

**A COMPARATIVE STUDY OF DIFFERENT
COLLECTORS IN THE FLOTATION OF RARE
EARTH MINERAL**

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**A COMPARATIVE STUDY OF DIFFERENT COLLECTORS IN THE
FLOTATION OF XENOTIME**

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled 'A Comparative Study of Different Collectors in The Flotation of Rare Earth Mineral'. I also declare that it has not been previously submitted for the award of any degree or diploma or other similar title of this for any other examining body or University.

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TABLE OF CONTENTS

DECLARATION.....	i
ACKNOWLEDGEMENT.....	ii
TABLE OF CONTENTS.....	iii
LIST OF TABLES	vi
LIST OF FIGURES	vii
LIST OF SYMBOLS	x
LIST OF ABBREVIATIONS	xi
ABSTRAK	xii
ABSTRACT	xiii
CHAPTER 1 INTRODUCTION.....	1
1.1 Background to Rare Earth Minerals.....	1
1.2 Occurrence of REE in Malaysia.....	2
1.2.1 On-shore Alluvial (Placer) Xenotime and Monazite.....	2
1.2.2 Ion Adsorption Clays	2
1.2.3 Marine Sediment Deposits	3
1.3 Rare Earth Minerals Extraction Method	3
1.4 Problem Statement	4
1.5 Objectives of Research.....	5
1.6 Scope of Study	5
1.7 Contributions and Industrial Relevance of the Current Research	6
1.8 Outline of Thesis	6
CHAPTER 2 LITERATURE REVIEW.....	8
2.1 Introduction	8
2.1.1 Positions in Periodic Table.....	8
2.2 Global Distribution of Rare Earth Deposits	9

2.3	Application of Rare Earth Elements.....	11
2.4	Xenotime Mineral	11
2.4.1	Mineralogy of Xenotime	13
2.4.1(a)	Specific Gravity	13
2.4.1(b)	Magnetic and Electrostatic Response	14
2.4.1(c)	Crystal Structure	15
2.5	Froth Flotation of Xenotime Minerals	17
2.5.1	Temperature	18
2.5.2	pH.....	20
2.5.3	Reagent.....	22
2.5.3(a)	Collectors	23
2.5.3(b)	Depressants	28
2.6	Industrial Flotation of Rare Earth Minerals	32
2.6.1	Bayan Obo Rare Earth Mine	32
2.6.2	Mountain Pass Rare Earth Mine.....	35
CHAPTER 3 METHODOLOGY.....		39
3.1	Introduction	39
3.2	Materials and Chemicals	39
3.3	Overview of Research Work	40
3.3.1	Feed Sample Preparation and Characterization	41
3.3.2	Flotation of Xenotime	42
3.3.3	Characterization of Flotation Products.....	43
3.4	Preparation of Feed Sample	44
3.4.1	Grinding	44
3.4.2	Sieving.....	45
3.4.3	Mixing.....	45
3.5	Sample Characterization	46

3.5.1	X-ray Fluorescence (XRF) Analysis	46
3.5.2	X-ray Diffraction (XRD) Analysis.....	47
3.5.3	Particle Shape Analysis.....	47
3.5.4	Particle Size Analysis (PSA).....	48
3.6	Froth Flotation of Xenotime.....	50
CHAPTER 4 RESULTS AND DISCUSSION.....		53
4.1	Characterization of Flotation Feed Sample	53
4.1.1	XRF Analysis of Feed Sample	53
4.1.2	XRD Analysis of Feed Sample	54
4.1.3	Particle Shape Analysis of Feed Sample.....	54
4.1.4	Particle Size Analysis of Feed Sample.....	56
4.2	Froth Flotation.....	57
4.2.1	Effects of Collectors.....	57
4.2.2	Effect of Collector’s Concentration	60
4.2.3	Effect of Depressant	64
CHAPTER 5 CONCLUSION AND FUTURE RECOMMENDATIONS.....		69
REFERENCES.....		71

LIST OF TABLES

	Page
Table 2.1 Major Applications of Rare Earth Elements (Charalampides et al., 2015)	12
Table 2.2 Physical Characteristics of Xenotime and Major Gangue Minerals ..	13
Table 2.3 Nitrogenous Collectors Used in Rare Earth Flotation (Luo et al., 2002)	25
Table 2.4 Distribution of REOs in Bayan Obo Deposit (Li and Yang, 2014). ..	33
Table 3.1 List of Chemicals	40
Table 3.2 Flotation Experimental Variables	52
Table 4.1 Composition of Minerals in Feed Sample.....	53
Table 4.2 Particle Size Analysis Result for Feed Sample	56

LIST OF FIGURES

	Page
Figure 1.1	Principle of Froth Flotation (Wills et al., 2006).....4
Figure 2.1	Periodic Table of Elements. Rare Earth Elements are Highlighted in Orange (Dahlgren and Coint, 2019).....9
Figure 2.2	Global Rare Earth Resources (Chen, 2011) 10
Figure 2.3	Atomic Arrangement of Xenotime (Yunxiang et al., 1995) 16
Figure 2.4	Crystal Phase of Xenotime (Yunxiang et al., 1995)..... 17
Figure 2.5	Adsorption densities of xenotime a function of pH with different concentration of octano-hydroxamic acid solution after shaking for 20 hours at room temperature and 80°C (Zhang, 2016)..... 18
Figure 2.6	Microflotation recoveries of xenotime and gangue minerals with 0.0005M octano-hydroxamic acid as a function of pH at room temperature (Zhang, 2016).....21
Figure 2.7	Microflotation recoveries of xenotime and gangue minerals with 0.0005M sodium oleate as a function of pH at room temperature (Zhang, 2016).....21
Figure 2.8	Satellite Image of Bayan Obo Mining Area in 2021.....33
Figure 2.9	Beneficiation Flowsheet of the Bayan Obo Deposit Ore (Li and Yang, 2014).....35
Figure 2.10	Satellite Image of the Mountain Pass Mining District, CA in 2021 ..36
Figure 2.11	A flowsheet for the flotation beneficiation of bastnaesite ore at Mountain Pass (Pradip and Fuerstenau, 1991).....36
Figure 3.1	Feed Sample Preparation and Characterization Flowchart41
Figure 3.2	Flotation of Xenotime Flowchart42
Figure 3.3	Characterization of Flotation Products Flowchart.....43
Figure 3.4	Ground Sample in Ring Mill.....44

Figure 3.5	Jones Rifle Splitter	45
Figure 3.6	Hitachi TM3000 Scanning Electron Microscope.....	48
Figure 3.7	Malvern Particle Size Analyzer	49
Figure 3.8	Denver Flotation Cell.....	50
Figure 3.9	Conditioning Process	51
Figure 3.10	Froth Flotation Process	51
Figure 3.11	Milipore Pump Filtration System	51
Figure 4.1	The XRD Pattern for Feed Sample	54
Figure 4.2	Particle Shape of Feed Sample in Different Degree of Magnification	55
Figure 4.3	Particle Size Distribution Graph	57
Figure 4.4	Grade of Xenotime and Selected Gangue Minerals with 0.0005M HXM vs. 0.0005M SOT, without Depressant.....	58
Figure 4.5	Grade of Xenotime and Selected Gangue Minerals with 0.0005M HXM vs. 0.0005M SOT, with Depressant.....	59
Figure 4.6	Effect of HXM Concentration on The Minerals' Grade without Depressant.....	60
Figure 4.7	Schematic representation of the mineral-solution interface in the presence of anionic collector: (a) Single ion adsorption at low concentration. (b) Hemi-micelle formation at higher concentrations. (c) Multilayer adsorption. (Gaudin and Fuerstenau).....	61
Figure 4.8	Effect of SOT Concentration on The Minerals' Grade without Depressant.....	62
Figure 4.9	Effect of HXM Concentration on The Minerals' Grade with Depressant.....	63
Figure 4.10	Effect of SOT Concentration on The Minerals' Grade with Depressant.....	64

Figure 4.11	Effect of Sodium Silicate on The Minerals' Grade with 0.001M HXM	65
Figure 4.12	Effect of Sodium Silicate on The Minerals' Grade with 0.001M SOT	66

LIST OF SYMBOLS

g	Gram
kg	Kilogram
μm	Micrometer
$^{\circ}\text{C}$	Degree Celsius
%	Percentage
M	Molarity

LIST OF ABBREVIATIONS

XRF	X-Ray Fluorescence
XRD	X-Ray Diffraction
SEM	Scanning Electron Microscopy
PSA	Particle Size Analysis
REE	Rare Earth Element
REM	Rare Earth Mineral
HREE	Heavy Rare Earth Element
LREE	Light Rare Earth Element
HXM	Octano-hydroxamic Acid
SOT	Sodium Oleate
SS	Sodium Silicate

A COMPARATIVE STUDY OF DIFFERENT COLLECTORS IN THE FLOTATION OF RARE EARTH MINERAL

ABSTRAK

Aplikasi unsur nadiir bumi (REE) dalam pelbagai bidang telah menyebabkan permintaan untuk mineral mengandungi REE (REM) meningkat. Xenotime (YPO_4) sebagai sumber yttrium (Y) sering diperlukan untuk sifat superkonduktornya dan juga sebagai bahan tambahan dalam aloi. Pengapungan buih yang merupakan kaedah asas untuk memproses mineral kompleks yang biasanya mengandungi unsur nadiir bumi. Penyelidikan ini dilakukan untuk membandingkan keberkesanan antara dua surfaktan yang berbeza (asid oktano-hidroksamik dan natrium oleat) dan kesan kepekatan dalam pengapungan xenotime. Kajian pengapungan mineral dijalankan menggunakan peralatan pengapungan bangku dengan keadaan pH 7 dan pada suhu bilik. Sampel suapan juga dianalisis menggunakan analisis saiz zarah (PSA), pembelauan sinar-x (XRD), fluorescene sinar-x (XRF) dan mikroskop pengimbasan elektron (SEM). Dengan ketiadaan depresan, asid oktano-hidroksamik menunjukkan selektiviti yang lebih kuat dalam mengapungkan xenotime berbanding natrium oleat. Penambahan kepekatan surfaktan dalam pengapungan akan menambahkan gred xenotime tetapi aplikasi pada kepekatan yang terlalu tinggi adalah memudaratkan. Kepekatan optimum bagi pengapungan xenotime adalah pada 0.001M. Secara keseluruhan, penambahan natrium silikat sebagai depresan akan menambahkan gred xenotime dan berhasil menekan silika dan alumina. Namun begitu, ia tidak menunjukkan sebarang kuasa depresan terhadap hematit. Pengetahuan yang diperoleh daripada penyelidikan ini diharapkan dapat memberi panduan dalam memilih surfaktan yang sesuai untuk pemulihan xenotime dalam industri.

A COMPARATIVE STUDY OF DIFFERENT COLLECTORS IN THE FLOTATION OF RARE EARTH MINERAL

ABSTRACT

Application of rare earth elements (REE) in various fields had caused the demand for REE-bearing minerals (REM) to spike in these recent years. Xenotime (YPO₄), a source of yttrium (Y) is often sought for its high-temperature superconductors properties and also as an additive in alloys. Froth flotation as a fundamental method for processing complex minerals is commonly applied in the beneficiation of rare-earth-bearing minerals. This research program was designed to compare the effectiveness between two different collectors (octano-hydroxamic acid and sodium oleate) and its concentration on xenotime flotability. The froth flotation study is carried out using bench flotation equipment with the condition of pH 7 and at room temperature. Samples were also characterized using Particle Size Analysis (PSA), X-ray Diffraction (XRD), X-ray Fluorescence (XRF) and Scanning Electron Microscopy (SEM). In the absence of depressant, octano-hydroxamic acid shows better selectivity in the flotation of xenotime than sodium oleate. On the other hand, sodium oleate produces better grade of xenotime with the presence of depressant. Increases in concentration will improve xenotime grade but at higher concentration it can be detrimental. Optimum concentration for xenotime flotation was found at 0.001M. Overall, the addition of sodium silicate as depressant can significantly increase xenotime grade and successfully depress silica and alumina. However, it shows no depressing power on hematite. The knowledge gained from this work will be beneficial in selecting appropriate collectors for xenotime recovery in the industry.

CHAPTER 1

INTRODUCTION

1.1 Background to Rare Earth Minerals

The rare earth elements (REEs) consist of the 15 elements with atomic numbers ranging from 57 to 71 in the Lanthanide Group of the Periodic Table, as well as yttrium (39) and scandium (21), all of which exhibit similar chemical characteristics and behaviour. Light rare earth elements (LREEs) include atoms with atomic numbers between 57 and 63, whereas heavy rare earth elements (HREEs) include elements with atomic numbers between 64 and 71 (Long et al., 2010).

The scientific knowledge and technological use of rare earth elements (REEs) have made remarkable breakthroughs in the past five decades, despite being generally unfamiliar. Due to their distinct chemical and physical features, many new applications were discovered over the years. Rare earth elements are significant in today's industry because of their broad use and diverse applications. For instance, classic halophosphors which are comprised of Sb and Mn used in the displays for computers, phones and fluorescent lamps can be substituted to more energy-efficient phosphors made up of Eu, Y, and Tb (Tiesman, 2010).

These elements are frequently found associated as rare earth oxides, with bastnaesite and monazite being the most common minerals. Separating pure elements from the material is the foremost concern with rare earths. As rare earth elements are more common than many other metals, such as gold, the name "rare" does not refer to their scarcity, but rather to the difficulty of obtaining a pure REE (Abaka-Wood et al., 2016). To date, the most common commercially extracted RE-bearing minerals are bastnaesite, monazite, xenotime and loparite.

1.2 Occurrence of REE in Malaysia

According to Akademi Sains Malaysia (ASM), Malaysia has good sources of REEs and REMs occur in various forms and types of deposits, namely:

- i. On-shore alluvial (placer) xenotime and monazite
- ii. Ion adsorption clays containing REEs
- iii. REMs and REEs in marine sediments
- iv. REMs in primary sources

1.2.1 On-shore Alluvial (Placer) Xenotime and Monazite

In earlier times, Malaysia's REMs specifically monazite and xenotime production has always been associated with alluvial, or placer, tin mining. These two REEs are commonly extracted from the re-treatment of tin tailings (also known as amang). Currently, Malaysia's engagement in the RE mineral business is almost solely restricted to the production of monazite and xenotime through the processing of domestic and imported amang.

Monazite and xenotime are widespread across the Peninsula in the stream sediments draining granitic regions and as part of the heavy mineral assemblages in the alluvium along the coast, particularly in the Kinta and Kuala Lumpur tin deposits (ASM, 2019). Both minerals have been extracted profitably as a by-product of alluvial tin mining, despite the fact that they have not been discovered in quantities high enough to be mined independently.

1.2.2 Ion Adsorption Clays

High concentrations of REEs also can be found in ion-adsorption type clays. To date, only the reserves in south China have been exploited commercially, although similar deposits have also been discovered abroad, such as in Laos and Vietnam. Rare earth clay deposits are often associated with tin-bearing granites and

are typically found in tropical regions with hot, humid climates and extensive weathering. The special feature of these deposits is that they are free from radioactive materials, since thorium and uranium are not present. Malaysia has comparable climatic conditions and a vast swath of severely weathered tin-bearing granite. For these reasons, it has been determined that the potential of rare earth clay deposits in this country should be further explored in the future.

1.2.3 Marine Sediment Deposits

Territorial waters in Malaysia, particularly in west coast receive significant amount of sediments carried by rivers that flow through granitic regions. Although the sediments are not identical to deep-sea mud, which has become one of the recognised worldwide REEs sources, it may be beneficial to check previously obtained offshore samples for any signs of REEs mineralization.

On the basis of location, the occurrences of REMs and REEs in marine sediments may be divided into two types: near-shore sediments and international seabed. Jabatan Mineral and Geosains Malaysia (JMG) and numerous other parties had conducted marine sediment surveys indicate that xenotime and monazite indeed exist in marine sediments, but at a quantities that are too low to be extracted at a profit (ASM, 2019).

1.3 Rare Earth Minerals Extraction Method

REEs are commonly found in REMs in small amount, thus a highly selective extraction method needs to be adapted. There are few popular ways in the beneficiation processes of rare earth mineral ores, however, froth flotation is more favourable due to its ability to process a wide range of fine particle sizes and can be tailored to the mineralogy of a specific deposit.

According to Wills et al. (2006), flotation is a physico-chemical separation process that utilizes the difference in surface properties of the valuable minerals and the unwanted gangue minerals. The process of minerals being recovered by flotation from the pulp comprises three mechanisms: (1) selective attachment to air bubbles (or "true flotation"), (2) entrainment in the water which passes through the froth, and (3) physical entrapment between particles in the froth attached to air bubbles (often referred to as "aggregation"). Figure 1.1 provides simple graphical explanation on the principle of froth flotation.

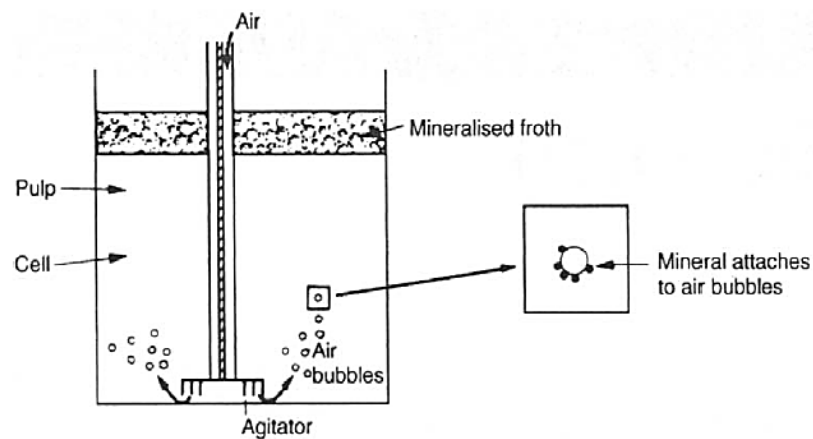


Figure 1.1 Principle of Froth Flotation (Wills et al., 2006)

1.4 Problem Statement

In recent years, REEs has gained enormous attention from the public, economic, and scientific study due to their advancement in modern defence systems, electronic applications, and green technologies. The growing economic and strategic importance of these sectors, coupled with uncertainty in the global supply of REEs from China, have led to concerns about the future availability of many of these metals. Several countries such as USA, the EU and Canada have classified REEs as a critical resource due to these supply concerns and the increasing demand (Marion et al., 2020).

The samples obtained from tailings of tin processing in Kedah were said to contain rare earth minerals (REMs) such as xenotime, monazite and other gangue minerals. However, the concentration of these minerals in the sample are unknown. Hence, characterization of sample needs to be carried out using x-ray diffractometer (XRD), x-ray fluorescence (XRF), scanning electron microscopy (SEM) and particle size analysis (PSA).

The extraction of xenotime using flotation process from the gangue minerals had been done by some of the researchers by using sodium oleate and octano-hydroxamic acid as collectors and pentahydrate sodium silicate and ammonium lignosulfonate as a depressant (Zhang, 2016). However, a comprehensive study has not been made to compare the effectiveness of different collectors' concentrations on the xenotime recovery. The purpose of the test is to compare the effect of different collectors on xenotime recovery.

1.5 Objectives of Research

The main objectives of the research are:

1. To characterize the samples obtained from a site in Kedah.
2. To study the effect of different collector types and concentrations in the flotation of xenotime with and without depressant.

1.6 Scope of Study

This research is carried out to characterize the sample obtained and to determine the concentration of xenotime and other gangue minerals associated in the ore. The characterization step includes the usage of XRD analysis to determine the crystallographic structure of a material, XRF spectrometer to determine the elemental

composition, SEM to analyze the microstructure and Malvern particle size analyzer to measure the particle size.

The samples were then used for the flotation study of the effect of different collector types and concentrations in separating xenotime minerals from the gangue minerals.

1.7 Contributions and Industrial Relevance of the Current Research

In 2010, after China had announced its export quotas on REs, many countries came to attention regarding this resource scarcity problem considering its demand in energy efficiency and high technologies. Since then, countries around the world including Malaysia had step up their research on this topic to combat the issue. However, to date, China is still the main producer of terbium, dysprosium, and yttrium.

Malaysia has promising sources of heavy REEs including xenotime which is a yttrium-bearing mineral and this resource should be utilized well to the country's advantage. Thus, sophisticated processing routes of rare earth minerals must be developed and explored to fully manipulate this resource. This is also ensured that Malaysia has its own resource of rare earths without heavy reliance to imports from other countries. In conclusion, this research can contribute some information and data to further enhance the effectiveness of xenotime flotation in the industry.

1.8 Outline of Thesis

This dissertation consists of five (5) chapters, started with Chapter 1 where a brief overview of the research is written. It consist of a general explanation of the research's background, as well as a brief description of the scope of study and the research's purpose.

Then, followed by Chapter 2, where literature on research studies is reviewed and discussed. In this chapter, the rare earth minerals background, flotation technique, reagents used, and parameters involved in this research were analyzed and explained in detail.

Methodology of experimental work is listed in Chapter 3 with detailed description of the experiment carried out based on the objectives selected, including an explanation of the sample and flotation work preparation, equipment setup (bench flotation cell), and characterization analysis methods to be used.

Chapter 4 consist of analysis data and results' discussion. Interpretation, explanation, and comparison of the experiment's data and results obtained from all the characterization tests are documented in this chapter.

Conclusion of the experiment and future recommendations are written in Chapter 5. The research findings were summarized and some recommendations were made to improve the experiment so that the data and results obtained are more accurate and reasonable for future research.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Rare earth elements (REEs) represent a set of 17 elements, which include 15 lanthanides (La-Lu), yttrium (Y), and scandium (Sc) (Meija et al., 2016, Xiao et al., 2016). REEs enriched in REE-bearing minerals of igneous rocks, such as apatite, allanite, monazite, titanite, xenotime and etc. in the lower mantle during magmatic differentiation (Castor and Hedrick, 2006), except continental rifts, which contain carbonatite and kimberlites (Hoshino et al., 2016). REE deposits are generally divided in accordance with their mineralogy and geneses: primary deposits associated with igneous and hydrothermal activities and secondary deposits assembled through sedimentary processes and weathering (Lusty and Walters, 2010).

2.1.1 Positions in Periodic Table

The REEs are mainly classified into two groups: light-group REE (LREE) and heavy-group REE (HREE).

The LREE are defined as the elements lanthanum, with atomic number 57, through gadolinium, with atomic number 64; they all contain an increasing number of unpaired electrons in the f subshell, from 0 to 7. The HREE are terbium, with an atomic number of 65, through lutetium, with an atomic number of 71, and yttrium, with an atomic number of 39.

All of the HREE differ from the first eight lanthanides in sense that they have paired electrons (a clockwise and counter-clockwise spinning electron) in the f subshell unlike LREE which have no paired electrons in the f subshell. Yttrium is a member of the HREE group due to its identical ionic radius and chemical characteristics. Scandium is likewise trivalent, but its other qualities are not similar

enough for it to be classified as an LREE or an HREE, thus coloured yellow in Figure 2.1.

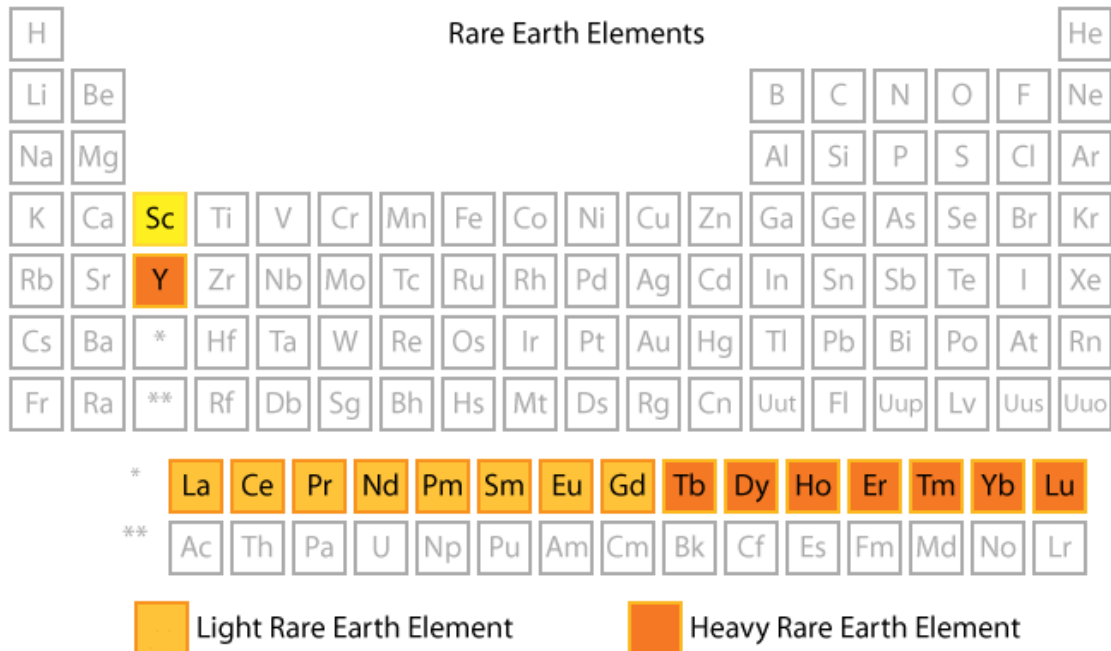


Figure 2.1 Periodic Table of Elements. Rare Earth Elements are Highlighted in Orange (Dahlgren and Coint, 2019)

2.2 Global Distribution of Rare Earth Deposits

In estimation, about 34 countries was known to possess a substantial amount of rare-earth resources (as shown in Figure 2.2) and in fact, REEs are widely scattered throughout the Earth's crust (Chen, 2011), besides coexisting with other mineral deposits. Alas, only a small handful are economically viable to mine, such as at the Bayan Obo mine in China where bastnaesite is extracted together with iron-bearing minerals (Long et al., 2010a). Hopefully as the technology advances in the future, more rare-earth deposits can be discovered and profitably exploited.

In contrast to Australia, where the main REMs existed are monazite and xenotime, many rare-earth deposits in the US and China are mostly rich in bastnaesite. Meanwhile, promising xenotime resources can be found in southern China and

Malaysia (Haque et al., 2014). Other than land-based deposits, Dubinin (2004) also had considered and suggested that the largest sources of REEs in the future may be the ocean sediments produced by hydrothermal plumes in the East Pacific Rise and the Juan de Fuca Ridge.

Despite the fact that many rare-earth resources have been discovered worldwide, only few are currently in use with the three most significant are Mountain Pass in the US, Bayan Obo in China, and the recently opened Mount Weld in Western Australia (Malik, 2015). Currently, China is known to home around 55% of rare-earth resources which has made them the biggest supplier of rare-earth metals in the world. This gave them the ability to dominate the market through supply, mining, and refining, which leads to the closure of numerous mines outside of China.



Figure 2.2 Global Rare Earth Resources (Chen, 2011)

2.3 Application of Rare Earth Elements

The beginning of rare earth industry boom started in the early 1960s upon the discovery of the intense red luminescence of Eu when excited by electrons, which was soon utilized in colour television. Since then, rare earth industry had witnessed a significant growth thanks to the huge increase of academic research, development and worldwide interest. REEs played a huge role in human civilization and everyday life.

REE exceptional physical and chemical properties are the features which make them ideally suited for, and critical in, high technology and green technology applications. Neodymium (Nd), dysprosium (Dy), terbium (Tb), europium (Eu), and yttrium (Y) are the five REEs crucial to green technology (Y).

The vast variety of REEs uses, from defense technology to our everyday household and also in industrial uses and products, such as in computers, lasers, chemical processing, proves their significance in fueling Industry 4.0 as well as in the Internet of Things. Table 2.1 lists some of the main uses of REEs.

2.4 Xenotime Mineral

One of the main yttrium-bearing minerals, known as xenotime, is frequently discovered in placer deposits alongside carbonate, uranium ore, iron ore, or weathered clays. It is also widely distributed as an accessory mineral in a variety of rock types, including those found in magmatic, sedimentary, and metamorphic environments. However, it is most frequently found in carbonates, hydrothermal mineral deposits, and certain alkali magmatic rocks. Other sizable but less significant yttrium resources were found in sedimentary phosphate deposits, niobium-tantalum deposits, apatite-magnetite deposits, and non-placer xenotime-monazite deposits (Chelgani et al., 2015; Zhang, 2016). Xenotime, which is essentially a primary source of HREE (e.g. Eu and

Gd) and small amount light rare earth elements (LREE) (La to Eu), is located at the one end of a compositional solid-solution with monazite (Cheng et al., 1994; Kolitsch and Holtstam, 2004).

Table 2.1 Major Applications of Rare Earth Elements (Charalampides et al., 2015)

REE	Symbol	Application
Scandium	Sc	High-strength Al-Sc alloys, electron beam tubes
Yttrium	Y	Capacitors, phosphors, microwave filters, glasses, oxygen sensors, radars, lasers, superconductors
Lanthanum	La	Glasses, ceramics, car catalysts, phosphors, pigments, accumulators
Cerium	Ce	Polishing powders, ceramics, phosphors, glasses, catalysts, pigments, misch metal, UV filters
Praseodymium	Pr	Ceramics, glasses, pigments
Neodymium	Nd	Permanent magnets, catalysts, IR filters, pigments for glass, lasers
Promethium	Pm	Sources for measuring devices, miniature nuclear batteries, phosphors
Samarium	Sm	Permanent magnets, microwave filters, nuclear industry
Europium	Eu	Phosphors
Terbium	Tb	Phosphors
Dysprosium	Dy	Phosphors, ceramics, nuclear industry
Holmium	Ho	Ceramics, lasers, nuclear industry
Erbium	Er	Ceramics, dye for glass, optical fibers, nuclear industry
Ytterbium	Yb	Metallurgy, chemical industry
Lutecium	Lu	Single crystal scintillators
Thulium	Tm	Electron beam tubes, visualization of images in medicine
Gadolinium	Gd	Visualization of images in medicine, optical and magnetic detection, ceramics, crystal scintillators

2.4.1 Mineralogy of Xenotime

Although there are hundreds types of rare earth bearing minerals discovered, it is uncommon for them to be extracted as main product due to inadequate concentration. Primarily, rare earths are obtained as the by-products of other industrial minerals. The three dominant minerals according to abundance, high rare-earth content and practicability to processing on an industrial scale are monazite, bastnaesite and xenotime.

Xenotime as one of the three major REMs are often found in beach placers occur in Australia, Southern China, India, and Malaysia. In this research, xenotime is associated with other major gangue minerals such as alumina, silica, hematite and rutile in the feed sample. Table 2.2 lists the composition and some physical properties of the minerals.

Table 2.2 Physical Characteristics of Xenotime and Major Gangue Minerals

Mineral	Empirical Formula	Molecular Weight	Crystal System	Specific Density	Hardness
Xenotime	Y(PO ₄)	183.88	Tetragonal	4.75	2.5
Alumina	Al ₂ O ₃	101.96	Trigonal	4.10	9.0
Silica	SiO ₂	60.080	Orthorhombic	2.65	7.0
Hematite	Fe ₂ O ₃	159.69	Hexagonal	5.30	6.5
Rutile	TiO ₂	79.866	Tetragonal	4.25	6.0

2.4.1(a) Specific Gravity

In mineral processing, particularly gravity separation process, the specific gravity of the mineral is an important parameter that need to be taken into consideration. The viability of gravity separation to separate two or more minerals (having different specific gravity) using a fluid medium, significantly relies on how each of them moves in reaction to gravity and one or many additional factors, such

"buoyancy". The concentration criterion (CC) provides a general guide to determine the efficiency of gravity separation (Burt, 1987) :

$$CC = \frac{Dh - Df}{Di - Df}$$

Where: Dh = Sp. Gr. of heavy particle

Di = Sp. Gr. of light particle

Df = Sp. Gr. of fluid medium (usually water, $Df = 1$)

If $CC > 2.5$, the separation is considered relatively easy; if $2.5 > CC > 1.25$, the separation is considered difficult or possible; and if $CC < 1.25$, the separation is considered impossible except for heavy liquids.

The specific gravities of xenotime and the major gangue minerals are 4.75 for xenotime, 4.1 for alumina, 2.65 for silica, 5.3 for hematite, and 4.25 for rutile. If water is used as the fluid medium, the CC for separating xenotime against each gangue mineral is 1.2, 2.27, 1.15, and 1.15, respectively, indicating that only silica is relatively easy to separate from xenotime by gravity separation. However, the sample is dried slime from the tailings of tin processing which made water unsuitable as medium for separation.

2.4.1(b) Magnetic and Electrostatic Response

At room temperature, xenotime has a paramagnetic response and non-electrostatic response. Alumina is diamagnetic and non-electrostatic response. Silica is non-magnetic and non-electrostatic response. Hematite responds weakly to magnet but have electrostatic response. Lastly, rutile is diamagnetic and have electrostatic response. This indicates that it is possible to separate hematite and rutile by electrostatic separator, however, this pre-treatment is not carried out in this experiment.

2.4.1(c) Crystal Structure

Each mineral has its own unique and distinctive arrangement of atoms, ions or molecules in its crystalline solid (or liquid) known as crystal structure. Crystals are classed into four groups: (1) ionic crystals; (2) molecular crystals; (3) atomic crystals and (4) metal crystals, based on the distinct properties of bonding energy and intrinsic patterns to connect mass points in minerals. Majority of the rare-earth minerals are ionic crystals. From previous study, it is widely believed that crystal structure dictates the microstructure and surface chemistry of the mineral. Thus, the crystal structure of a mineral directly affects the minerals' floatability and the selectivity of flotation reagents.

The correlations between mineral's crystal structure and its floatability have been studied previously by some researchers. In 1975, Manser discovered that the adsorption of anionic collector increases when the cationic metal ions on the surface of silicate minerals increases. They also found that the bigger the activated area of -SiOH and SiO^- on the surface, the more cationic collector could be adsorbed.

Study on the correlations between crystal structure and flotation behaviors of silicate minerals also carried out by Fuerstenau and Raghavan in 1977. They concluded that most silicates were ionic crystals and its flotation performance is at best when chemical bond is formed between the collector and cationic metal ions on the mineral's surface. Other research shows that the increasing amount of broken Al-O bonds and the increasing ratio of Al-O to Si-O bonds both had significant effects on the isoelectric point (IEP), point of zero charge (PZC), and flotation recoveries of diaspore, kaolinite, pyrophyllite, and illite (Hu et al., 2003).

To date, comprehensive researches on the characterization of xenotime crystal structure are still lacking. According to Yunxiang and others (1995), the structure of

xenotime is tetragonal, with $a = 6.89 \text{ \AA}$, $b = 6.03 \text{ \AA}$, $c = 6.03 \text{ \AA}$ and $a:c = 1:0.875$ and has equal numbers of PO tetrahedra and REO₈ polyhedra. It possesses a regular REO₈ polyhedron that accommodates the smaller HREE elements, which is the most common coordination number for the respective groups of REEs. The fundamental atomic arrangement of xenotime has the structure that the [001] chains are formed of alternating rare-earth (RE) polyhedra and phosphate tetrahedra (so-called polyhedron-tetrahedron chains).

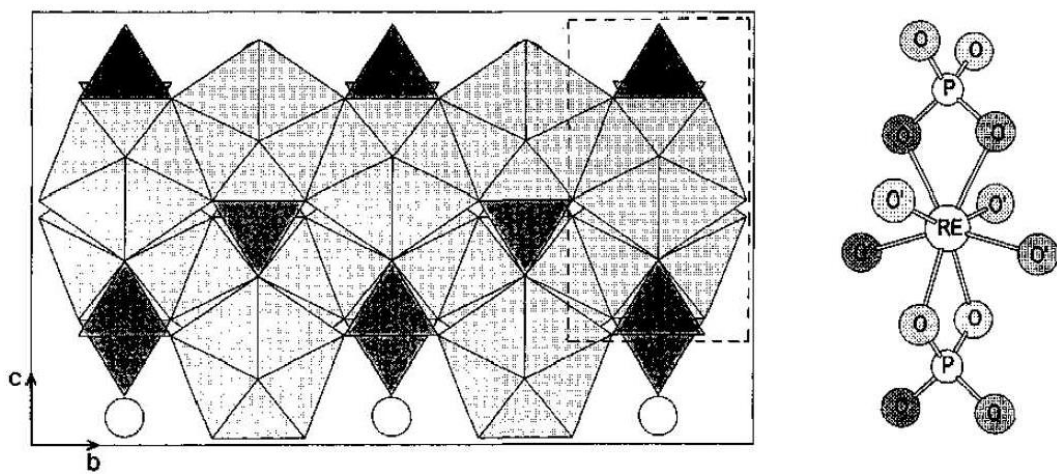


Figure 2.3 Atomic Arrangement of Xenotime (Yunxiang et al., 1995)

Figure 2.3 depicts the polyhedron-tetrahedron chains in the xenotime structures. The chains extend along by sharing tetrahedral edges with REE polyhedra and there are four chains per unit cell in the mineral. The chains are linked laterally by sharing edges of adjacent REO₈ polyhedra.

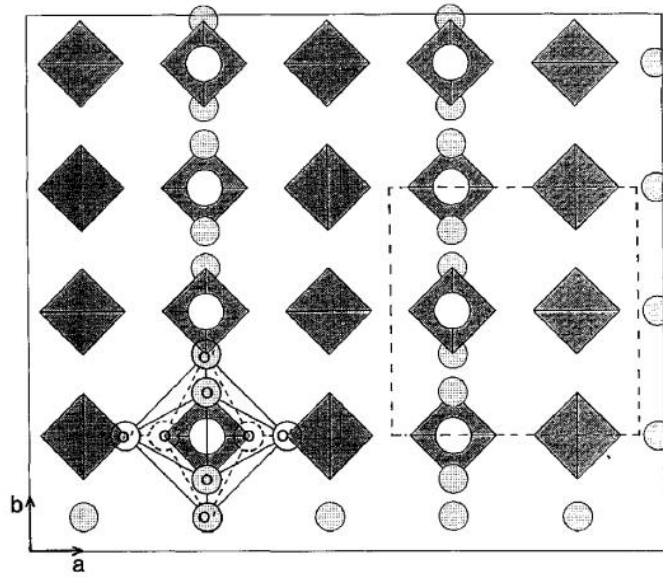


Figure 2.4 Crystal Phase of Xenotime (Yunxiang et al., 1995)

The crystal phase of xenotime illustrated in Figure 2.4 shows that the phosphate tetrahedra exist in planes perpendicular to a^* , with two such planes in the unit cell of each phase. Each of these tetrahedra represents the projection of a polyhedron-tetrahedron chain. The tetrahedra are in rows parallel to a and b , and the shared edges of the tetrahedron are parallel to a or b . The atomic arrangement accommodates the smaller HREE in the REO_8 polyhedron, the most common coordination for the HREE.

2.5 Froth Flotation of Xenotime Minerals

Froth flotation has been used to increase recovery and grade of xenotime due to its highly selective ability during extraction process. This process is also favourable because of its potential to process a wide range of fine particle sizes and can be tailored to the mineralogy of a xenotime. Recovery of xenotime depends on pH, flotation time, collector concentration, and temperature. According to certain studies, xenotime is somewhat more floatable than monazite (Cheng et al., 1993).

2.5.1 Temperature

Through previous research and studies, it is acknowledged that rise in temperature will enhance the adsorption of the collector in chemisorbing-types of flotation. This perhaps cause by the increase in the free energy in solid-liquid system which offers hydroxamate ions more active areas on the surfaces of ore to adsorb on. Zhang (2016) in his study to investigate the role of temperature in the adsorption of minerals including xenotime, found that the adsorption density for each mineral was much higher at 80 °C than those at room temperature (Figure 2.5).

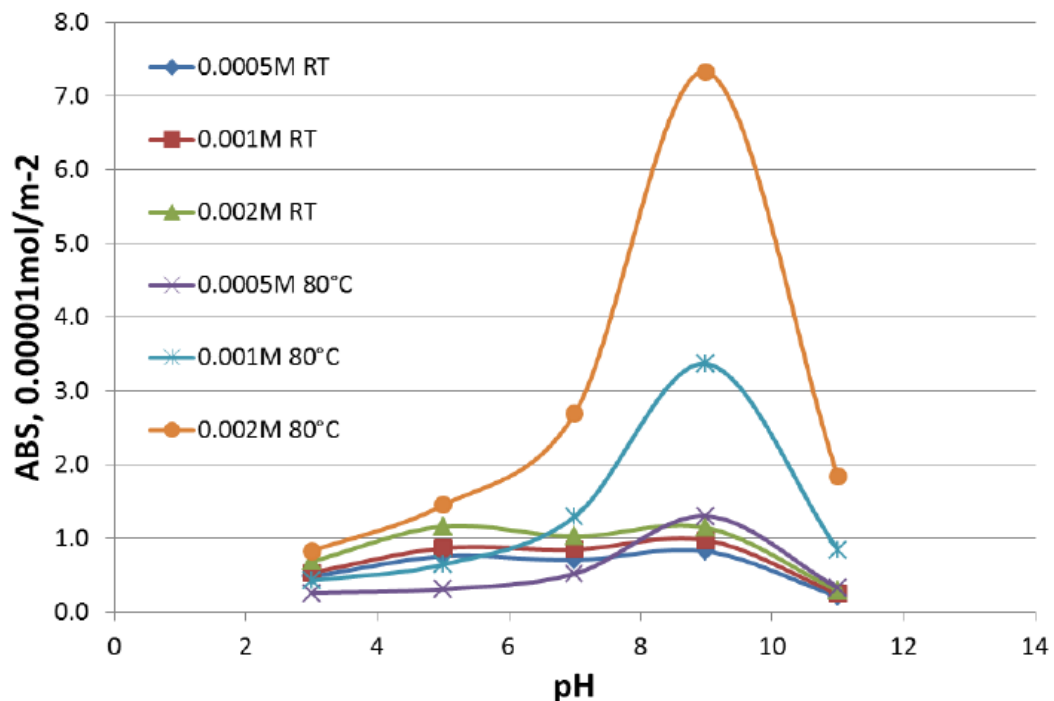


Figure 2.5 Adsorption densities of xenotime a function of pH with different concentration of octano-hydroxamic acid solution after shaking for 20 hours at room temperature and 80°C (Zhang, 2016)

The same observation also documented by Cheng et al. (1994), Zhang (2014) and Anderson (2015). From literature, the monolayer adsorption density of octano-hydroxamic acid was calculated to be $8.1 \times 10^{-6} \text{ mol.m}^{-2}$ at room temperature while relatively low adsorption densities were found for other minerals. The result thus indicate that octano-hydroxamic acid was monolayer-adsorbed on the surface of

xenotime in wide pH range from 5 to 9. Overall, it can be concluded that the adsorption density of octano-hydroxamic acid for each mineral increased at 80°C, suggesting that multiple layers of hydroxamic acid were adsorbed on the mineral surface. Cheng proposed that at elevated temperature, horizontal monolayers could appear promoting rise in the density which calculated to be $3.0 \times 10^{-6} \text{ mol.m}^{-2}$. Thus, number of layers of hydroxamic acid adsorbed on the surface also increases.

Additionally, after thermodynamic analysis, the comparison of the octano-hydroxamic acid's free energy for adsorption on the surfaces of minerals at ambient temperature and 80°C pointed to chemisorption being the mechanism of adsorption for this collector. Zhang stated that when using the concentration 0.001M of octano-hydroxamic acid at pH 9 as an example, the free energy of adsorption of octano-hydroxamic acid on the surface of minerals increased with an increase in temperature. The effect of temperature on the adsorption density using hydroxamate as the collector also evaluated by Anderson in 2015 and he concluded that the adsorption of hydroxamate was chemisorption.

Recent studies also demonstrate slight decrease in the bubble attachment time from 13.9 ms at 24 °C to 10.7 ms at 64 °C on xenotime, when the constant concentration of oleate (1×10^{-5}). Additionally, increase in concentration of oleate decreased the bubble attachment time to 3.9 ms (Cross and Miller, 1989). In the same work, Cheng et al. (1994) showed that increasing the conditioning temperature lowered the xenotime recovery when sodium oleate was present (which it is not logical). They discovered that at higher pH levels and high temperatures, oleic acid species predominate (oleic acid is a weak acid with little solubility; 16 mg/L at 25 °C). According to the adsorption isotherm studies, oleate molecules initially adsorb to xenotime surfaces in a vertical orientation at a temperature of 25 °C (having a cross-

sectional area of 21 Å), changing primarily to a flat orientation at a higher temperature (having a cross-sectional area of 42 Å). The recovery of xenotime at higher temperatures was shown to be reduced because oleic acid's solubility declined as temperature increased.

2.5.2 pH

According to Wang et al. (2005), at a specific pH range, mineral surface will be activated by dissolved lattice ions resulting many charged ions on the surface are exposed to collector ions. This can stimulate the adsorption of collector ions onto the mineral surface which can increase the efficiency of mineral's floatability. They also stated that a certain acidic conditions (lower pH value), recovery of mineral using flotation can decrease significantly as the desired mineral is suppressed. This condition may happen because cationic ion species dissolved on the mineral surface must compete with homo-charged collector ions for adsorption onto the mineral surface. The same consequence can also happen in certain alkaline condition (higher pH) as the concentration of collector ions in the solution decreases. pH are one of the variables that can influence the solubility of collectors on semi soluble salt minerals, thereby, affecting flotation behaviour.

Zhang (2016), in his study of xenotime flotation suggested that at pH below 3.90, the predominant species is Y^{3+} , while at pH above 3.90, $Y(OH)^{2+}$, $Y(OH)^{2+}$ and $Y(OH)_3$ become prevalent. This finding indicated that as the solution goes from acidic to alkaline, more Y^{3+} are hydrolyzed into $Y(OH)_3$. Thus, it is reasonable to conclude that at a relatively low pH, less available active area on the surface of xenotime because more Y^{3+} ions are dissolved on the surface. While at a relatively high pH, Zhang stated that more hydroxyl ions are competing with anionic collector ions for the xenotime surface, resulting less recovery. From the study, he conclude that good

recovery can be expected at pH range of 5 to 9 when octano-hydroxamic acid as the collector is applied (Figure 2.6). Sodium oleate has a narrower effective pH range of 7 to 9 to achieve maximum recoveries of xenotime when used alone (Figure 2.7).

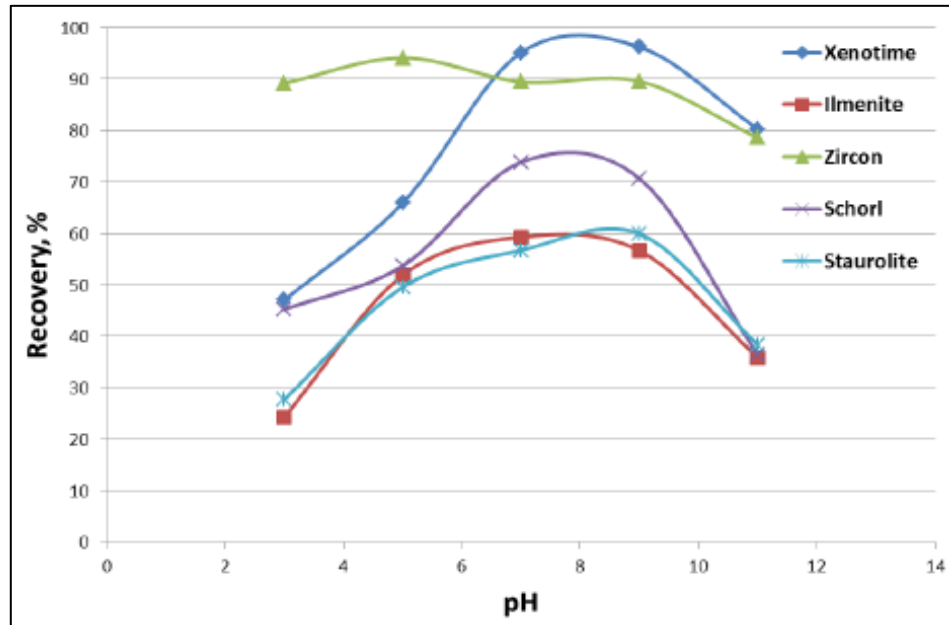


Figure 2.6 Microflotation recoveries of xenotime and gangue minerals with 0.0005M octano-hydroxamic acid as a function of pH at room temperature (Zhang, 2016)

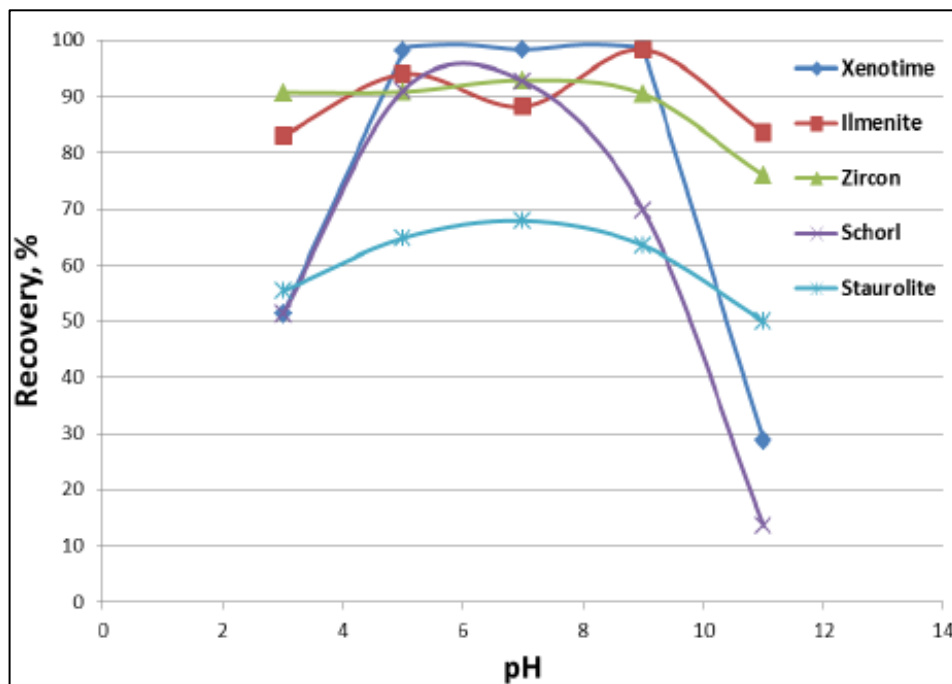


Figure 2.7 Microflotation recoveries of xenotime and gangue minerals with 0.0005M sodium oleate as a function of pH at room temperature (Zhang, 2016)

Chelgani and others (2015) concluded that the highest floatability of monazite grains in the presence of sodium oleate was observed at pH 8, and for xenotime at pH 7 to 8. When using hydroxamate, the highest selectivity of monazite grains was observed at pH 9, and for xenotime at pH 10. Although hydroxamate was found to have higher selectivity compared to sodium oleate in monazite and xenotime flotation, sodium oleate showed higher recoveries. The results indicated that the separation of xenotime from monazite could be achieved at pH 7.5, where monazite was floated and xenotime was concentrated in the roughing tail.

Abaka-Wood et al. (2019) studied the flotation recovery of rare earth oxides from hematite–quartz mixture using sodium oleate as a collector. In his findings, maximum flotation recovery of both monazite and hematite occurred at alkaline pH 9 condition. The selectivity of monazite over hematite was enhanced at pH 9 and shown to reduce with the increase of sodium oleate dosage.

2.5.3 Reagent

Various reagents have been evaluated and adapted in flotation of rare earths in previous research and commercial purposes. The process of selecting reagents is a key factor in determining the success of flotation. Different ore type and properties requires different reagent thus this process can be seen as tedious and daunting task. Both experience and statistical method need to be taken into account during the selection process. The abundance of reagents offered in the market had made the task even more lengthy as all the available choices need to be considered. Previous study provides researchers with statistical information that will be extensively used for reagent selection in further investigation.

Flotation reagents classified into the following categories (Thompson, 2002):

- 1) Collectors. These reagents are used to render minerals hydrophobic once adsorbed on the surface of mineral particles, forcing the desired minerals toward be collected by air bubbles in the froth phase.
- 2) Depressants. These reagents are used to render the gangue minerals hydrophilic and keep the gangue minerals in the liquid phase.
- 3) Activators. These reagents are used before the collector to modify the particle surface for further collector adsorption.
- 4) Dispersants. These reagents are used to prevent micro-sized particles in the solution from aggregating allowing better floatation of the desired minerals.
- 5) Frothers. These reagents are used to decrease the surface tension of the pulp and develop a stable froth flow.

In several cases, versatile reagents such as sodium silicate (Na_2SiO_3) can act both as depressant and as dispersant for floatation of rare-earth-bearing silicates. Some collectors also can react as a frother and vice versa depending on ore type and dosage.

2.5.3(a) Collectors

Collectors or also known as surfactants are reagents used to render minerals hydrophobic. Once these reagents adsorbed on the surface of mineral particles, it forced the desired minerals to attach to the air bubbles and floated in froth phase. Floatation of REM is typically done using oxhydroxyl collectors, such as hydroxamates, carboxylates and phosphoric acid esters (Jordens et al., 2013). Oxhydroxyl collectors consist of an oxygen anion and a double-bonded oxygen as their functional group. According Bulatovic (2010), the main difference between these three oxhydroxyl collectors is the atom which oxygen atoms are attached (whether nitrogen, carbon or phosphorous). These collectors may be used along with diverse type of depressants and activators depending on the mineralogy of the ore.

2.5.3(a)(i) Hydroxamic acids

Hydroxamic acids which may be considered as derivatives of both hydroxylamines and carboxylic acids, have become very much favored and commonly used in flotation research for the past years. This collector can be represented by the general formula $R-CO-NOOH$ which the R typically represents an alkyl chain containing five to nine carbon atoms. Hydroxamic acids also known as nitrogenous collectors and is categorized as a group of chelating collectors, hence, means that the acid will form complexes with metal cations present at the minerals surface. Numerous studies have postulated that hydroxamate-metal complexation occurs by the substitution of the hydrogen atom of the hydroxyamide group with a metal cation and ring closure via the carbonyl oxygen atom (Marion et al., 2020).

Collectors are classified into three groups according to the types of nonpolar groups: alkyls, cyclanes, and aryls, as shown in Table 2.3. Due to their differences in molecular structures, different types of nitrogenous collectors perform are vary in froth flotation.

The metal cation attached to the acid to form complexes play a huge role in determining its stability. The most stable complexes formed with Fe^{3+} , Al^{3+} , Cu^{2+} , Cr^{3+} and Pb^{2+} , followed by rare-earth metal cations; and the weakest complexes are formed with alkaline-earth metal cations (Khairy et al., 1996, Sastri et al., 2003). Suggested by Pradip and Fuerstenau (1983), the larger the difference in stability constant between the complexes formed and surface cations, the greater the selectivity while according to Assis et al. (1996), the selectivity of hydroxamic acid collectors is more closely related to adsorption kinetics.