RARE EARTH ELEMENT INDETIFICATION FROM ELECTRONIC WASTE: SOLID PHASE SEPARATION (ACID LEACHING)

NUR ASHIKIN BINTI JAMIN

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UNIVERSITI MALAYSIA PAHANG

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ABSTRACT

Rare earth element (REE) commonly used as a significant component in electronic appliance such as Liquid-crystal display (LCD). Nowadays, rare earth element is being disposed rather than being recycled or reused. Due to the increased in demand, rare earth element become more economically profitable. Recycling or recovery of rare earth element from electronic waste will help to secure the effect on price, supply and quantity of the element. The aim of this research is to identify the rare earth element contain in the LCD. The separation process of solid phase extraction (SPE) or so called as leaching method were introduced to identify the rare earth in the LCD. The concentration of acid solution parameter was varied to examine the optimum condition for leaching process of LCD by chromatography analysis using X-ray Diffraction (XRD).

ABSTRAK

Unsur nadir bumi (REE) biasanya digunakan sebagai salah satu komponen penting dalam perkakas elektronik seperti paparan cecair kristal (LCD). Pada masa kini, unsur nadir bumi kebanyakkannya dilupuskan dan tidak dikitar semula atau digunakan semula. Disebabkan oleh peningkatan dalam permintaan, unsur nadir bumi menjadi lebih menguntungkan dari segi ekonomi. Kitar semula atau pemulihan unsur nadir bumi dari sisa elektronik akan membantu untuk mengurangkan kesan ke atas harga, bekalan dan kuantiti unsur. Tujuan kajian ini adalah untuk mengenal pasti elemen nadir bumi terkandung di dalam LCD. Proses pemisahan pengekstrakan fasa pepejal (SPE) atau dipanggil sebagai kaedah larut lesap telah diperkenalkan untuk mengenalpasti nadir bumi di dalam LCD. Kepekatan asid sebagai parameter telah diubah untuk memeriksa keadaan optimum untuk proses larut lesap LCD dengan analisis kromatografi menggunakan X-ray Zarina (XRD).

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m1	molarity of pure acid
v1	volume of pure acid
m2	molarity of diluted (desired) acid
v2	volume of diluted (desired) acid, usually using volumetric flask
M	molarity

LIST OF ABBREVIATIONS

HCL	Hydrochloric acid
HNO3	Nitric acid
HREE	Heavy rare earth element
H2SO4	Sulphuric acid
LREE	Light rare earth element
LCD	Liquid crystal display
MW	Molecular weight
REE	Rare earth element
REO	Rare earth oxide
XRD	X-ray diffraction

1 INTRODUCTION

The topic of Under Graduate Research Project is about Rare Earth Element Identification From Electronic Waste: Solid Phase Separation (Leaching Process). The rare earth elements are all metals and the group in the bottom part in the periodic table usually called as 'lanthanides' and widely used in our life. Rare earth application were various in production and usage of electronic goods that showed increase in trend for recent years and also the price declining, invention of new technologies and upgrading of new features had developed in our dumping area, together with domestic waste. By taking liquid crystal displays (LCD) as example composition that formed inside the waste is indium tin oxide (ITO). ITO is a clear and conductive liquid or film and acts as a coating on a 1mm glass sheet of monitor screen. By conducting this research, it helped in providing the knowledge about rare earth elements and enhanced it in leaching process.

1.1 Motivation and statement of problem

The rare earth element (REEs) are a group of 17 element listed in periodic table. According to U.S. Geologies Survey REE is a group consists of 15 lanthanides with atomic number from 57 to 71 (James B.Hedrick, 1997). Scandium and yttrium are included based on the same physiochemical characteristics and this metal are commonly found in the same assemblages as the lanthanides. REE occur together in geological deposits because this group shared a lot similar properties but have different distributions and concentration. The term 'rare' was a brought from metallurgical chemists from within 1940s (Gupta and Krishnamurthy, 2004). The least abundance REE, thulium (Tm_{69}), was nearly 200 times more common than gold. However they are commonly known as 'rare' because usually we can not find them in commercially viable concentrations this due to a very little tendency for REE to become concentrated in exploitable ore deposits. The concentration of pure REEs from mined rock is complicated, requires many stages, and affects the economic decisions in the industry.

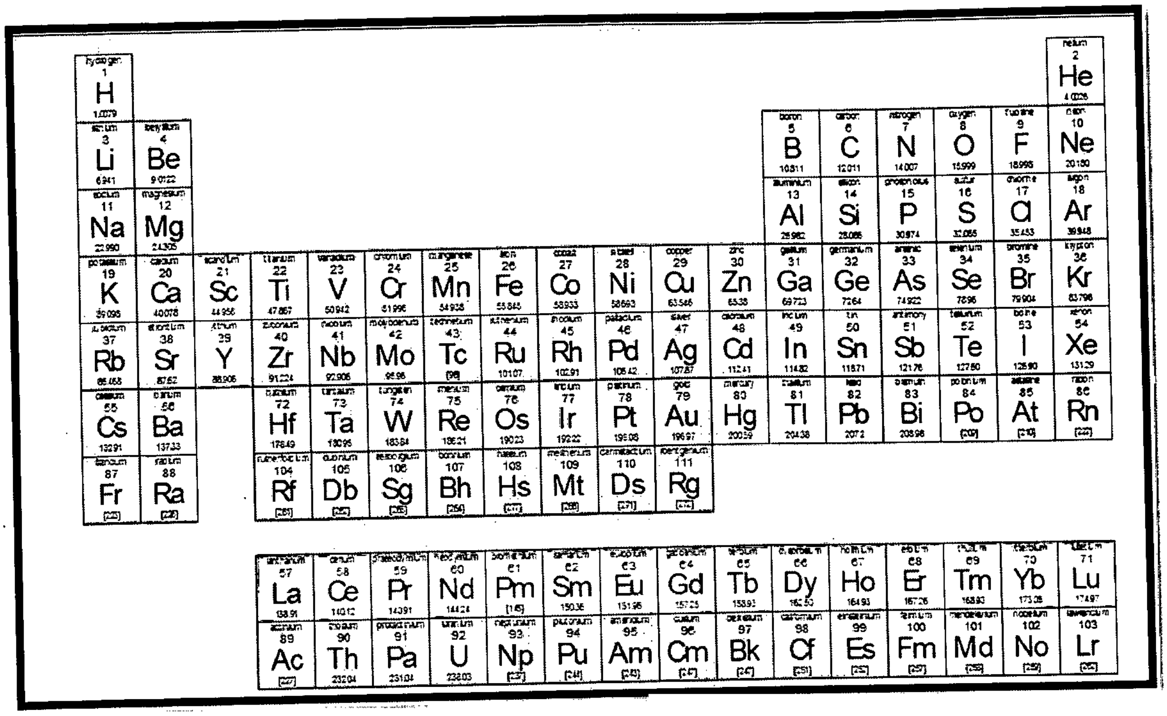


Figure 1.1-1 REE in periodic table

REEs were divided into two classes which is light rare earth element (LREEs) and heavy rare earth element (HREEs), categorized based on their electron configuration . Lanthanum through gadolinium with an atomic number from 57 to 64 categorized as LREE while terbium through lutetium with an atomic number 65 to 71, and also yttrium (atomic number 39) were included in HREE. Usually the HREEs are relatively less common in nature but more valuable. Xenotime for example is one of the sources of REE minerals but only a minor contributor to the production of REEs. Xenotime were produced as the by-product from tin-mining in Malaysia. However, an important scale of the Chinese rare-earth production is sourced from ion absorption clays, which themselves appear to have been derived from the deep weathering of source rocks containing xenotime (Simon, W. 2010).

The overall process to obtain REE from ore was very complicated and costly. (Refer Figure 1.2). At first, the ore (bastnaesite) containing minerals were taken out from the ground using usual mining procedures. The bastnaesite were then been removed by crushing the ore into smaller size then it was placed into a grinding mill. The fine sand or silt the different mineral grains from ore milling process then continue the bastnaesite separation process from other nonessential minerals.

Acid and vary solvent extraction separation steps was applied to separate the ore that contain REE into respective pure forms which then will be process to become metal. The metal then been processed into alloys that used for other application usually in technologies. This overall process may takes about 10 days. However mining in natural environment comprises the majority acquisition of REE and most mining operation result in large quantity (greater than 90%) of excess and unused material (EPA REE report,2012)

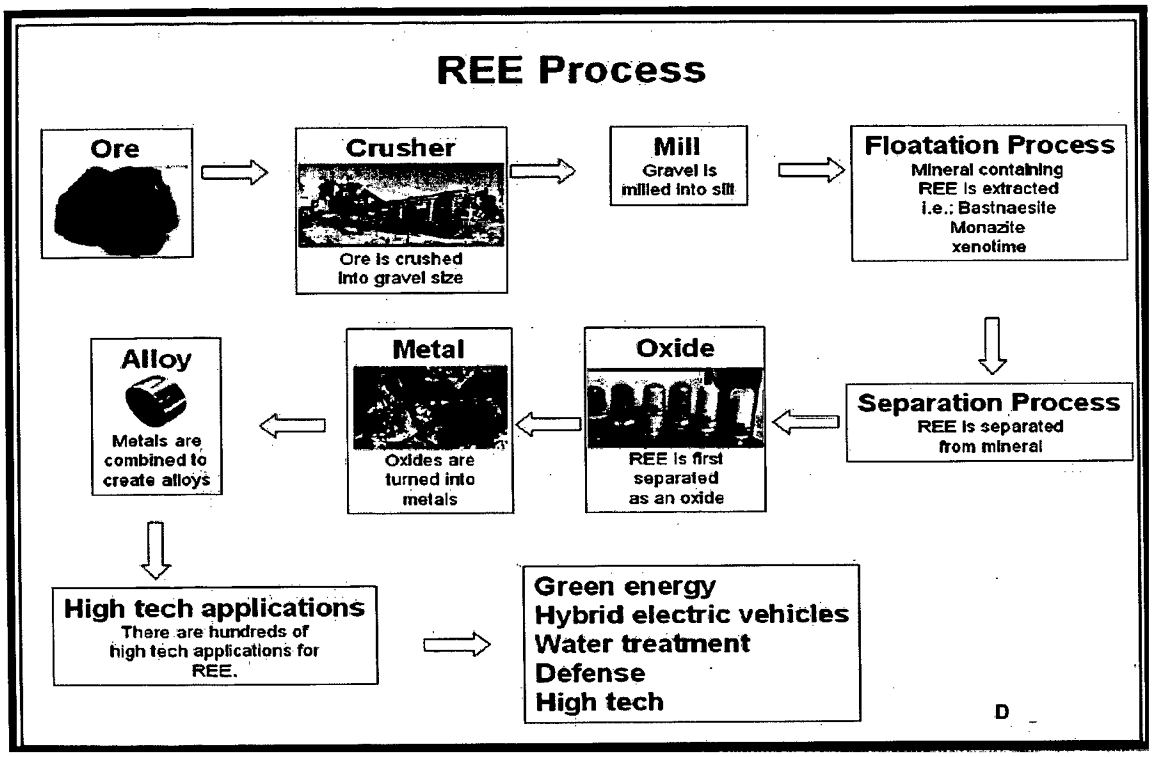


Figure 1.1-2 REE from the Ores

The REE history begin within the year 1751, the Swedish mineralogist and chemist Axel Fredrik Cronstedt (1722-1765) found an odd heavy reddish mineral (Cerite) in the quarry in Bastnas in Sweden. Almost 150 years (1788-1941) was took to indentify each of the REE. The history of REE metallurgy was divided into three stages: The Dark Ages (before 1950), The Enlightenment Age (1950-69) and The Golden Age (from 1970) (K.A. Gschniedner).

The REE special properties of luminescence, magnetism and electronics which now made REE critical varies and widen array or high technology invention application had construct an important part of the industrial economy of the 21st century. The Mountain Pass rare earth mine in California was once the largest REE supplier in the world until 1970s they supplied 100 percent of U.S. demand and 33 percent of the world's demand for rare earths. Active mining operations at Mountain Pass Mine were suspended in 2002.

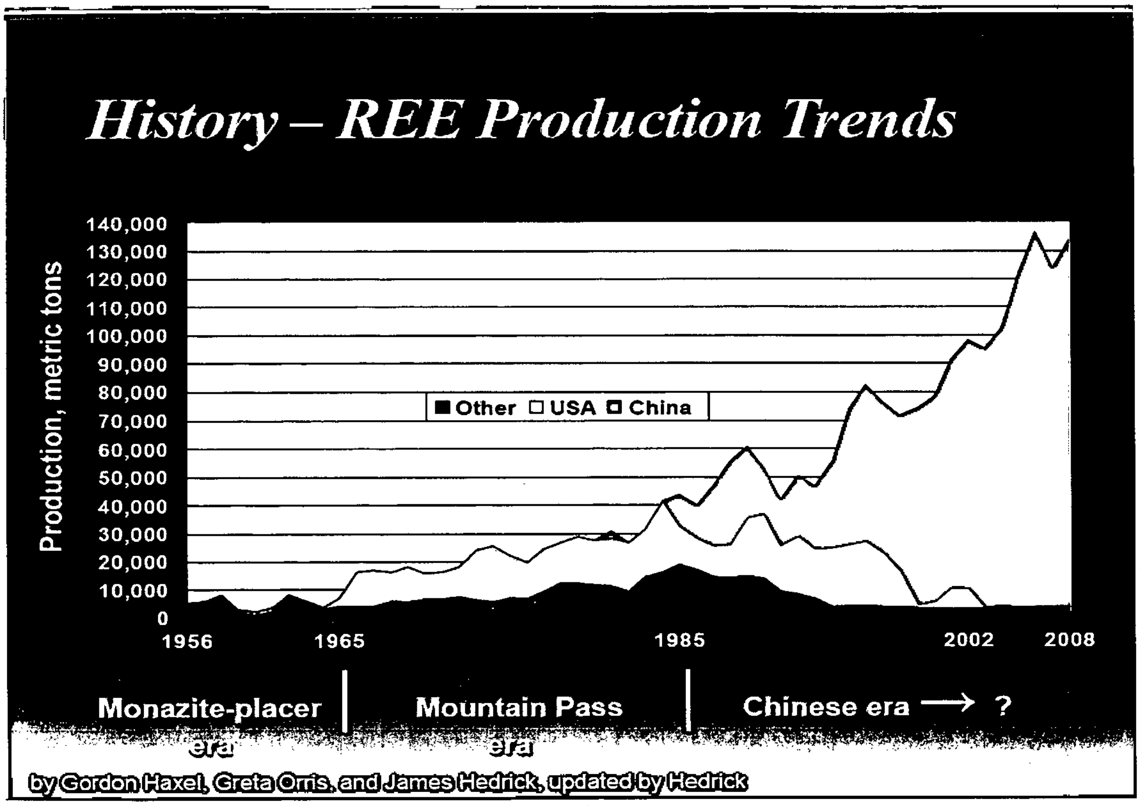


Figure 1.1-3 REE production trends

United States lead the rare earth oxide (REO) production from 1960 until 1980s. In the late 1970s, China started increasing production of REEs, and as projected in (Figure 1.3), rapidly became the world's dominant producer. As U.S. REE production has declined, China has become the world's leading producer of REEs and China is a dominant in producing over 90 percent of world production of rare earth element and has 36 percent reserves. While United States is one of the largest rare earth element consumers and importers and the demand will continue to increase as the expected trend (Koen Binnemans, 2013). As the demand increase, rare earth element becomes more economically profitable.

Nowadays, rare earth element is being disposed in a huge quantity rather than being recycled or reused. Rare earth element is being imported to European Union (EU) from a limited procedure. REE had already became an integrated in new technologies, especially within the clean energy, military, magnets, hybrid car batteries, catalyst, lighting luminescence and others electronics technologies. It is difficult to get an exact projection of demand in future, analysts have placed the lower and upper bounds for annual growth for total REE demand at 5% and 9% over the next 25 years (Alonso, Sherman, Wallington, Everson, Field, Roth & Kirchain, 2012). Additionally, rare earth metals are significant in alloying addition to steels. REEs is also very useful in the green energy sector. For example electric and hybrid cars may contain 20-25 pounds of REE, which is double that found in a standard gasoline vehicle (I Am Gold Corperation, 2012). REEs widely used in development of the braking systems and electric traction motors that consist of powerful magnets made from neodymium and dysprosium. REEs are also used to make high capacity wind turbines, advanced solar panels, high efficiency lighting, petroleum and pollution control catalysts for automobiles and high speed rails (Kennedy,J, 2009).

To overcome China REEs production domination and to fulfill the market demand the other minor producer country started doing a research in recovery of REE and recycling technologies of REE from an electronic waste. One of the electronics waste that can be used to recovery of REE is the liquid crystal display (LCD). Table 1-1.1 showed the application of the REE metal in general

Table 1-1.1: The application, potential supply issues for clean technologies of REE (EPA Report,2012)

Element	Applications
Scandium	Metal alloys for the aerospace industry.
Yttrium	Ceramics; metal alloys; lasers; fuel efficiency; microwave communication for satellite industries; color televisions; computer monitors; temperature sensors. Used by DoD in targeting and weapon systems and communication devices. Defined by DOE as critical in the short- and mid-term based on projected supply risks and importance to clean-energy technologies.
Lanthanum	Batteries; catalysts for petroleum refining; electric car batteries; high-tech digital cameras; video cameras; laptop batteries; X-ray films; lasers. Used by DoD in communication devices. Defined by DOE as near critical in the short-term based on projected supply risks and importance to clean-energy technologies.
Cerium	Catalysts; polishing; metal alloys; lens polishes (for glass, television faceplates, mirrors, optical glass, silicon microprocessors, and disk drives). Defined by DOE as near critical in the short-term based on projected supply risks and importance to clean-energy technologies.
Praseodymium	Improved magnet corrosion resistance; pigment; searchlights; airport signal lenses; photographic filters. Used by DoD in guidance and control systems and electric motors.
Neodymium	High-power magnets for laptops, lasers, fluid-fracking catalysts. Used by DoD in guidance and control systems, electric motors, and communication devices. Defined by DOE as critical in the short- and mid-term based on projected supply risks and importance to clean-energy technologies.
Promethium	Beta radiation source, fluid-fracking catalysts.
Samarium	High-temperature magnets, reactor control rods. Used by DoD in guidance and control systems and electric motors.
Europium	Liquid crystal displays (LCDs), fluorescent lighting, glass additives. Used by DoD in targeting and weapon systems and communication devices. Defined by DOE as critical in the short- and mid-term based on projected supply risks and importance to clean-energy technologies.
Gadolinium	Magnetic resonance imaging contrast agent, glass additives.
Terbium	Phosphors for lighting and display. Used by DoD in guidance and control systems, targeting and weapon systems, and electric motors. Defined by DOE as critical in the short- and mid-term based on projected supply risks and importance to clean-energy technologies.
Dysprosium	High-power magnets, lasers. Used by DoD in guidance and control systems and electric motors. Defined by DOE as critical in the short- and mid-term based on projected supply risks and importance to clean-energy technologies.
Holmium	Highest power magnets known.
Erbium	Lasers, glass colorant.
Thulium	High-power magnets.
Ytterbium	Fiber-optic technology, solar panels, alloys (stainless steel), lasers, radiation source for portable X-ray units.
Lutetium	X-ray phosphors.

Liquid crystal display (LCD) and Indium tin oxide (ITO)

Liquid Crustal Display (LCDs) had become more popular replacing the cathode ray tube (CRT) displays. Based on the report, which indicated that between 2004 until 2009 the Japanese producers of LCD tv increased their shipments to about five time (Figure) (METI,2010). From the view of ecological point, LCD may reduce the power consumption, emit less heat and therefore might cause fewer problem in air conditioning at office whenever many displays run at the same time. (Menozzi et al, 1999). Low power consumption gave the LCD an advantage with the potential of electromagnetic radiation for causing possible effects on biological matter (Nelson and Wullert, 1997). As well as the market of the LCD keep increasing (U.S. EPA, 1998), the life-cycle environmental impacts of LCD treatment methods are thus of interest to both manufacturers and consumers (Socolof and Kincaid, 2001).

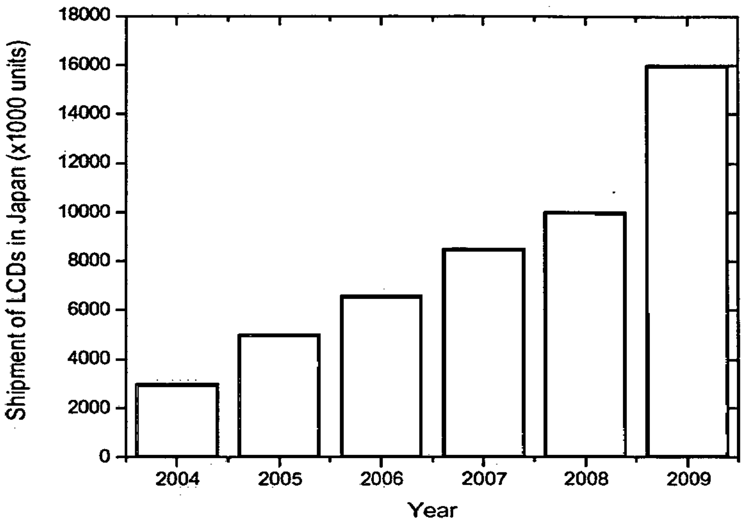


Figure 1-4: Shipments of Japanese producers for LCD TV sets. Source: METI, 2010.

The indium element (Z=49) is a soft and silvery white metal that was found to be discovered in 1863 by Ferdinand Reich and Theodor Ritcher and named due to the indigo color of its spectrum (M.J. Chagnon, 2010). While it is said to be nonhazardous in commercial use, the metal and the metalloid is known to be severely toxic and carcinogenic to humans and animals (B.Fowler et.al, 1993). The major sources of primary indium distribution are found in South America, Canada, China, South Korea and Japan. Canada has the potential to be the largerst sources of indium while China is currently the biggest indium producer where about 50 to 60% of the world's indium production (M.J. Chagnon, 2010). On the other hand, on the consumption side, Japan is the largest indium consumer, taking 60% of the world supply.

1.2 Objectives

The following are the objective of this research:

- The aim of this work is to identify REE from the electronic waste by double step leaching process.

1.3 Scope of this research

The following are the scope of this research:

- The recovery of REE from an electronic waste which is Liquid Crystal Display (LCD).
- To apply double step leaching in the process in REE recovery.
- Identify the REE from the electronic waste by using XRD

1.4 Main contribution of this work

The main contribution of this work is related to recovering or recycling process of REE from an electronic waste which is LCD.

1.5 Organisation of this thesis

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

Chapter 2 provides a description of the REE from previous finding based on LCD, the method of recovery and the acid leaching process.

Chapter 3 gives a review of the double stage leaching approach applied and the identification of REE by using XRD. The summary methodology of the experiment and the parameters to be study was reviewed in this aspect.

Chapter 4 is devoted to the finding.

2 LITERATURE REVIEW

2.1 Overview

To reduce a production of REE by mining the ores, on the other hand to lower the impact of import pressure from the major producer, China and the major consumer, United States it is necessary to other country to recover or recycled this minerals from the waste. REEs had been widely used in electronic equipment in for example liquid crystal display (LCD) as computer monitor. In future the demand for REE will expand as shown in figure 2.1.

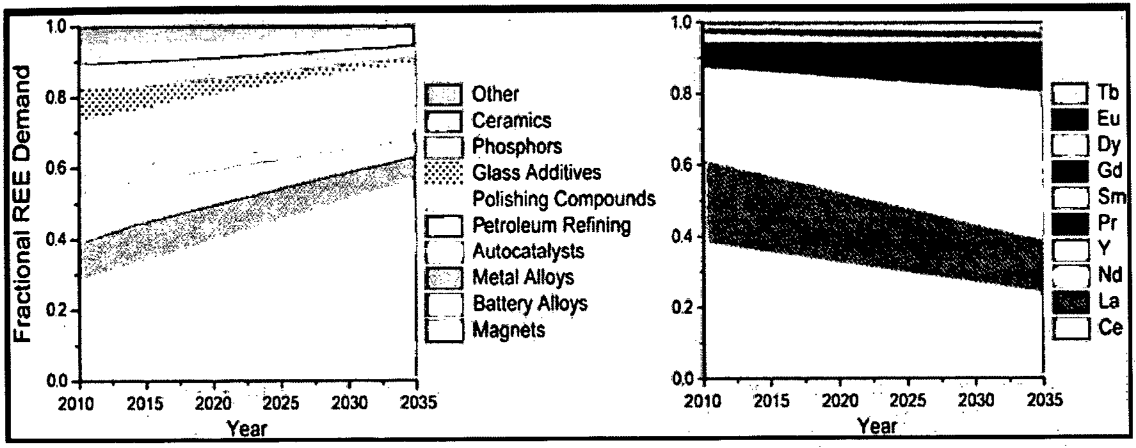
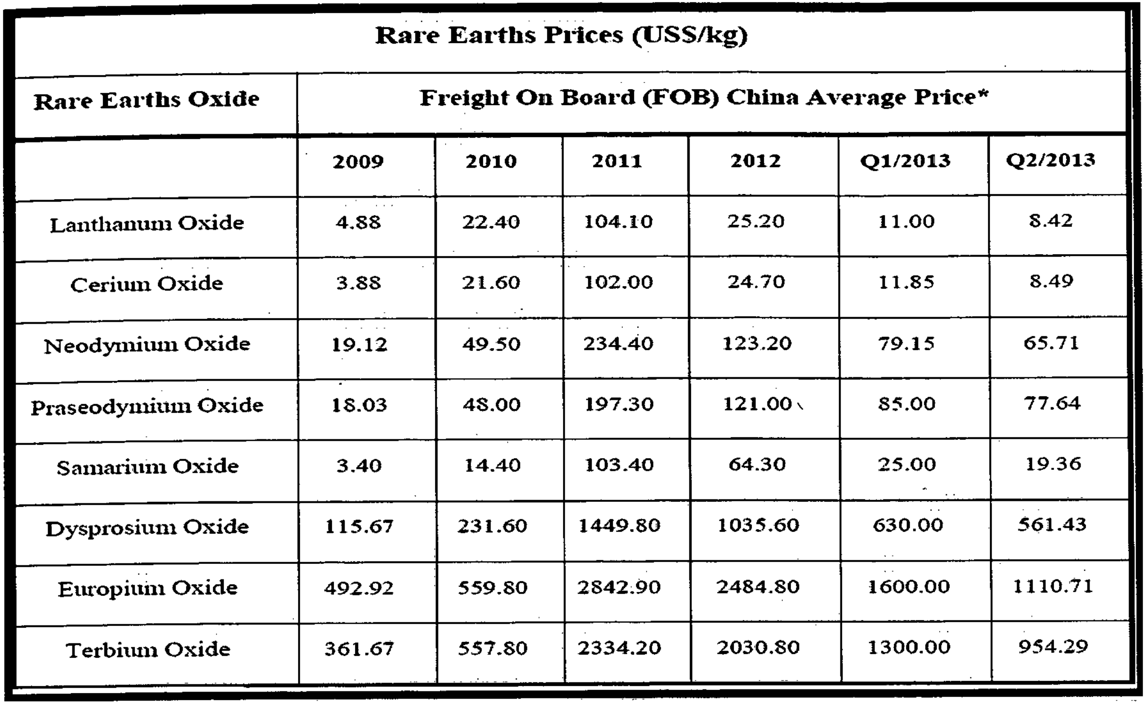


Figure 2.1: Average expert predictors on the REE demand up to 2035 (Kingsnorth,2010)

Table 2-1.1: Average prices for standard 99% purity of individual REO



Rare Earths Prices (USS/kg)						
Rare Earths Oxide	**Freight On Board (FOB) China Average Price***					
	2009	**2010**	**2011**	**2012**	**Q1/2013**	**Q2/2013**
Lanthanum Oxide	4.88	22.40	104.10	25.20	11.00	8.42
Cerium Oxide	3.88	21.60	102.00	24.70	11.85	8.49
Neodymium Oxide	19.12	49.50	234.40	123.20	79.15	65.71
Praseodymium Oxide	18.03	48.00	197.30	121.00	85.00	77.64
Samarium Oxide	3.40	14.40	103.40	64.30	25.00	19.36
Dysprosium Oxide	115.67	231.60	1449.80	1035.60	630.00	561.43
Europium Oxide	492.92	559.80	2842.90	2484.80	1600.00	1110.71
Terbium Oxide	361.67	557.80	2334.20	2030.80	1300.00	954.29

In order to oxidize the REE into leachable, a high temperature was indeed so that the REE can be extract by hydrometallurgical process (D. Voßenkaul, 2013).

Rare earth metallurgy divided into several method and technique :

a) Mining
   i) Open pit
   ii) Underground
   iii) In-situ
b) Milling
   i) Crushing and grinding
   ii) Mixing
c) Physical separation
   i) DMS (loparite, monazite)
   ii) Magnetic/ electrostatic separation (F/Ti impurities)
   iii) Flotation (bastnaesite, monazite)

d) Cracking and Precipitation
    i) Acid digestion
    ii) Alkaline cracking (monazite)
    iii) Heating
    iv) Precipitation (Na2SO4, CaCO3, Oxalic acid)
e) Rare earth separation
    i) Solvent extraction
    ii) Ion absorption
    iii) Acid leaching

2.2 Introduction

This section present the literature review based on the liquid crystal screen (LCD), previous finding on recycle and recovery of rare earth element (REE) and the acid leaching process finding.

2.3 Liquid Crystal Display (LCD) and Indium Tin Oxide (ITO)

LCD is divided into to categories, depend on the whether cold cathode fluorescent lamps or light-emitting diodes been used as the backlight unit. The categories are conventionally named as LCD and LED respectively. The general structure of the LCD is presented in (Figure 2-1). ITO is located in the LCD panel. The illustration of the layered structure of the key components in a panel is presented in (Figure). The majority of the weight were made up from the glass substrate layer, usually in the range of 1mm thickness, while the thickness of the liquid crystal, electrode (ITO) and color filter layers are 5 µm 150 nm and 2 µm respectively (B.Kopacek, 2009).

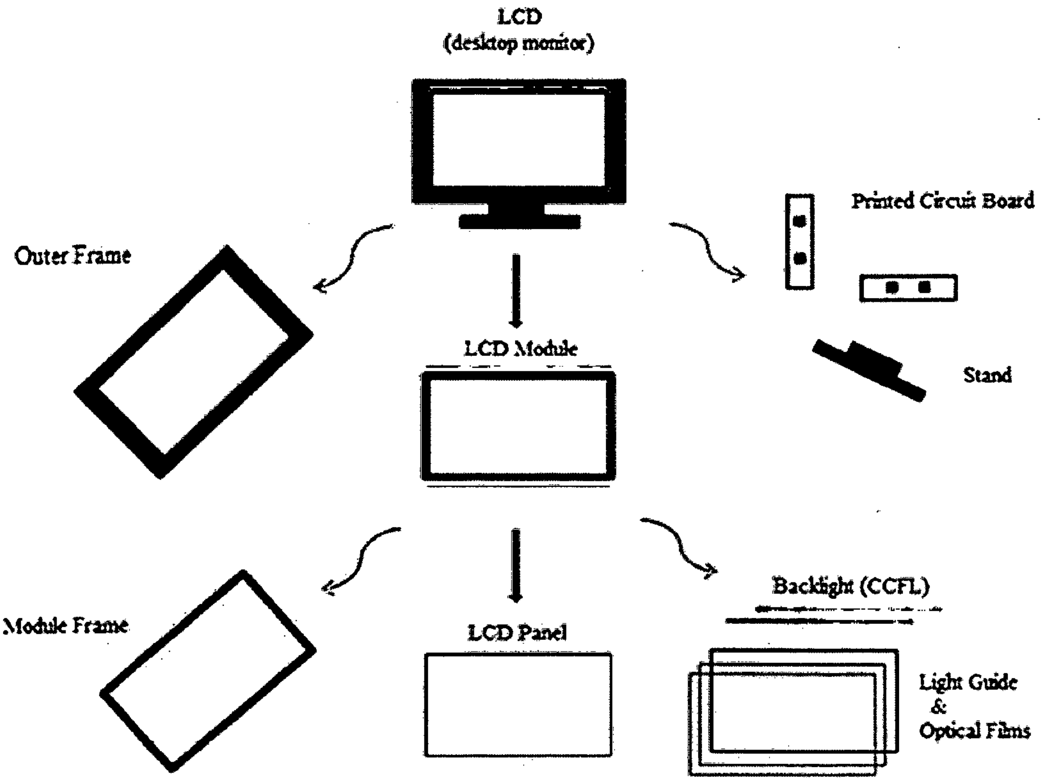


Figure 2-1: The main components within a LCD, and its general structure.

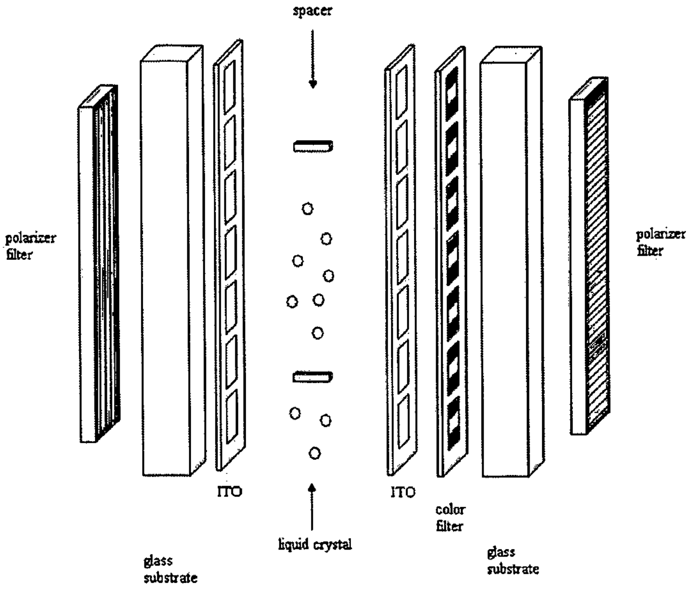


Figure 2-2: the internal structure and component of an LCD panel

ITO is a thin film acts as semiconductor optoelectronic material, processing special physical properties of visible light transmission, electric conduction, high hardness and chemically stable. Therefore ITO is widely used in a lot of optoelectronic equipments for transparent and conductive display LCD and plasma display panel (PDP), organic light emitting diode (OLED) and touch panel. Almost 60% indium production was used for the preparation of ITO films (Alfantazi A M, Moskalyk R R, 2003). Usually ITO film was prepared by DC magnetron sputtering technology using ITO targets. Nevertheless, 85% of the ITO target which need to be recovered could not be utilized for magnetron sputtering (Chen J et.al, 2003).

Wastern governments are awakening slowly to the threat of losing access to the key elements and expert panels in the EU and US have published the report (Critical raw material for the EU, 2010) that identified 14 raw materials and metal groups including all the rare earth and platinum group metal as well as antimony, beryllium, cobalt, gallium, germanium, graphite, indium, tungsten, niobium is abundant and rare earth crust. The expert team that compiled the report would see the recycling is more efficient rather than mining ores and keen to promote the research into recycling technically challenging products.

Globally, most primary indium is recovered as a by-product of processing zinc ores. As such it is considered as 'at risk' because its supply is dependent on prices of other commodities. Global secondary indium production increased significantly during the past several years and now accounts for a greater share of indium production than primary. This trend is expected to continue in the future. In 2007 (Department of Natural Resources and Mines, 2014) several major secondary indium producers in Japan and the Republic of Korea announced plans to further increase their recycling capacity. The indium market, however, remained in deficit as demand for the metal, supported largely by indium tin oxide (ITO) demand, continued to outpace supply. In 2007, year-on-year shipments of LCD television panels, which are a major use of indium, were forecast to increase by 47%, and LCD monitor panels to increase by 24%. Mainstream LCD devices were also trending toward larger panel sizes, which require more indium per unit (Department of Natural Resources and Mines, 2014).

Increased manufacturing efficiency and recycling (especially in Japan) maintain a balance between demand and supply. According to the United Nations Environment Programme, indium's end-of-life recycling rate is less than 1%. Demand increased as the use of the metal in LCDs and televisions increased, and supply decreased when Chinese mining concerns stopped extracting indium from their zinc tailings. In 2002, the price was US$94 per kilogram. Recent changes in demand and supply have resulted in high and fluctuating prices of indium, which from 2006 to 2009 ranged from US$382/kg to US$918/kg (Department of Natural Resources and Mines, 2014).

It has been estimated that there are fewer than 14 years left of indium supplies, based on current rates of extraction, demonstrating the need for additional recycling.

2.4 REE recycle and recovery

The electronic waste that contain REEs are typically being disposed rather than being recycled. All the scrap materials were labeled as hazardous waste and being disposed in a suitable area with safety handling guideline. Recovery and recycling of magnets will be more attractive in a future year as the demand of this high quality magnet does keep increasing as the expected trend a shown in figure 4. It is admitted that 300,000 tons of REEs was trapped in waste electric and electronics equipment (WEEE) waste streams in Japan today (EPOW, 2011a), and Japan is, as mentioned earlier, the only country in the world where there are some activity on recycling of rare earth magnets to date (Oakdene Hollins, 2010). Japan nowadays with the collaboration between Honda and Japan Metals & Chemicals Co., Ltd had already established the recovery of REE from recycled nickel-metal hydride batteries.

A novel technique was presented before for indium oxide recover without the difficulties described in method applied before. Efforts to recycle the valuable materials especially rare metal like indiums (G.Phipps et.al; 2008) from Liquid Crystal Display (LCD) wastes and indium tin oxide (ITO) targets have been investigated by many researchers. Most methods on indium recovery have concentrated via acid dissolution or acid leaching (J.Li et.al, 2009 and Y.Liet.al, 2011), and indium recovery has been reported.

LCD glass substrate cannot be reused because unresolved thin films cannot be peeled from the glass surface. The glass used for LCD panel is made of high quality glass and is expensive due to the difficulty to produce high silica content, low density, large flat panels, good surface quality, high heat resistance, and dimensional stability glass panels. Sub- critical water (sub-CW) has been utilized for recovery and/or production of valuable resources from solid waste and is gaining interest due to its potential as solvent with hydrolysis power and catalyst for organic reaction. This technique is based on the use of water as medium, at temperatures between its boiling point (100 °C) and its critical point (374 °C) and at pressures high enough to maintain the liquid state (Hiroyuki Yoshida et.al, 2014). Sub-critical water treatment in are action time of 5min and temperature of 360 1C showed a remarkable 83% (337mg/kg- GL) indium recovery from CF glass, but7% (22mg/kg-GL)in TFT glass. Optic microscopic images and TOC analysis implied that sub- CW treatment caused exfoliation of ITO covered with organic multilayers, which did not dissolve in the sub-CW. This phenomenon is very advantageous because indium can simply be separated from CF glass and easily recovered by filtration. High purity indium product can then be produced just by burning the filtered material, which is small amount, economically. Transparent and quality glass was simultaneously recovered from CF glass (Hiroyuki Yoshida et.al, 2014).

Table 2.2: Recycling operations, technologies utilized current status and benefits (EPA Report, 2012)

Company	Target Feedstock/ Element	Technology to Be Used	Anticipated Time to Commercialization	Benefits (Cost and Environmental)
Hitachi	Rare earth magnets from air conditioner compressors and hard disk drives	Automated separation process and dry extraction process	Anticipates recycling will meet 10% of its need by 2013 when facility goes online	Dry extraction method that allows processing without acids; resulting waste water problem. Automated separation process is faster than manual. Cost savings anticipated.
Toyota	Hybrid car batteries	Unknown	Ongoing	Main driver is supply concerns
Japan's Shin-Etsu Chemical	Air conditioners	Plans to recycle recovered REEs into magnets	2011	No information readily available.
Showa Denko KK	Dysprosium and didymium (a mixture of praseodymium and neodymium)	No information readily available.	Estimated output of 800 tons from recycling facility	No information readily available.

2.5 *Acid leaching*

Leaching process will involve the interaction between the sorbent, analyte and the solvent. Leaching rate of rare earth element basically influence by the solvent concentration, temperature, time, liquid to solid ratio and also by the stirring agitation speed during mixing between rare earth element and the solvent. Leaching rate is directly proportional to those factors. In leaching, there are transport process between solvent and the surface of element. Leaching mechanism of rare earth is ion exchange between positive-ion in solution and the surface of rare earth material (A. Żwir-Ferenc,2006). Due to the factor that will affect the leaching rate, the solvent must have high concentration and have high saturation limit and selectivity in order to produce an optimum quality of extracted product. The most suitable solvent usually used in leaching of rare earth element was an acidic solution such as HCl, H_2SO_4, and HNO_3.