of the reminder of the thesis is outlined as follow:

Chapter 2 summarizes all the researched and worked that have been done by previous researches. All the research is related with the separation process of rare earth element using fluidized bed column.

Chapter 3 presents a detailed procedure for the effect of pressure on the performance of gas-solid fluidized bed for the separation of rare earth elements in order to recycle the unwanted waste of printed circuit board (PCB). Flow of methodology also had revealed in this chapter.

Chapter 4 is one of the parts of research methodology. This chapter presents a detailed about the design of the gas-solid fluidized bed column.

Chapter 5 This chapter describes and discusses the results obtained from each step in research methodology.

Chapter 6 draws together a summary of the thesis and outlines the future work which might be derived from the model developed in this work.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter summarizes all the researched and worked that have been done by previous researches on separation of rare earth elements. A general view on the study of separation process of rare earth elements in the chipboard of electronic waste using fluidized bed column is described and followed by the previous worked of the researches on separation of rare earth elements.

2.2 Overview

This research presents the experimental studies of separation process of rare earth elements from chipboard of electronic waste chipboard using fluidized bed column in order to recycle the unwanted waste of electronic device. During the last decade, China RE industry has made significant progress and become the most main producers in the world (Chunhua et al., 2006). Despite their global distribution, REE are mined mainly in China where this country produced 95,000 tons REE in 2011, down from 129,000 tons in 2009 (Wubbeke, 2013). According to Tse (2013), China's share of global production decreased from 95 percent in year 2009 to 86, downstream production around the global is critically dependent on Chinese percent in 2012. Addition, in 2011, about 68 percent of the REE mined in China used in the country where North East Asia consumed 16 percent with USA 10 percent and others only 6 percent due to the Chinese near monopoly on REE processing and production supply. But in 2010, China as the most important producers in the world decided to tighten its export quotas for rare earth

elements (Wubbeke, 2013; Szumigala, 2011). This is become a problem since China is less and less interested in exporting its REE. According to Binnemans (2013), these quota may cause serious problems for REEs user outside of China, and, hence, also for the development of a more sustainable, low-carbon economy.

Due to their similar chemical properties, making the separation process of REE from concentrates is a very difficult and at the same time increasing the price of the REEs (Szumigala, 2011; Morais & Ciminelli, 2004). Separation technique is one of the way to overcome the limitation of REEs such as ion exchange, fractional crystallization and liquid-liquid extraction (Szumigala, 2011). But Gupta and Krishnamurthy (2005) stated that, some process are laborious, inefficient and quite difficult. So, the fluidized bed column has been introduced since this way is simple and easy to handle. Furthermore, the demands on REEs keep increase every years that will increase their price (Szumigala, 2011). Hence, recycling method should implement to overcome this situation. By recycling, waste material will be reduced and at the same time reduced cost of the process. In this work, in order to find the effect of pressure in separation process, fabricated fluidized bed column has been using. Meanwhile, recycling is one of the best options to do as the demand for rare earth element is increasing years by years in order to sustain this metal in the future.

2.3 Previous works on separation of REEs on various types of anion-exchangers in the $C_3H_7OH-7 M HNO_3$ system

Since the REEs are difficult to separate and this process are expensive as their physico-chemical properties are similar (Hubicki & Olszak, 2002), the researches was done their research on separation process. Hubicki & Olszak (2002) have done this research on separation of Y, Nd, and Sm by frontal analysis on strongly basic anion-exchangers: Wofatit SBW, Wofatit SBK and Lewatit MP 5080. However, their work was limited only on Y, Nd, and Sm elements in the RE. The objective of this worked was to know which is the best basic anion-exchanger among three in separation process of REEs. In this work, they focus on separation of nitrate complexes of Y from Nd and Sm from Nd on different anion-exchanger in 2-propanol and 1-propanol. Besides that,

the separation of frontal analysis was carried out in glass column of 2-cm diameter with the determination of the percentage of Nd in Y and Sm by using spectrophotometer Specord M 40 supplied by Zeiss, Germany. However, in this work, Wofatit SBW and SBK proved completely useless where the last anion-exchanger; Lewatit MP 5080 is the best results of separation obtain. Meanwhile, according to Kutun et al., (2000), sodium trimetaphosphate ($\text{Na}_3(\text{PO}_3)_3$) is a very suitable new elution agent for the separation of RE and thorium on strongly basic anion-exchange resins.

2.4 Previous work on separation of lanthanum and cerium using a coated solvent-impregnated resin

Nowadays, from the view point of resource sustainability, rare earth metals becomes an attractive issue on development of effective processes (Nishihama et al., 2013). Nishihama et al., (2013) have done their research on separation of La and Ce, using a solvent impregnated resin (SIR) containing 2-ethyl-hexyl phosphonic acid mono-2-ethylhexyl ester, that coated by polyvinyl alcohol (PVA) crosslinked by glutaraldehyde or divinyl sulfone. In their research, they have to coat the SIR with a thin polymeric film to prevent leakage of the extractant. Kabay et al., (2010) stated that, although this coating provides high stability to SIR, the coating procedure is complex and they conclude that the PVA is the simplest among others polymers. Besides that, they focus on separate La and Ce element, found in vehicle catalyst where they want to investigated the effect of crosslinking agents, glutaraldehyde and divinyl sulfone, and their concentration. Furthermore, they use Inductively coupled plasma atomic emission spectrometer (ICP-AES) in order to know the concentration of metal ions. Additionally, in this research they use 100, 200, and 500 mm height with 10 mm diameter for column use. At the end of this research, they found that, glutar-aldehyde possesses suitable loading and elution capacities, even with repeated operation.

2.5 Previous work on separation of rare earth with a polymeric microcapsule membrane

From Kondo and Kamio (2002), they stated that in this recent years, lanthanoids have been in important demand for various functional materials. Although each of the elements is need to be separated and purified in high purity for the application to functional materials, it is very difficult to separate them. Same with others researches, Kondo and Kamio (2002) also have done their research on separation of lanthanoids using the column packed with the microcapsules containing acidic organophosphorus compound as an extractant. In their research, microcapsules containing EHPNA (MC-EHPNA) was packed in glass column by a micro-tube pump at a constant flow rate. Besides that, they use inductively coupled plasma spectrometer (ICPS) in order to find the concentration of lanthanoids. Furthermore, they focus on La, Ce, Pr, Sm, Eu, Gd, Ho, Er, and Y as the elements to be separated. Additionally, they examined the effect of pH in the feed solution on column operation. For example, at low pH, Sm could be separated from Gd during the overshoot. From this research, they have found that it will possible to apply the column packed with the microcapsules as a separation unit for REEs.

2.6 Previous work on separation of rare earth elements by tertiary pyridine type resin

The separation of REEs are developed for the industrial use of REEs (Hubicka & Drobek, 1997), and for the analyses and partitioning of REEs including the fission products generated in nuclear reactors (Lee et al., 2001). According to Suzuki et al., (2006), there are variously method in separation process but there are some problems, such as complicated methods, tight separability condition, restriction on separable REEs, remain of organic material, and so on. They already have done their research on the separation technique based on the chromatography using tertiary pyridine resin with alcoholic inorganic acid solution system. In order to separate the REEs under optimal

condition, the effects of the nitric acid concentration, the methanol concentration, and the alcoholic species on the adsorption were explored. Besides that, they use ICP-AES in order to find out the concentration of REEs. In their research, they have find out that the separation factors strongly depends on the methanol concentration.

2.7 Previous work on separation of rare earth elements by anion-exchange chromatography using ethylenediaminetetraacetic acid (EDTA) as mobile phase

Fernandez and Alonso (2008) stated that, REEs are important indicators in many geochemical cycles. According to Balaram (1996), the development and the improvement of analytical methods for rapid, sensitive and selective determination of REEs is due as the most geochemical studies require on-line and/or off-line REE separations. Fernandez and Alonso (2008) also stated that, typical cation or mixed bed exchangers (anion and cation exchange) are commonly used in the separation of REEs. They also mention the use of ICP-MS detection has increased in the last recent years whereas traditionally, REE are detected by post-column spectrophotometric reaction with strongly absorbing chromophores such as PAR or Arsenazo-III. They have done their research on separation of REEs, that form anionic complexes which can be separated isocratically by anion-exchange chromatography using EDTA as the mobile phase. Besides that, they have used ICPMS as the detection method of REEs. The objective in their research is to study of the different parameters which affect the chromatographic retention of REEs on the anion-exchange column. From their reseacrh, they have developed an anion-exchange separation procedure for the lanthanide elements as the cationic Ln^{3+} ions on acidic solution could pre-concentrated on cation-exchange columns and later eluted by EDTA onto the separation column. But this process seem very complicated as need more procedure.