HYDROMETALLURGICAL TREATMENT OF BEYLİKAHIR RARE EARTH PRECONCENTRATE

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ABSTRACT

HYDROMETALLURGICAL TREATMENT OF BEYLİKAHIR RARE EARTH PRECONCENTRATE

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The aim of this research was to determine the optimum hydrometallurgical parameters to extract the rare earth elements from a bastnasite containing ore in Beylikahır, Eskişehir. The total rare earth oxide (REO) content of the deposit was estimated to be 1 million tons with an average concentration of 3.14% REO. The rare earths were mainly contained in bastnasite mineral. The other major constituents of the ore were calcium fluoride, barite, calcite and minor amounts of thorium, iron and manganese containing minerals. The bastnasite mineral occurred either as cement material between fluorite and barite particles or was intimately associated with these minerals. The rare earth elements were enriched considerably in sub-sieve sizes.

After extensive research about physical concentration of this ore, various metallurgical routes were followed for the extraction of rare earth elements (REE) from the preconcentrate obtained by attrition scrubbing, screening and desliming by cyclones. Among the metallurgical routes tested, the most promising was sulphuric acid baking and subsequent water leaching. The results of the acid baking and leaching experiments indicated that rare earth elements leach recoveries up to 90% were easily obtainable and hydrofluoric acid recovery as a by-product was also possible. Later, the optimum conditions of recovery of REE's from the pregnant leach solution by precipitation as double sulphate by adding sodium sulphate and conversion to hydroxide by NaOH addition were determined. Then, the separation of cerium from the other REE's after drying and oxidation of Ce^{3+} to Ce^{4+} and hydrochloric acid leaching was carried out. Finally, the separation of relatively heavier REE's from light rare earths by solvent extraction was investigated.

Key words: Rare earths, leaching, precipitation, solvent extraction

ÖZ

BEYLİKAHIR NADİR TOPRAK ÖNKONSANTRESİNİN HİDROMETALURJİK YÖNTEMLERLE İŞLENMESİ

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Bu araştırmanın amacı, Eskişehir'in Beylikahır bölgesinde bulunan bastnazit içeren cevherden, nadir toprak elementlerinin üretimi için gerekli olan optimum hidrometalurjik parametrelerin belirlenmesidir. Cevher yatağının, toplam nadir toprak oksitleri içeriğinin 1 milyon ton olduğu tahmin edilmektedir ve bu cevher ortalama % 3,14 nadir toprak oksitleri içermektedir. Nadir toprak elementleri büyük oranla bastnazit mineralinde bulunmaktadır. Cevherde bulunan diğer ana mineraller florit, barit, kalsit olup, ayrıca az miktarda toryum, demir ve manganez içeren mineraller bulunmaktadır. Bastnazit minerali florit ve barit minerallerinin arasını çimento maddesi olarak doldurmakta veya bu minerallerle iç içe bulunmaktadır. Nadir toprak elementleri elek altında zenginleşmektedir.

Bu çalışmalarda daha önce yapılmış olan zenginleştirme çalışmaları sırasında elde edilmiş olan düşük tenörlü bastnasit önkonsantresi kullanılmıştır. Kompozit cevhere uygulanan aşındırmalı yıkama ve şlam atma ile elde edilmiş olan çok ince yapılı bastnasit önkonsantresi düşük tenörlü olduğu için, daha çok literatüre geçmiş konvansiyonel olmayan metalurjik yöntemlerin, bu önkonsantreye uygulanması söz konusu olabilmektedir. Geniş araştırmalardan sonra, bu önkonsantreden nadir toprak elementlerinin üretimi için çeşitli metalurjik yollar takip edilmiştir. Test edilen metalurjik metodlardan en iyi sonuç vereni sülfürik asit ile kavurma ve su liçidir. Asit ile kavurma ve su liçi deneylerinin sonuçları göstermiştir ki; nadir toprak elementlerinin liç verimi kolaylıkla % 90'a ulaşabilmektedir, ayrıca ara ürün olarak hidroflorik asitin de üretilebilmesi mümkündür. Daha sonra, yüklü liç çözeltisine sodyum sülfat ekleyerek nadir toprak elementlerinin çöktürme ile çift sülfat olarak elde edilmesi için ve NaOH ekleyerek hidroksite dönüşüm için gerekli optimum parametreler belirlenmiştir. Bundan sonra, seryum diğer nadir toprak elementlerinden ayrılmıştır. Bu amaçla hidroksit kurutulmuş, Ce^{+3}, Ce^{+4}'e yükseltgenmiş ve hidroklorik asit ile liç edilmiştir. Son olarak, nisbeten ağır nadir toprak elementlerinin, hafiflerden solvent ekstraksiyon ile ayrıştırılmasına çalışılmıştır.

Anahtar kelimeler: Nadir topraklar, liç, çökelme, solvent ekstraksiyon.

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CHAPTER 1

INTRODUCTION

The International Union of Pure and Applied Chemistry (IUPAC) defined rare earths as comprising the lanthanides from lanthanum to lutetium together with yttrium and scandium. Thus, the rare earths comprise a group of 17 elements in the periodic table. These 17 elements and their atomic numbers are shown in Table 1.1. Scandium, yttrium and lanthanum appear in the column IIIB of the periodic table as seen in Figure 1.1. The rare earth elements with atomic numbers of 58-71 seem to have properties that are characteristic of lanthanum and are placed at the bottom of the periodic table and called the lanthanides. The term lanthanons is used when lanthanum is also included [1-4].

The rare earth elements, being chemically similar to one another, invariably occur together in the source minerals and behave as a single chemical entity. The lanthanons are a set of essentially trivalent elements, with many resemblances to the other members of group IIIB of the periodic table and some resemblance to the alkaline earth elements despite the difference in valency. Group IIIB includes a very homogenous set of elements; scandium, with a small ionic radius, is somewhat divergent in properties and does not occur with the lanthanons, but yttrium, lanthanum, the other lanthanons and actinium are all very similar [5]. The lanthanides are subdivided into two groups;

1. The Cerium or Light group: La, Ce, Pr, Nd, Pm, Sm and Eu

2. The Yttrium or Heavy group: Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Y

Table 1.1. The Rare Earth Elements, Their Symbols and Atomic Numbers

Element	Symbol	Atomic Number
Lanthanum	La	57
Cerium	Ce	58
Praseodymium	Pr	59
Neodymium	Nd	60
Promethium	Pm	61
Samarium	Sm	62
Europium	Eu	63
Gadolinium	Gd	64
Terbium	Tb	65
Dysprosium	Dy	66
Holmium	Ho	67
Erbium	Er	68
Thulium	Tm	69
Ytterbium	Yb	70
Lutetium	Lu	71
Yttrium	Y	39
Scandium	Sc	21

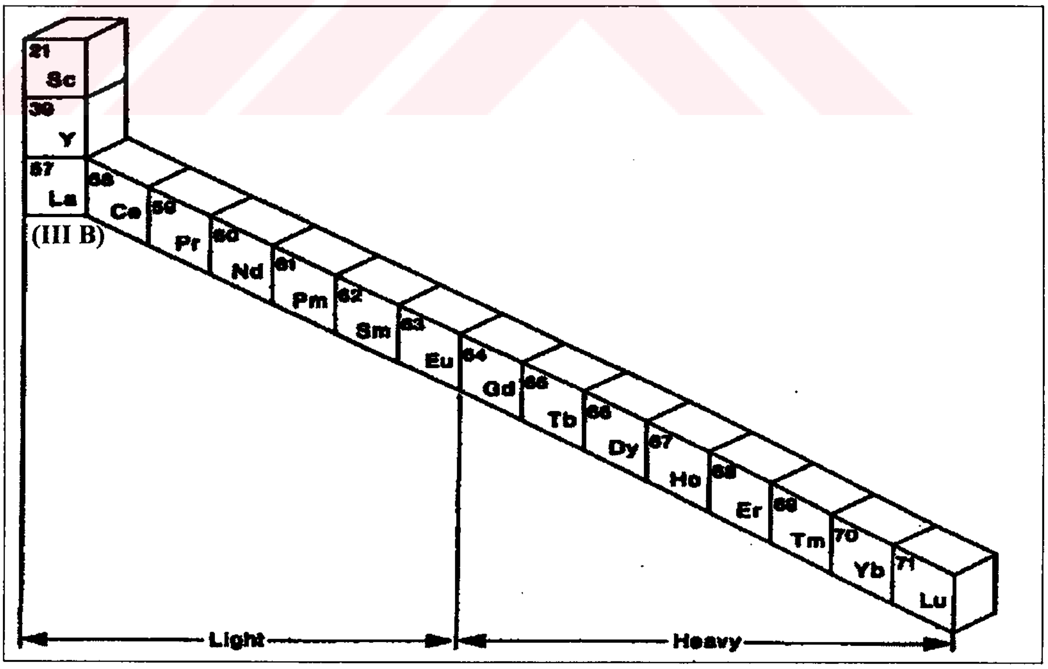


Figure 1.1. The Position of Rare Earths in the Periodic Table (Group IIIB)

This subdivision was originally based on the differences in solubility between double sulphates of the lanthanides and sodium or potassium. However, there are also periodic variations of some properties within the lanthanide series. For example, the atomic and ionic radii decrease continuously as the atomic number is increased. This phenomenon, which is known as the " lanthanide contraction " is attributed to the gradual decrease in the basicity of the elements in the transition from cerium to lutetium and is the cause of the different solubility of the lanthanides and the stability of their complex compounds. This property is utilized in the separation of rare earths from each other. Some properties of the elements are given in Table 1.2.

Table 1.2. Some Properties of the Rare Earth Elements [5]

Elements	At. Wt.	Abundance (ppm)	Valency states in solution	Composition & colour of normal oxide	Colour of ions in solution	Ionic radius °A
La	138.9	18	3^+	La_2O_3 White	Colourless	1.04
Ce	140.1	46	$3^+,4^+$	CeO_2 Cream	Ce^{3+} Colourless Ce^{4+} Orange-red	1.02 0.92
Pr	140.9	5.5	$3^+,4^+$	Pr_6O_{11} Black	Green	1.00
Nd	144.3	24	3^+	Nd_2O_3 Blue	Purple	0.99
Pm	145.0	Nil	3^+	Pm_2O_3	Pink	
Sm	150.4	6.5	$2^+,3^+$	Sm_2O_3 Cream	Sm^{2+} Orange Sm^{3+} Pale yellow	1.11 0.97
Eu	152.0	0.5	$2^+,3^+$	Eu_2O_3 Very pale pink	Eu^{2+} Pale yellow Eu^{3+} Pale pink	1.06 0.96
Gd	156.1	6.4	3^+	Gd_2O_3 White	Colourless	0.94
Tb	158.9	0.9	$3^+,4^+$	Tb_4O_7 Dark brown	Pale pink	0.92
Dy	162.5	5.0	3^+	Dy_2O_3 Yellowish white	Pale yellow	0.91
Ho	164.9	1.2	3^+	Ho_2O_3 Pale yellow	Yellow-orange	0.89
Er	167.2	4.0	3^+	Er_2O_3 Rose	Red	0.87
Tm	168.9	0.4	3^+	Tm_2O_3 Very pale green	Pale green	0.86
Yb	173.0	2.7	$2^+,3^+$	Yb_2O_3 White	Yb^{2+} Pale green Yb^{3+} Colourless	0.93 0.85
Lu	175.0	0.8	3^+	Lu_2O_3 White	Colourless	0.84
Y	88.9	28	3^+	Y_2O_3 White	Colourless	0.88

The lanthanides are silvery-white metals. Some of them are pale yellow. They have close-packed hexagonal or face centred cubic crystal lattices, with the exception of samarium (rhombohedral) and europium (body-centred). Most of the cerium group elements have more than one allotropic modification. The pure lanthanides are ductile and worked without difficulty. The tensile strengths and modulus of elasticity of the metals in the yttrium subgroup (except ytterbium) are higher than those of the metals of the cerium subgroups [6]. All of the rare earths are characterized by high density, high melting point, high electrical conductivity and high thermal conductance [7].

Rare earths have been of considerable technical and commercial interest during the past three decades because of the unique properties of their compounds that can be used as phosphors, magnets, superconductors, lasers, ceramics, and semiconductors. So, within the scope of this thesis work, the hydrometallurgical extraction of rare earths from Beylikahır deposit located in the mid-west of Turkey was studied and the results obtained have been presented as well as discussed in detail.

CHAPTER 2

LITERATURE REVIEW

2.1. Reserves and Locations of Rare Earth Element Resources

The natural resources of lanthanides are quite large. Their total content in the Earth's crust is 0.015%, i.e., the same as the content of copper. So the term “rare earths” is a misnomer. They were originally called rare because they were discovered in isolated monazite crystals in certain types of granite. “Earth” is an old chemical name for oxides and refers to the fact that the metals always occurred in the oxide form. In the Earth’s crust the most commonly found lanthanides are La, Ce and Nd. Lanthanides with odd atomic numbers are less abundant than their immediate neighbours with even atomic numbers. Thus, given the choice, an even-numbered element should be selected for specific applications because it would be more available [7-9].

The rare earths do not occur naturally as metallic elements. Their strong affinity for oxygen causes them to form mostly oxides, although other combinations are possible. An exception is promethium, which does not have a stable isotope and is not found in nature. Because of their reactivity, it is difficult to refine the rare earths to a pure form. Due to their chemical similarity, it is even more difficult to separate them into individual elements or compounds.

More than 250 lanthanide containing minerals are known. Of these 60 to 65 are lanthanide minerals, i.e., minerals in which the total concentration of the lanthanide elements is higher than 5 to 8%. These minerals consist of phosphates, fluorides or fluorocarbonates, silicates, etc. The minerals usually contain some thorium and occasionally some uranium [6].

The rare earths are widely distributed in low concentrations throughout the Earth's crust. They occur as mixtures in many massive rock formations, e.g., basalts, granites, gneisses, shales, and silicate rocks. More than 95% of the REO occurs in three minerals. Monazite and bastnasite are the important minerals for the light rare earths, and xenotime for yttrium and the heavy rare earths. Some of the important rare earth containing minerals are given in Table 2.1.

Table 2.1. Some of the Important Rare Earth Containing Minerals [2,10]

Mineral	Composition
Bastnasite	$LnFCO_3^*$
Monazite	$(Ln,Th)PO_4$
Xenotime	$LnPO_4$
Euxenite	$(Ln,Ca,U,Th)(Nb,Ta,Ti)_2O_6$
Apatite	$(Ln,Ca)_5((P, Si)O_4)_3(F,Cl,OH)$
Gadolinite	Be_2FeLn_2,Si_2O_{10}
Loparite	$(Ln,Na,Ca)(Ti,Nb)_2O_6$
Uraninite	$(U,Th,Ln,Pb)O_2$
Brannerite	$(U,Ca,Fe,Th,Ln)(Ti,Fe)_2O_6$
Doverite	$CaLn(CO_3)_2F$
Pyrochlore	$(Na,Ca,Ln)_2Nb_2O_6(F,OH)$
Allanite	$(Ca,Ln,Th)_2(Al,Fe,Mg)_3.Si_3O_{12}(OH)$

*The symbol Ln in the formulas represents elements 57-71 including yttrium.

The chemical compositions of the most common rare earth minerals are given in Table 2.2. Monazite and bastnasite are the minerals used commercially to supply most of the rare-earth chemicals. Monazite is a brown, dense phosphate mineral. There are extensive deposits of enriched monazite sands on beaches in many parts of the world, e.g., along the southwest coast of India and the east coast of Brazil; in uplands of Australia, South Africa; in the CIS (formerly Soviet Union); and in the United States in Idaho, South Carolina and Florida [1,10].

Table 2.2. Chemical Compositions of the Most Common Rare Earth Minerals [11]

Element	Monazite	Bastnasite	Xenotime
La	22.0 %	33.3 %	1.3 %
Ce	47.3	49.2	3.2
Pr	5.1	4.3	0.5
Nd	17.9	12.0	1.6
Sm	2.8	0.8	1.2
Eu	0.1	0.1	trace
Gd	1.7	0.2	3.5
Tb	0.2	trace	0.9
Dy	0.6	trace	8.5
Ho	trace	trace	2.0
Er	trace	trace	6.5
Tm	trace	trace	1.1
Yb	trace	trace	6.9
Lu	trace	trace	1.0
Y	2.1	0.1	61.8

Bastnasite is a fluorocarbonate of cerium and the rare earth metals and contains hardly any thorium. There is a large bastnasite deposit at Mountain Pass, California. The ore contains about 60% carbonates (mainly calcite), 20% barite, 10% rare earth fluorocarbonates, and 10% other minerals including silica.

The world's largest deposit of rare earths is found at Bayan Obo in Inner Mongolia, China where bastnasite and monazite co-occur as associated minerals in iron ore. The main minerals are iron, rare earths, and niobium as well as fluorite. Bastnasite and monazite account for about 70% and 30%, respectively, in the rare earth fraction of the ore and Bayan Obo deposits contain an estimated 36 million tons of rare earth oxide [2,12].

Eskişehir-Beylikahır ore deposit, which is investigated in this study, is located in the mid-west of Turkey. The complex ore of hydrothermal origin contains rare earths mainly in bastnasite mineral. The total rare earth oxide reserve of the ore deposit has been estimated to be 1 million tons with an average grade of 3.14% REO, 37.5% CaF_2, 31.0% $BaSO_4$ [13].

As stated in the literature, commercially significant rare earth mineral deposits are found throughout the world [2,10,14-18]. In spite of the large number of mentioned locations, about 80% of world rare earth reserves are concentrated in the People's Republic of China (PRC), 11 % in North America, and 5% in India. The major minerals constituting these reserves are monazite, bastnasite, and xenotime; in Canada the uranium ores; and in the CIS apatites and loparite.

The rare earth element scandium does not occur in the rare earth minerals. The major source of scandium is uranium ores that contain about 0.1% scandium. Some scandium is also recovered as a by-product of wolframite. Scandium content in wolframite is of the order of 500-800 ppm and this is considered an important potential resource in the USA. The only mineral that contains a large percentage of scandium is thortveitite. This mineral is very rare and is not counted as an important source of scandium. Slags from blast furnaces used in the production of cast iron and tin smelting have also been sources of scandium.

Several rare earths are found in the elements formed in the fission of uranium and plutonium. The fission products from nuclear reactors are the only source of promethium.

Commercial mining of rare earth reserves began about a hundred years ago. Monazite was the major rare earth source from the beginning of the industry until 1965. Thereafter bastnasite production equalled or exceeded monazite production. At present, bastnasite is the world's major source of rare earths and constitutes 62% of world output of rare earth minerals.

Production began from the Mountain Pass deposit in the 1950s and this has remained the only source of bastnasite for over three decades. The only reported production of bastnasite outside the USA was the occasional very minor production in Burundi. Production began in China in the 1980s. In China bastnasite is produced as a by-product of iron ore mining in Bayan Obo. Chinese mine production capacity was about 6000 tons of REO in 1982 and rose phenomenally to over 400000 tons of REO (six times the world demand) in 2000 [19,20]. Bastnasite accounts for the major fraction of Chinese output. China is the only country that also owns ion-adsorption rare earth clay minerals [21].

The major amount of monazite is obtained as by-product from the extraction of ilmenite, rutile, or zircon in Australia, Brazil, India, or from placer cassiterite mining in Malaysia. Since 1967 Australian beach sand deposit has become the major source of monazite supply and in 1988 Australia continued to dominate, contributing nearly 37% of the total world monazite production [2].

Xenotime production is less than 1% of the total tonnage when it is compared with monazite or bastnasite. It is recovered essentially as a by-product of processing tin ore in Malaysia, Thailand, and China. Processing of heavy mineral sands also yields minor amounts of xenotime in Australia. Some xenotime has also been recovered in Brazil from the Ptinga alluvial tin mine [2].

2.2. Applications, Productions and Consumptions of Rare Earth Elements

The lanthanides are used as metals, alloys, and chemical compounds in various branches of technology: ferrous and non-ferrous metallurgy, production of glass and ceramics, the chemical industry, medicine, nuclear and agriculture. They still have other potential uses, the number of which increases as the properties of lanthanides, their alloys, and compounds become known [6,7,10,22-25].

The end uses of rare earths come under two broad categories. Those using mixed rare earths: either naturally occurring mixtures or mixtures enriched with respect to a particular rare earth element or elements, and those using individual rare earths in various levels of purity. Rare earths consumption in mixed form constitutes, on a volume basis, about 95% of the total rare earths consumed. However, the separated rare earths, which account for only 5% in terms of quantity, constitute 50% of the financial value of the total rare earth consumption. The major rare earth consuming countries are the USA and Japan.

The addition of lanthanides as mischmetal (complex alloy of rare earth metals) or rare earth silicide (Ln-Fe-Si) improves the quality of carbon, stainless and high speed steels; they increase the mechanical strength, corrosion and oxidation resistance, and refractoriness, improve the workability of the steels. The rare earths also play a leading role in the production of nodular cast iron. The addition of lanthanide metals to various aluminium and magnesium alloys increases their high-temperature strength.

The largest single use of rare earths, in which the naturally occurring rare earth mixture is used, is in the manufacture of rare earth containing, zeolite cracking catalyst required in the petroleum refining process.

The introduction of lanthanides in the composition of glass, produce glasses that absorb ultraviolet and infrared light. A mixture containing cerium and other rare earth oxides is used for decolourising glass. On the other hand, neodymium, praseodymium, and also erbium oxides are used for colouring glasses. CeO_2 or other mixed rare earth oxides make excellent abrasives for glass polishing in the manufacturing of optical glass, mirrors and lenses. The rare earths have a variety of applications in ceramics as well.

Lanthanides with a large thermal neutron capture cross-section are of utmost importance for nuclear technology. The oxides of these metals are components of ceramic shields used in atomic reactors.

In electronics, lanthanides are used as components of non-sputtering gas absorbers. A number of rare earth phosphors have been developed for conversion of X-Ray radiation to visible light. Another application of rare earths is the field of hydrogen energy systems for storage purposes. In recent years, the use of rare earths as micro-fertilizers has been developed in China.

Rare earths entered into hi-tech epoch in early 1980s following the inventions of rare earth hi-tech new materials such as NdFeB magnet, NiMH rechargeable batteries and Y-Ba-Cu-O high temperature superconductor and so on. Driven by the rapid growth of hi-tech industries, rare earth industry entered into the fast development period in 1990s. The consumption of rare earth in the world has soared up from 33000 tons of REO in 1990 to 75000 tons of REO in 1999, showing an increase of 2.3 times with an annual average growth rate of 9.6%. The driven force has been the rare earth new materials. The major users of the magnets are the computer-led hi-tech industries that the experts in the fields predict will be kept at a high growth rate in the coming decade, so will the magnets. Another example is rare earth NiMH rechargeable batteries. The turnout of the cells in Japan alone reached 868 million pieces in 1999 from 72 million pieces in 1993, increased by 11 times in 7 years with an annual average growth rate of 51%. Other rare earth new materials includes phosphors, advanced ceramics, fiber optics, magnetostrictive alloy, auto catalysts, magnetooptics, magnetic refrigeration alloy, fertilizers and so on. Some have already become the leading consumers of rare earth, and others will do soon. Supply statistics showed that the global consumption of rare earth in 1999 was 75000 tons of REO. And in that year, China's turnout of rare earth products was 60000 tons of REO, domestic consumption was 16000 tons of REO and export of rare earth was 50000 tons of REO. The total of domestic consumption and export in China was 66000 tons of REO. Therefore, China has provided 88% of the world's total rare earth consumption in 1999, becoming the sole leading supplier of rare earth on the international market. USA used to be the largest rare earth producer and consumer in the world before the emergence of China's rare earth in the middle of 1980s. But now it has stepped down from the position of leading rare earth supplier, yet remains as the leading consumer of rare earth in the world. There may be many factors contributing to the reduction of rare earth production in USA, but the key one is the cost for Molycorp, the leading rare earth producer at Mountain Pass, California in USA is the only company in the world that recovers rare earths as the only target mineral, hence its production cost can not compete against that in China where most of the rare earth products are recovered as by-products. As a matter of fact, USA has become a rare earth importing country in recent years. In 1999, the US import of rare earth from China reached 17600 tons, becoming China's second largest rare earth export partner in the world (only next to Japan). Australia and India are two major owners of the proven monazite reserves in the world where monazite is recovered as by-product of processing heavy minerals. Monazite contains radioactive elements such as uranium and thorium, thus challenging the environment when being processed. The recent report says that a high grade rare earth deposit is discovered in Australia with low content of radioactive elements and the deposit is now at the stage of process development, and the owners of the mine aim at sharing several percentage of the world's raw material market. If yes, it could be regarded as the return of Australians on the global rare earth market since the shut down of its monazite operation in 1990s because of the shift of Rhone-Poulenc's raw materials from Australian monazite concentrate to Chinese rare earth chloride and carbonate. It is reported that CIS, owns 19 million tons of REO of rare earth reserves, but 98% of the reserves are located in Russia, which are not only scattered in many deposits, but also contain low grades of rare earth in composite minerals. In addition, the disintegration of the former Soviet Union has made its originally well established rare earth facilities belong to different CIS countries now and each country owns a certain section, thus having slowed down the development of rare earth industry in CIS as a whole. It will take time if the CIS countries try to well establish its own rare earth facilities in each country, but it seems rather risky to invest heavily in the basic rare earth facilities now because of the impact of the low price rare earth products from China, which are readily available in large quantities. France does not have rare earth resources of its own. Rhodia, the only rare earth processor in France, is the world's largest producer of high purity rare earth individuals. The company used to import monazite concentrate from Australia. The company's purchase then was several thousand to ten thousand ton of the concentrate per annum. But now, it has shifted its raw materials from the Australia monazite to the Chinese rare earth chloride/carbonate. There are several other countries reporting to have rare earth resources such as Brazil, South Africa, Namibia and Turkey. But they do not appear to develop the resources in a short run, again because of the pressure from China's rare earth products. As stated above, the world's total consumption of rare earth was some 75000 tons of REO in 1999. North America, mainly USA, took the largest share, accounting for 27% of the world total consumption, which was followed by Japan and China, taking 22% of the total each. Other southeast countries excluding China and Japan and Europe took 13%, respectively and the balance 3% was taken by the rest of the world. These data showed that 84% of the world rare earth consumption in 1999 went to Asia-Pacific regions, becoming the largest rare earth consuming markets, yet there reserves large rooms for rare earth applications in other continents such as Africa and Latin America. Statistics shows that the total rare earth consumption in USA, China and Japan has accounted for over 70% of the world total in recent years. USA is the world's largest rare earth consumer by country, Japan's rare earth applications have demonstrated the highest value of rare earth application in the world, and China is the largest developing country in the world with some special features in rare earth application. Therefore, to look into the rare earth applications in details in the three countries will help one gain a general picture of rare earth applications in the world as a whole, and predict the future development trend of rare earth applications [19,20]. The details of rare earth applications in the three countries are as follows:

China: Metallurgy/machinery: 32%, Catalysts: 24%, Glass/ceramics: 11%. New Materials: 14% and Others: 19%.
Japan: Catalysts: 6%, Glass/ceramics: 49%, New Materials: 42% and Others: 3%.
USA: Metallurgy/machinery: 8%, Catalysts: 72%, Glass/ceramics: 3%, New Materials: 12% and Others: 5%.

2.3. Mining and Mineral Dressing of Rare Earth Minerals

Mining of hard-rock deposits is by open-pit and underground methods. At Mountain Pass, California and at Bayan Obo, China, for example, open-pit operations are standard drill, blast, load, and haul to the mill. World resources of economically exploitable rare earth oxide are estimated to be about 100 million tons in place, composed of 93% in primary deposits and 7% in placers [10]. So there will be no difficulty in supplying REO at present consumption rates. Some of the present working deposits especially in China have sufficient reserves for many years.

Usually, the rare earth deposits are complex and from a large majority of these deposits, the rare earth minerals are recovered as by-products. From the processing point of view, the following are the major factors that affect the selection of a treatment process for the concentration of rare earth oxides:

a) Type and nature of the deposit (i.e., beach sand, vein type, igneous and complex ores) and its complexity.
b) Type and nature of other valuable minerals present with REO.
c) Type and nature of gangue minerals present in the deposit (slimes, clay, soluble gangue, etc.).
d) Type and composition of individual REO minerals.

Flotation is the standard method for recovering REO minerals from finely grained complex ores, while physical methods such as gravity and magnetic/electrostatic separations are currently employed for the treatment of REO containing coarse beach sand and placer deposits.

2.3.1. Flotation of Rare Earth Minerals

The flotation properties of bastnasite are relatively well known. Various collectors have been used or proposed to recover it, such as fatty acids (oleic), hydroxamates and dicarboxylic acids. The flotation method employed for the recovery of bastnasite largely depends on the gangue composition of the ore, and the chemical composition of the bastnasite itself.

Some of the gangue minerals associated with bastnasite, such as calcite, barite, celestite, etc., have flotation properties similar to bastnasite and therefore separation of the bastnasite from these gangue minerals using conventional fatty acid flotation, is rather difficult [26-29].

The major production of bastnasite by flotation originates from the USA and China. The bastnasite mined from Mountain Pass and the rare earths containing iron ores of Bayan Obo have to be crushed before they are concentrated by exploiting gravimetric, magnetic, or surface wettability differences. The Mountain Pass concentrator of the Molycorp Corporation treats a complex carbonate ore consisting of bastnasite, barite, calcite, strontianite and quartz. The flowsheet and reagent scheme of the Mountain Pass concentrator is well documented, and is quite unique and it is outlined in Figure 2.1.

Depression of gangue minerals is accomplished by additions of soda ash, sodium fluorosilicate and ammonium lignin sulphonate. These reagents are added stepwise in a pulp heated to 70°C to 90°C and the six-stage conditioning is carried out for about 120 minutes. The bastnasite is recovered with additions of tall oil (0.40 kg/t). High-grade bastnasite (~60% REO) is recovered at an overall REO recovery of 65-70%.

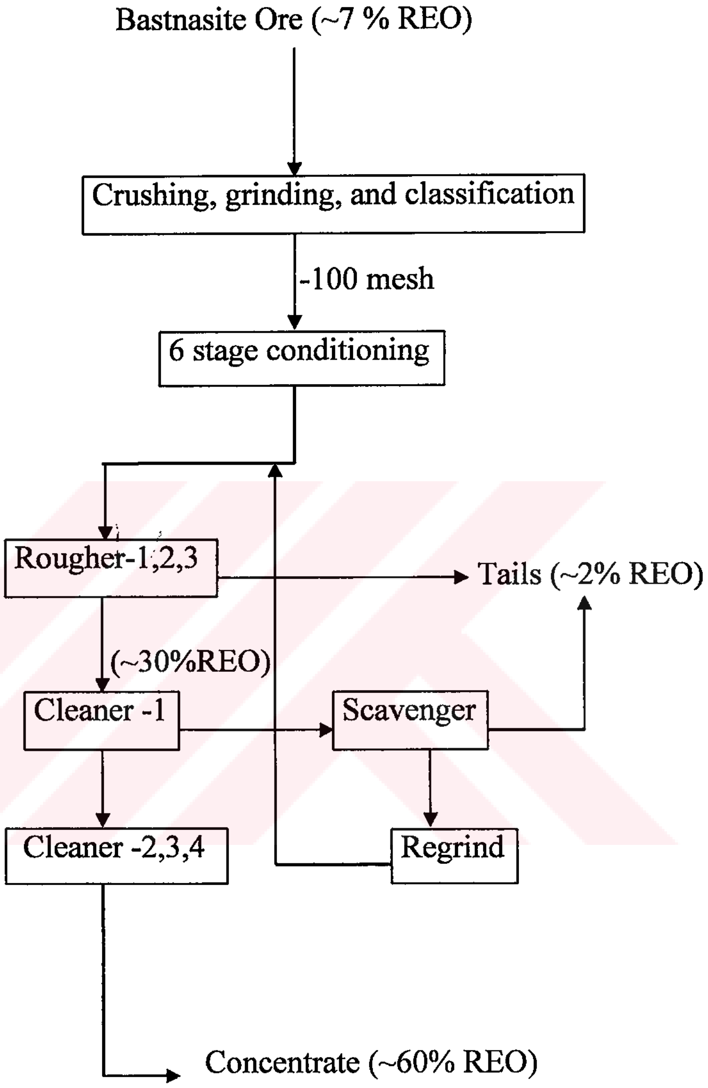


Figure 2.1. Physical Beneficiation of Mountain Pass Bastnasite [2]

Numerous minerals occur intimately intergrown in the rare earth bearing Bayan Obo iron ore. In physical beneficiation, in addition to the rare earths, magnetite, fluorite, hematite, and niobium oxide are recovered as valuable products. The rare earths are obtained from the non-magnetic tailings of hematite processing and are concentrated by flotation as seen in Figure 2.2. The flotation concentrate contains both monazite and bastnasite with overall REO content of 56%. For separating bastnasite and monazite slight difference between their specific gravities is made use of in the shaking table. While the bastnasite concentrate thus obtained is of high grade (68% REO), the monazite product has only 47% REO. The low monazite content has been attributed to its extremely intimate intergrowth with associated strata. The total recovery of the rare earths from the ore is about 72%.

Recent development work carried out by Lakefield Research led to the development of new techniques coupled with a collector specifically developed for the flotation of varieties of bastnasite that effectively recovers bastnasite from very complex ores similar to Mountain Pass. A rare earth ore was beneficiated using a double reverse gangue flotation followed by bastnasite flotation. This flowsheet gave a bastnasite concentrate assaying 62% REO at 88% recovery [30].

In the placer deposits, monazite occurs as a minor constituent along with sillimanite, garnet, magnetite, while the major minerals are ilmenite, rutile, zircon, and quartz. Occasionally trace quantities of other minerals such as cassiterite, chromite, picotite, baddeleyite, cinnabar, and native metals such as gold and platinum are also present. The beach sand deposits exhibit a considerable variation in mineralogy and chemical composition depending on the location. The flowsheets for their beneficiation are therefore variable in detail. However, as the task is essentially the separation of already crushed minerals with quite similar physical properties, the flowsheets have several features in common. An outline of the major steps in the processing is given in Figures 2.3 to 2.5 for various plants around the world [30]. The separation of individual minerals is achieved by exploiting the small gravimetric differences or the slight differences in magnetisability and surface ionisation potential between the various co-occurring minerals. Among the beach sand minerals, the specific gravity of monazite is the highest. Ilmenite, xenotime, and monazite in decreasing order of magnetisability, behave as magnetic materials. In electrostatic separation, ilmenite and rutile behave as conducting materials and others non-conducting.

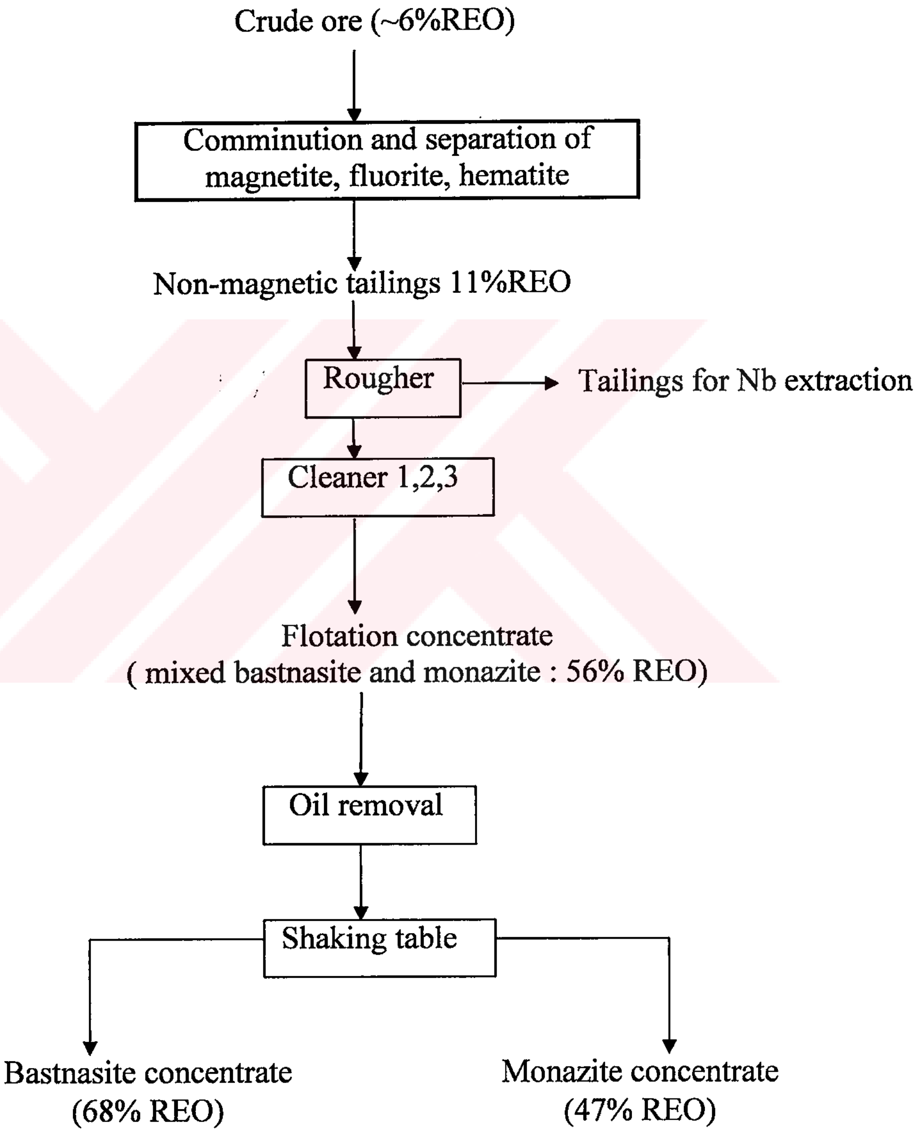
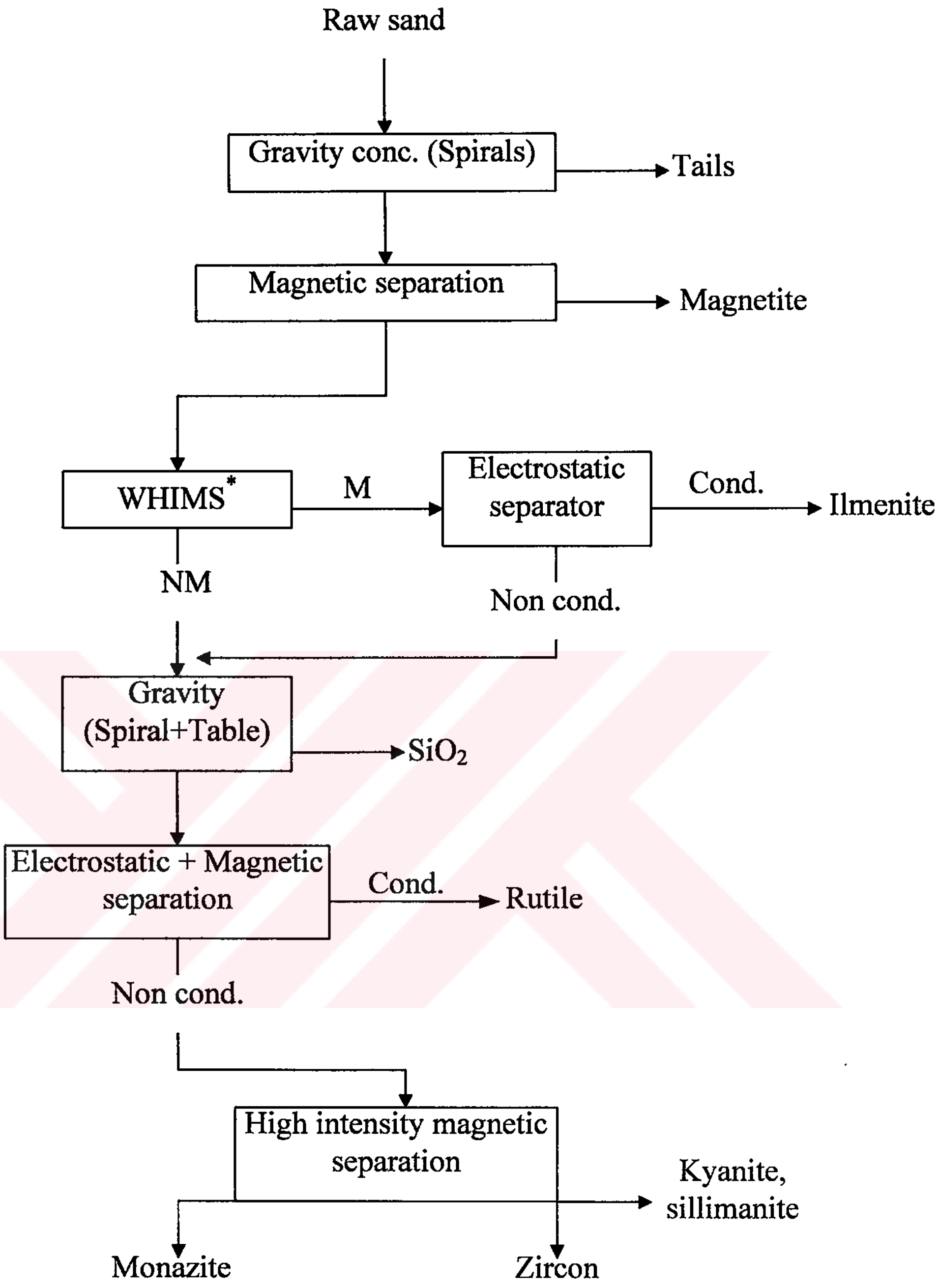


Figure 2.2. Physical Beneficiation of Bayan Obo Ore [2]



* Wet high intensity magnetic separation

Figure 2.3. Treatment Flowsheet of a Coarse Heavy Mineral Sand from Congolone, Mozambique [30]

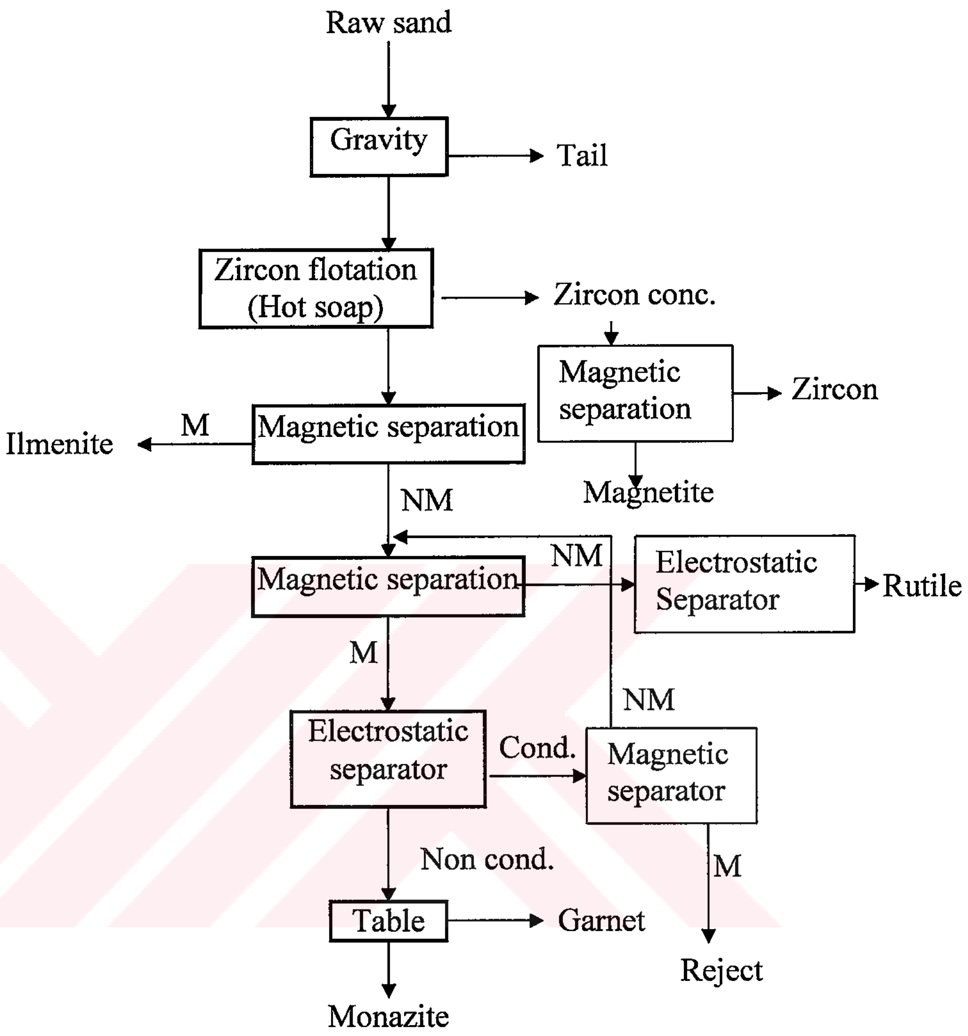


Figure 2.4. Treatment Flowsheet of the Zircon Rutile Ltd., Australia [30]

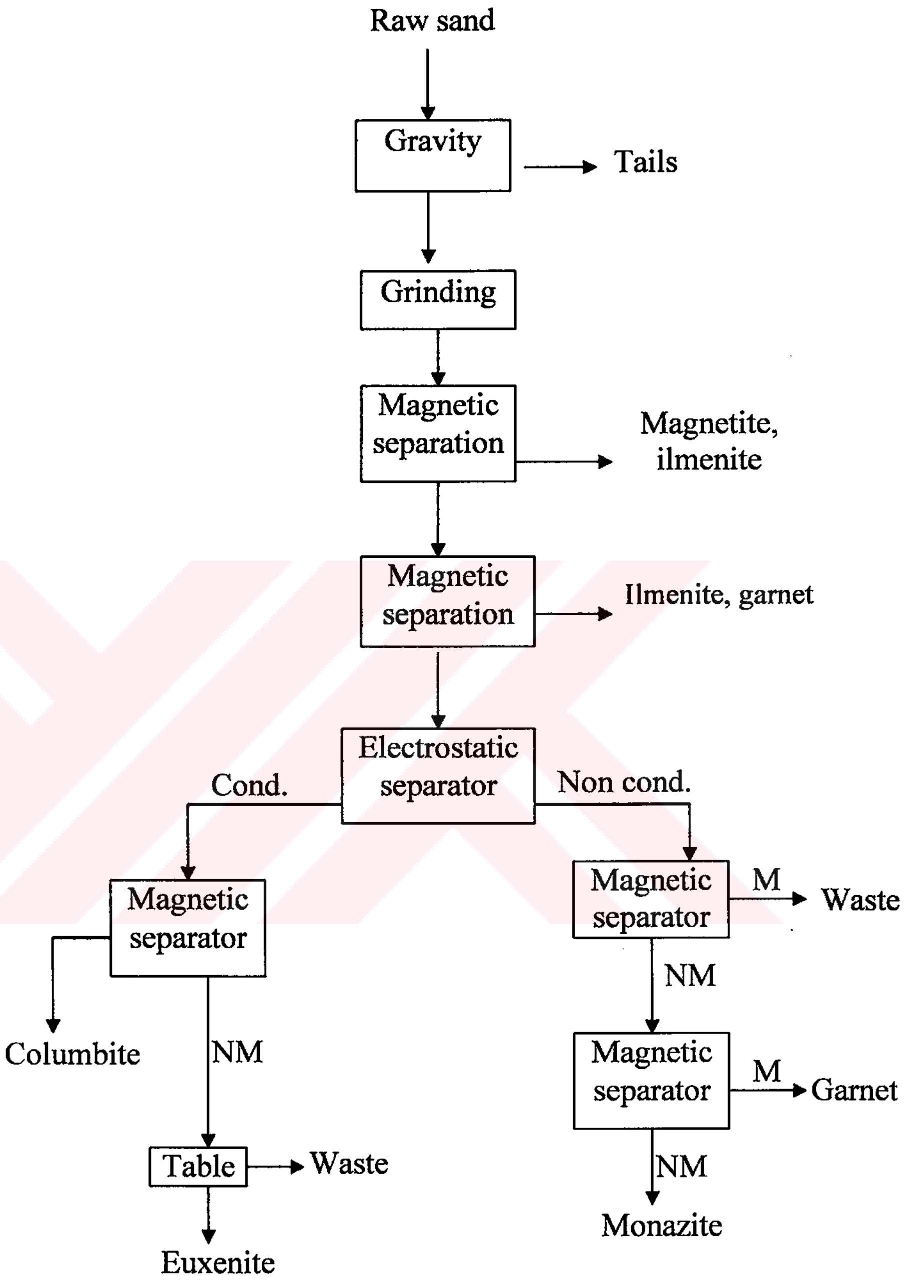


Figure 2.5. Treatment Flowsheet of a Black Sand from Bear Valley, Idaho [30]

2.4. Hydrometallurgical Processes for Bastnasite Containing Ores

Since the rare earth ore found in Turkey is of bastnasite type only the hydrometallurgical treatment of this mineral is explained in detail below. Metallurgical treatments start either with crude ore or bastnasite concentrate and are summarised in two parts: conventional processes and other processes.

2.4.1. Conventional Processes

Generally, a bastnasite concentrate containing about 60% REO, which has been produced by mineral dressing processes, is used in these conventional processes.

2.4.1.1. Upgrading of Concentrate

In concentrates that have been produced by flotation, bastnasite is present with calcite ($CaCO_3$) and other carbonate minerals because all of them show similar physical properties. At Mountain Pass, the bastnasite concentrate is obtained by hot flotation and contains approximately 60% REO. It is leached at pH 1 with 10% HCl solution in order to remove the above mentioned carbonate minerals. After leaching, $CaCl_2$ leach solution is separated by thickeners and drum filters from an enriched bastnasite concentrate with 68-72% REO [31-35]. Flowchart used in Mountain Pass is given in Figure 2.6.

2.4.1.2. Calcination of Upgraded Concentrate

The bastnasite concentrate upgraded with weak hydrochloric acid leaching is treated by a calcination process.

The purposes of calcination:

i. Decomposition of fluorocarbonates present in concentrate, formation of REO and elimination of CO_2, so obtaining of a higher grade bastnasite concentrate (85-90 % REO).

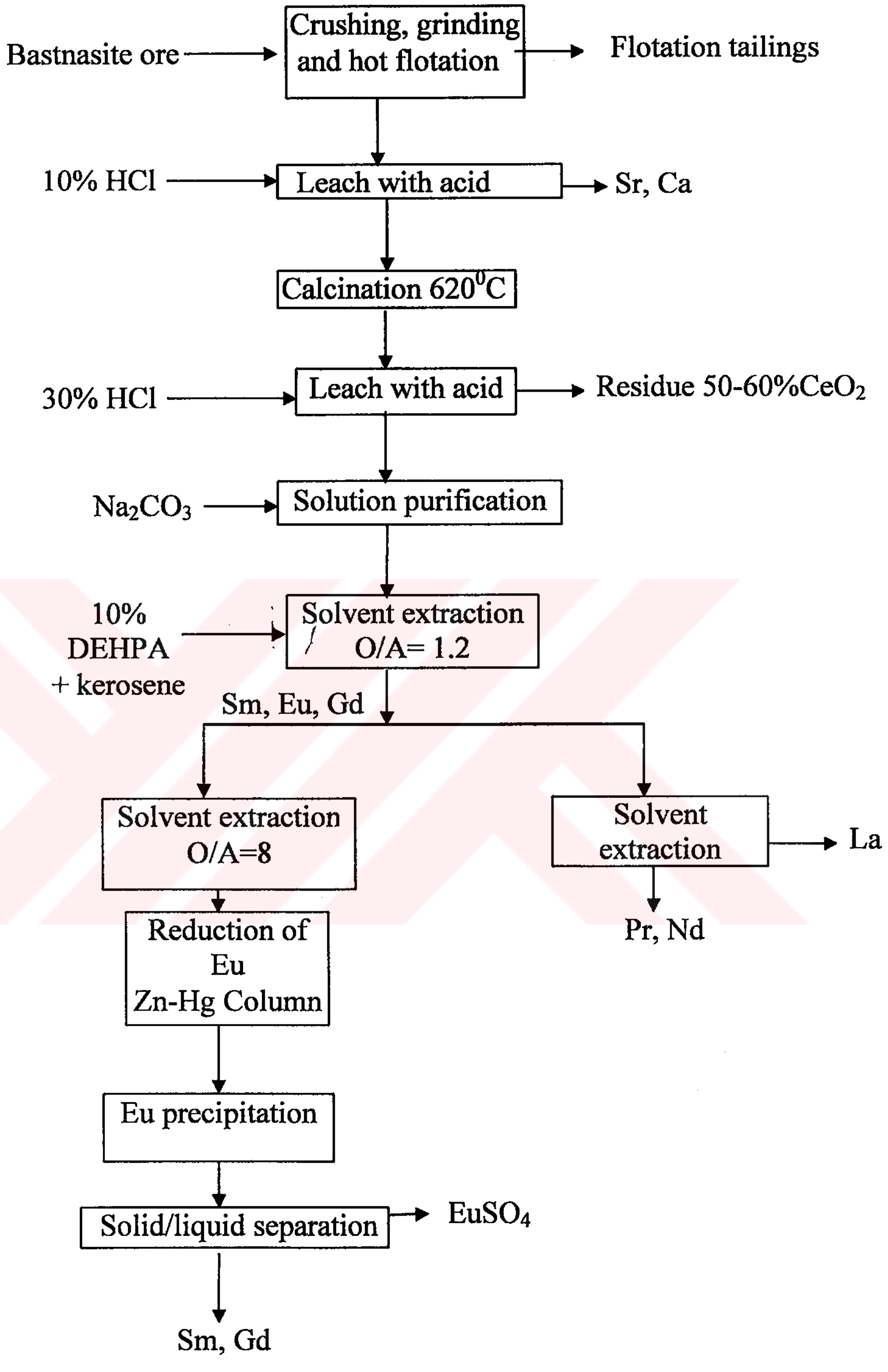


Figure 2.6. Flowchart of Mountain Pass [2]

ii. Oxidation of Ce^{3+} to Ce^{4+}, so formation of CeO_2 (ceric oxide) which does not dissolve at high acid concentrations, therefore production of a high grade CeO_2 concentrate can be easily achieved by the following leaching process [36-43].

Calcination process is carried out in an 8-hearth Herreshoff type multi-layer furnace in an oxidizing medium at 620°C. Calcination duration is taken as three hours and sulphur content of fuel should be as low as possible. In the calcined concentrate; cerium is present as CeO_2 and most of the other rare earths are present as 3+ valency oxides (except Pr and Tb). Calcined bastnasite concentrate which is produced at Mountain Pass contains about 90% REO. The chemical analysis of the concentrate shows that it contains 29% La_2O_3, 44% CeO_2, 4% Pr_6O_{11}, 10% Nd_2O_3, 0.8% Sm_2O_3, 0.11% Eu_2O_3, 0.15% Gd_2O_3, 0.2% (Tb_4O_7 + Dy_2O_3 + Ho_2O_3 + Er_2O_3 + Tm_2O_3), 0.01% Yb_2O_3, 3.3% BaO, 3.0% SiO_2, etc.

2.4.1.3. Leaching of Calcined Concentrate

In the Mountain Pass process, the calcined concentrate is leached with 30% hydrochloric acid solution at 32°C. Leaching process is selective, so cerium 4+ does not dissolve and it accumulates in the leach residue. The other rare earth oxides dissolve in the leach solution and pass into liquid phase. Four-step washing in thickeners and filtration follows the leach process. So a leach residue is obtained which contains 70% REO and more than 90% of it is CeO_2 and ThO_2. On the other hand, the pregnant leach solution contains 100 g/l REO.

Rare earth metals are present as chlorides in the pregnant leach solution. In order to extract rare earth elements (except cerium) from the pregnant leach solution, first of all it must be purified. Therefore, Na_2CO_3 is added to solution, so pH of solution is adjusted and impurities are precipitated and they are removed from the pregnant leach solution.

2.4.1.4. Solvent Extraction Process

The old processes for the separation of rare earth elements from each other are fractional crystallisation, fractional precipitation, selective oxidation or reduction and ion exchange. But nowadays these old methods are replaced by solvent extraction (SX). This method takes advantage of the relative affinities of the rare earth elements for a liquid solvent and an aqueous feed solution. Lanthanides contain 16 rare earth elements and their physical and chemical properties are very similar, therefore separation of these elements from each other is very difficult. Actual separation for individual rare earth elements is relatively small per contact; since multiple contacts are required to achieve acceptable extraction rates, numerous mixer-settler reaction cells are needed for the entire process. For example, 1000 stage-wise solvent extraction is used in order to separate REE from each other in La Rochelle factory of Rhone-Poulenc Corporation in France [44]. Mixer-settler solvent extraction system is used in this factory and automation of it has been completed, so very few workers work in the factory. Another mixer-settler solvent extraction system is present in China where 700 stage-wise solvent extraction is used in the separation of rare earth elements [45].

Organic phase used in solvent extraction processes can be chosen according to properties of pregnant leach solution. For example, while tributyl phosphate (TBP) is used in nitrate medium, di-2-ethyl hexyl phosphoric acid (DEHPA) or 2-ethylhexyl hydrogen 2-ethylhexyl phosphonate (PC-88A) is preferred in chloride systems. Several investigations have shown that the extractability of DEHPA and PC-88A increased with the increasing atomic number of REE or decreasing ionic radius. Thus, the relative extractability of rare earths with DEHPA from acid solutions increases in the order of La<Ce<Pr<Nd<.....<Lu and this effect is more marked for pH=1 than pH=3. The use of DEHPA has been limited by the formation of a gelatinous third phase when the metal concentration of the solvent phase became too high. PC-88A can reduce the cost of mineral acid in the stripping stage or back extraction, and in the process that follows, PC-88A can also save the cost of alkali in neutralizing an acidic aqueous solution. These

organic reagents are used after dilution with kerosene or a similar liquid without a modifier [46-49].

A component, say Ln_A is distributed between the two phases and will have a distribution coefficient (D_A), measured at equilibrium:

D_A= (Concentration of A in organic phase)/(Concentration of A in aqueous phase)

For two components, Ln_A and Ln_B, both distributed between the organic and aqueous phases, a separation factor can be defined:

$$\beta_B^A = D_A / D_B$$

The closer this factor approaches “1” the more difficult it will be to separate those two elements. With TBP, the separation factors vary between 1 and 1.9, depending on the concentration of various nitrates in the system. Separation factors of up to 2.5 are reported with DEHPA. The degree of separation is maximized by optimisation of operating conditions. To achieve any relatively complete separation, i.e. for two lanthanides adjacent in the periodic table in order to produce material of 99.99% or higher purity for the one element without contamination by the other, many SX cells must be linked in series into a chain as mentioned before. The aqueous feed flows one way while the organic flows the other. In commercial practice 50 or more cells will form a circuit. The most difficult separation tends to be that between Nd and Pr, and, in SX behaviour, yttrium fits into the Ln series near Dy or Ho.

Passing a mixed Ln and Y feedstock through an SX circuit will result in a cut into two fractions. A single element could be cut off from one end of the group or, alternatively, the mixed feedstock can be split into two fractions, each still containing several elements. The choice will depend on economics, on the relative demand for the mixture or the single element [3].

The diagram given in Figure 2.7 indicates the material flow paths within a typical SX circuit. Here the desired product, A, is preferentially concentrated in the organic phase and, after removal of the contaminants B and C in the scrub section, is stripped from the organic by an acid stream.

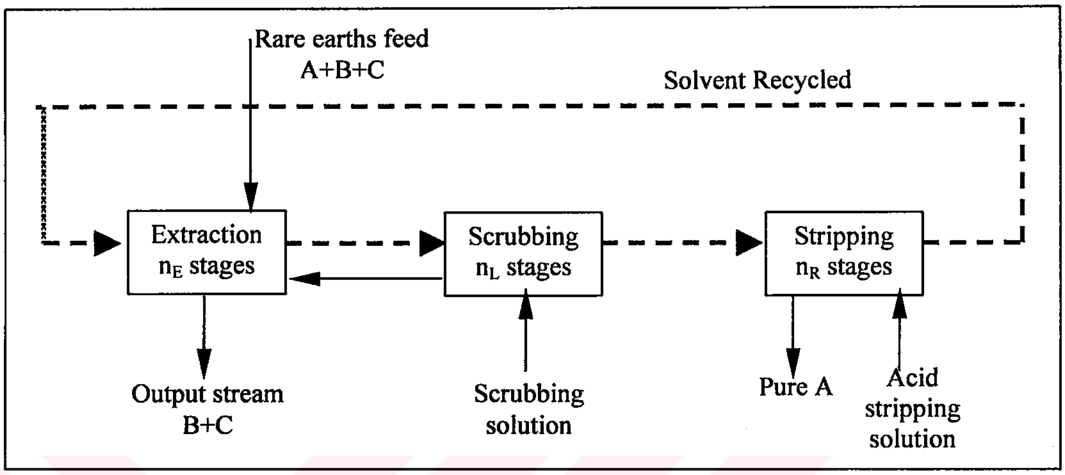


Figure 2.7. Liquid-Liquid Counter-Current Extraction Simplified SX-Circuit [3]

The solvent used in order to extract rare earth metals from chloride solution is 10% DEHPA in kerosene at Mountain Pass Corporation. Organic phase to aqueous phase ratio (O/A) is 1.2 in the first step. In this step, the light rare earths (La, Nd, Pr) are separated from the relatively heavier rare earths (Sm, Eu, Gd). Counter-current extraction in mixer-settler stages is carried out in large plywood boxes coated with epoxy-fibreglass and polyvinylchloride for protection against HCl. While the heavier rare earths like Sm, Eu and Gd are preferentially extracted to organic phase, the light rare earths are kept in aqueous phase during the extraction process. In the second step, La, Pr and Nd are separated from each other in a similar way. The heavy rare earths go through two further solvent extraction steps. The first separates a europium oxide product, and the second separates samarium from gadolinium as given in Figure 2.6. After the separation processes, REE are stripped from organic phase and precipitated as hydroxide, carbonate or oxalate [44,45,50,51]. A simplified flowsheet of Yao Lung Chemical Plant located in China is given in Figure 2.8.

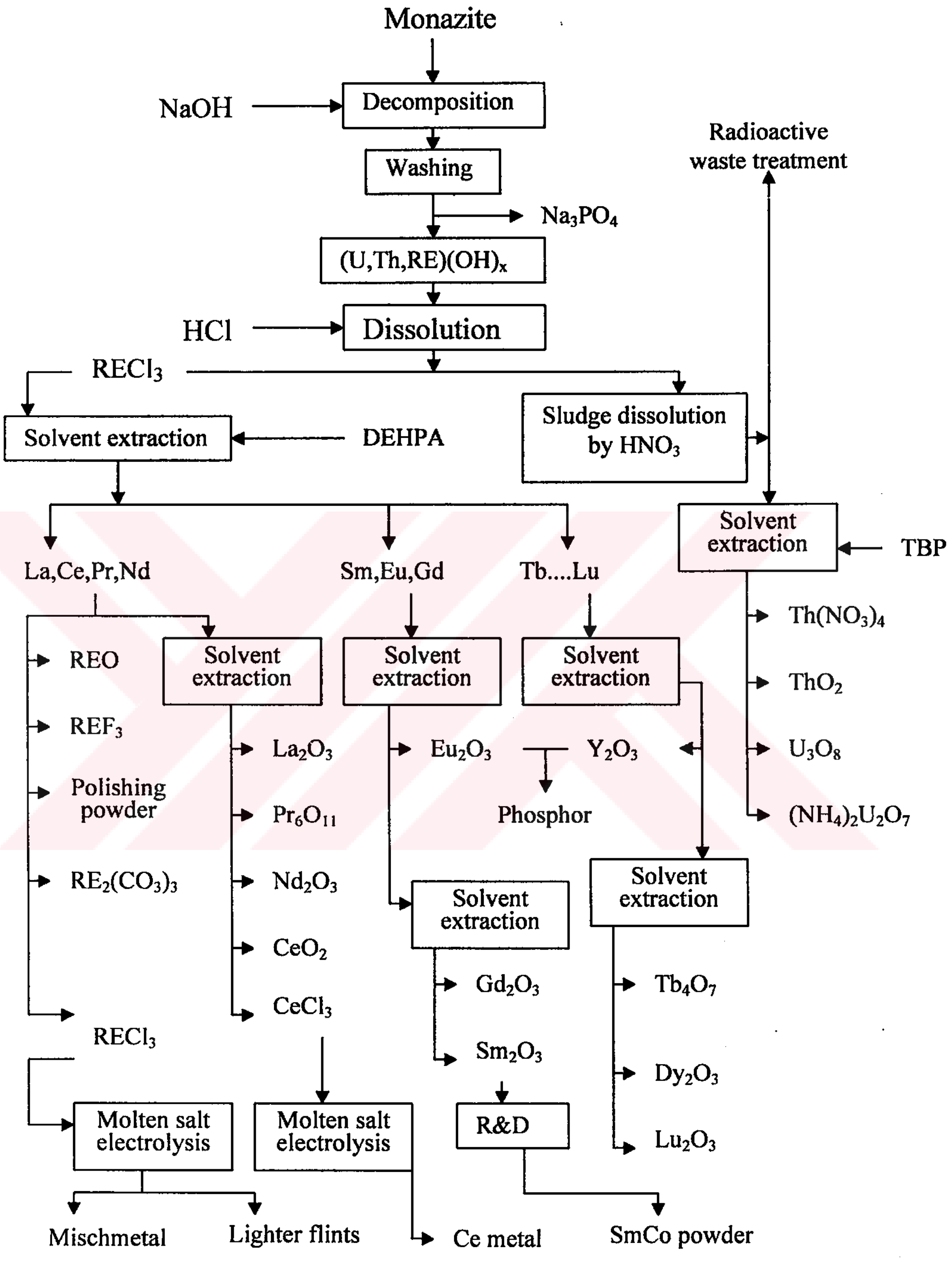


Figure 2.8. A Simplified Flowsheet of Yao Lung Chemical Plant Located in China [45]

In this plant, DEHPA is used for the separation of rare earths by solvent extraction. A reagent called P-507 has recently appeared on the Chinese market. As compared with the conventional DEPHA, this extractant has manifested many outstanding merits, such as easy stripping, lower solubility in water, good phase disengagement behaviour and especially much greater separation factors for neighbouring rare earths [45].

There are numerous other publications related to the use of solvent extraction for the separation and purification of rare earth elements [52-78]. In these publications various extractants such as tributyl phosphate, organophosphorus acids such as DEHPA, phosphonic and phosphinic acids, carboxylic acids such as Versatic acid and Naphthenic acid, various amines have been used.

2.4.1.5. Reduction and Rafination Process

Several processes have been developed for the production of rare earth metals of different purities. These methods include: (a) reduction of anhydrous rare earth chlorides or fluorides; (b) reduction of rare earth oxides, and (c) fused salt electrolysis of rare earth chlorides or oxide-fluoride mixtures. A qualitative picture as to which reactive element is useable as reducing agent for rare earth metals preparation is given by the free energies of formation of the oxides, fluorides, and chlorides, and their dependence on temperature. In the oxide systems, the order of stability is $CaO > Ln_2O_3 > MgO > Al_2O_3 >> SiO_2$, whereas among the fluorides it is $CaF_2 > LnF_3 > LiF > NaF > MgF_2 >> AlF_3$, and among the chlorides, $KCl > NaCl \approx LiCl \approx CaCl_2 > LnCl_3 > MgCl_2 >> AlCl_3$. The indicated order of stabilities, however, can be changed in real systems by changing the activities of one or more of the reactants or products. When no such change is effected, the above data indicate that calcium is the only choice for the reduction of rare earth oxides and fluorides, whereas the chlorides can also effectively be reduced with lithium, sodium, or potassium [2].

In the purification of rare earth metals, vacuum melting, electron beam melting, electrorefining and zone refining are used. By using these techniques, rare earth metals of different levels of purity can be obtained.

2.4.2. Other Metallurgical Processes

Metallurgical processes other than the conventional ones are summarized in the following paragraphs. These are generally about bastnasite ore (3-10% REO) and low grade concentrates.

2.4.2.1. Calcination and Nitric Acid Leaching

According to this process, bastnasite ore containing 7-10% REO is calcined at 800-900°C, and the calcined ore is ground to -10 mesh (1.65 mm), and then it is leached with 57 % nitric acid. The REE reporting to pregnant leach solution is filtered from leach residue and they are obtained from the pregnant leach solution by TBP solvent extraction method [2]. Rare earth metals recovery of this process is above 98%, but the industrial application of this process to bastnasite is absent. In Poland and Russia, HNO_3 leach process is applied to waste which is generated during the production of phosphoric acid from apatite and in the past it was applied to apatite in Finland.

2.4.2.2. Sulfating Roasting and Water Leaching

In this process, ground bastnasite is mixed with 98% H_2SO_4 and heated to 200°C. The added H_2SO_4 amount is twice of the calculated stoichiometric equivalent. During this heating (baking) process, the rare earth metals are converted to rare earth sulphates [5]. The reaction may be conducted in digesters, in rotary kilns, or in pugmills [40,79]. In order to obtain complete conversion, the heating of the mixture is continued up to 900°C and CO_2, HF and SiF_4 gases evolved from the system during this stage as seen in Figure 2.9.

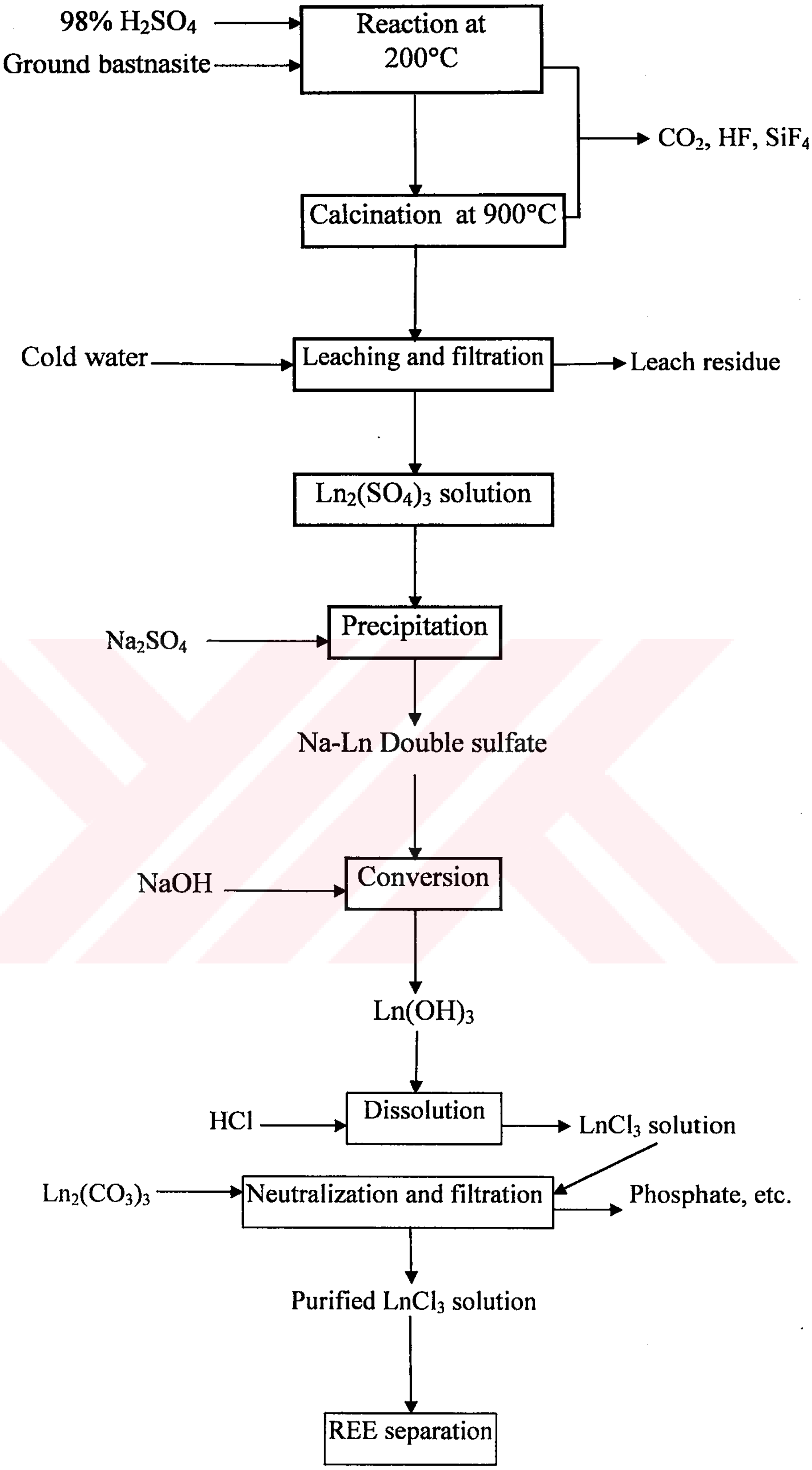


Figure 2.9. Acid Treatment of Bastnasite [5]

After the baking operation with acid, the rare earth metal sulphates are leached with cold water. After leaching, the pregnant leach solution is separated from insoluble gangue minerals by filtration. The pregnant leach solution contains about 50g/l REO from which sodium-lanthanon double sulphate is precipitated by the addition of sodium sulphate. Conversion to hydroxide with sodium hydroxide, dissolution in hydrochloric acid and neutralization to remove phosphate yields an acceptable lanthanon chloride solution.

The advantage of this process is elimination of barium and calcium. But disadvantages are; it requires calcination and HF production during the process. Some firms use this process in industrial scale in order to eliminate Fe, Pb, Si and Ba from bastnasite concentrates.

i. Mountain Pass Application

Sulphating roasting and water leach process was applied to Mountain Pass rare earth ore by USBM and positive results were obtained. In the first step, the bastnasite ore was leached with 10% HCl solution to remove calcium prior to reaction with sulphuric acid; otherwise, the calcium would report with the barium-strontium fraction, where it was difficult to remove. So REO grade of ore was increased from 7.05% to 12.4% REO.

Then the HCl-leached ore was reacted with concentrated H_2SO_4 at 150°C for 4 hours. The mixture was cooled, and the acid was separated from the residue by centrifugation. Barium and strontium were recovered from the concentrated H_2SO_4 by carefully adding the acid to an equal volume of water. The residue containing the rare earths was mixed with enough additional H_2SO_4 to give a thick paste and roasted at 650°C for 2 hours to convert the rare earth elements into sulphate. The cooled calcine was water leached to recover the soluble rare earth sulphates. As a final step, the rare earth metals were precipitated as oxalate and it was calcined at 600°C in order to obtain REO. Solvent extraction method could be applied to the rare earth sulphate solution in order to increase the quality of the rare earth product or to recover individual rare earth elements [34]. Flow diagram of this research done by USBM is given in Figure 2.10

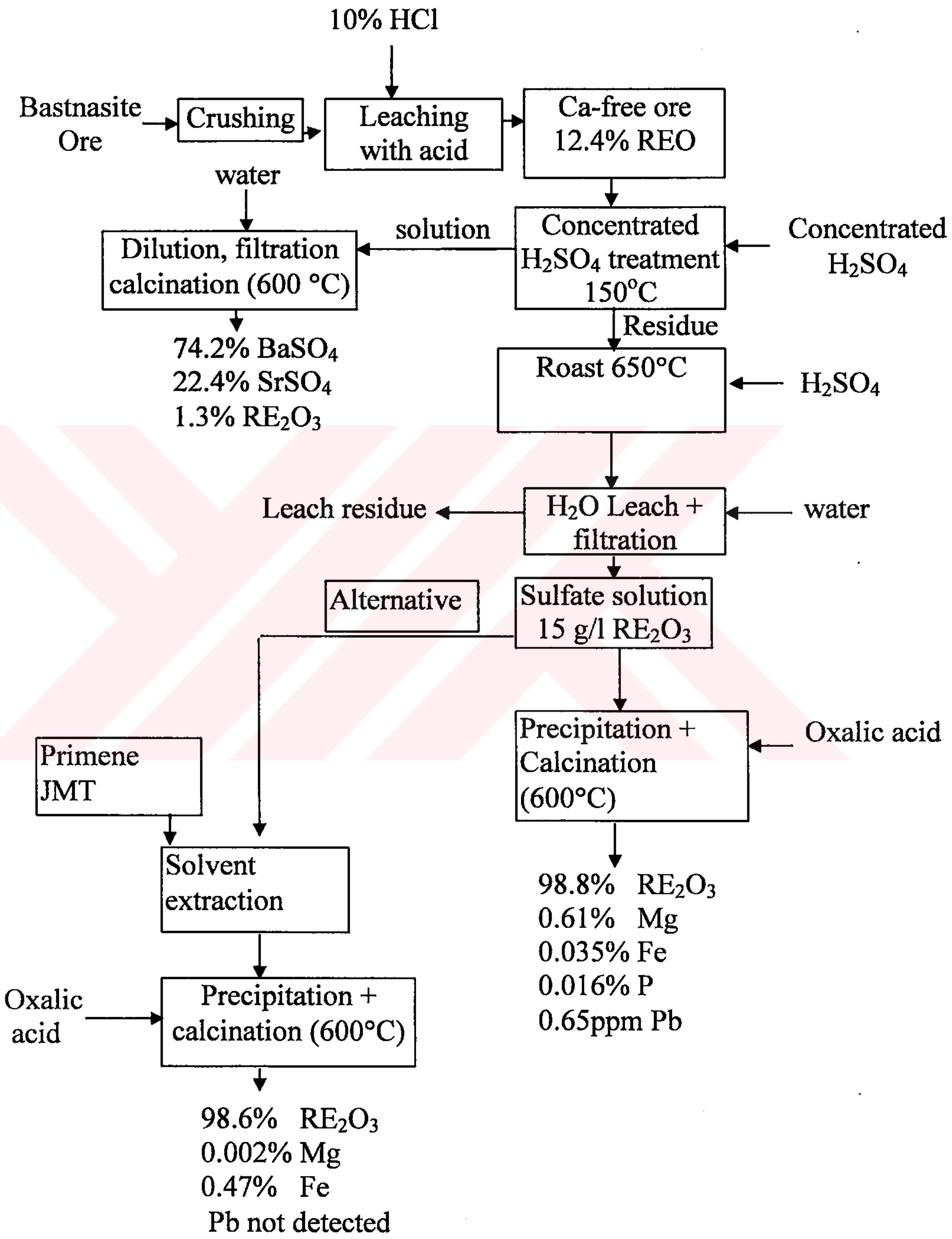


Figure 2.10. Flow Diagram for Treatment of Mountain Pass Ore Developed by USBM [34]

If this flowchart were to be applied to Mountain Pass ore, it would not require the flotation process to obtain a bastnasite concentrate.

ii.Vietnam Dong Pao Application

Mineral dressing of bastnasite type Dong Pao ore in Vietnam is very difficult because it has a very complex mineralogical structure. The concentrate which is produced from this ore, contains 32.8% REO, 29.3% $BaSO_4$, 7.5% CaF_2, 4.6% SiO_2, 6.0% Fe_2O_3, 3.3% MnO. The conventional metallurgical processes cannot be applied to this concentrate due to its high content of gangue minerals. Therefore, the developed process comprises the following steps [80,81]:

1. Comminution of the dried bastnasite concentrate.

2. Mixing of bastnasite concentrate with certain amount of H_2SO_4. Production of agglomerates due to the exothermic reaction.

3. Baking of agglomerates up to 200-300°C to remove fluorine and to obtain rare earth sulphates.

4. Leaching of rare earth sulphates and iron sulphates with cold water.

5. Removal of insoluble components like barite, quartz, MnO_2 and $CaSO_4$ by filtration.

6. Precipitation of rare earths as double sulphates from the pregnant leach solution by adding sodium sulphate and filtration.

7. Conversion of rare earth double sulphates to rare earth hydroxides by NaOH addition and separation of hydroxides from sodium sulphate solution by filtration.

8. Clarification of $NaSO_4$ solution from impurities (Fe^{+3}, Mn^{+2}, Zn^{+2} and Ca^{+2}) by addition of oxidizing agents, NaOH and soda.

9. Recovering of Na_2SO_4 from filtrate by cooling, crystallisation, filtration or centrifugation.

iii. Chinese Application

Preconcentrate containing 30% REO, which is obtained from Bayan Obo ore reserve, is mixed with hot H_2SO_4 and the mixture is calcined at 500-600°C and then the produced rare earth sulphates is leached with water and they are taken into leach solution. After the solid/liquid separation, the rare earth metals are precipitated as rare earth double sulphates with sodium sulphate addition and converted to rare earth hydroxides using NaOH. Finally, a rare earth chloride solution is obtained by leaching of the rare earth hydroxides for the following solvent extraction separation [50].

2.4.2.3. Direct Calcination

This process is suitable for ores which contain rare earth carbonates and alkali earth metal compounds; calcite, barite and $BaCO_3$. The aim of this method is the conversion of rare earth carbonates to other compounds especially to oxides which have high density so that they can be separated from gangue minerals by the use of density differences.

When crushed ore is heated to above 1000°C, rare earth carbonates decompose and convert to oxides. In this process CO_2 is eliminated from the system. In order to complete the elimination of CO_2, calcination duration should be more than 2 hours at 1000°C. The advantages of the process are; it does not require grinding, so dust lost is very low.

An ore, which contains 48.8% REO-barite mixture, was used in this research. After the calcination, the grade of mixture was raised to76.6% and then its grade was increased to 92.9% by shaking table. This process may be applied to low grade ores [82].

2.4.2.4. Calcination with Sodium Hydroxide

Another method that might be applied to bastnasite ore is calcination with sodium hydroxide. The bastnasite concentrate can be treated with caustic soda, to convert the fluoride components to hydroxide such as $Ln(OH)_3$. The rare earth hydroxides are then leached with HCl and insoluble $BaSO_4$ is separated from leach solution by filtration.

This process has been applied to a concentrate containing 70% REO which was produced at Mountain Pass. In this process, bastnasite concentrate containing 70% REO was leached with 30% HCl without calcination. So some part of the REE passed into solution as chlorides and leach residue was reacted with NaOH. As a result, the rare earth fluorides present in leach residue were converted to rare earth hydroxides and NaF by NaOH. The insoluble $Ln(OH)_3$ was filtered and used in neutralization of rare earth chloride leach solution. Sodium fluoride was obtained as by-product [2].

2.4.2.5. Direct Chlorination of Bastnasite

According to this process rare earth ores containing 7-10% REO can be chlorinated at high temperature. The process essentially consists of conversion of the components in the ore to chlorides by reaction with carbon and chlorine at 1000-1200°C followed by separation according to their volatility. The anhydrous rare earth chlorides are recovered in a molten form [2,83,84].

2.4.2.6. Rare Earth Metal-Silicon Alloy Production

In this process which is applied in China and other countries, bastnasite concentrate containing 30% REO is used in order to produce a REE-Si-Fe alloy. Bastnasite concentrate, coke, scrap iron and silica are mixed and smelted at 1600°C in a submerged arc furnace. Finally, a rare earth silicide alloy containing 30% REE-Si-Fe is obtained with 60% recovery [85-87]. This alloy is used in steelmaking process in order to control the sulphur content of the steel.

CHAPTER 3

PREVIOUS STUDIES ON BEYLİKAHIR ORE AND SAMPLE CHARACTERIZATION

3.1. Introduction

In this chapter, the previous studies related to the geology, mineralogy, mineral processing and hydrometallurgy of Beylikahır ores are summarized. Also, the physical, mineralogical and chemical characterization of Beylikahır ore and preconcentrate are given in detail.

3.2. Previous Studies

Geological studies on a hydrothermal type rare earth deposit located in Beylikahır region of Turkey started in 1959. The complex type of rare earth deposit was found at seven different locations in the area, namely, Devebağırtantepe, Küçükhöyüklütepe, Yaylabaşı, Köyyeri, Kocayayla, Kocadevebağırtan and Canavarini Sırtı. Detailed geological investigations of Devebağırtantepe and Küçükhöyüklütepe were completed in 1984. As a result of these studies, the total rare earth oxide (REO) content of the deposit was found to be 1 million tons with an average concentration of 3.14%REO. The proven and probable reserve of the bastnasite type rare earth deposit was estimated to be about 30 million tons [13,88-90].

Various mineralogical, mineral processing and hydrometallurgical investigations were carried out on Beylikahır ore samples by the Turkish Mineral Exploration and Research Institute starting from the date of 1974. Initial work was focused on the recovery thorium from Beylikahır rare earth ore. Due to the complex nature of the ore some other studies were done in order to recover the fluorite and barite [91-97]. In more recent years, the emphasis has changed to the recovery of rare earths as well as other products [98-102]. A number of masters thesis and Ph.D. work were also carried out related to Beylikahır deposit [103-107]. During the last ten years, some mineral processing as well as hydrometallurgical studies were also undertaken in Italy [108]. Most of these studies indicated that due to the complex nature of the ore, the concentration of rare earth minerals in a bastnasite concentrate was only possible at subsieve sizes. The grade of the bastnasite concentrate was very low and it was not easily marketable. On the otherhand, the physical concentrations of barite and fluorite minerals by gravimetric and flotation methods were found to be possible.

The most detailed study on Beylikahır ore samples was done at the Mining Engineering and Metallurgical Engineering Departments of Middle East Technical University. The details of this study is summarized below since the preconcentrate used in this Ph.D. work was obtained during that investigation [109].

3.3. Production of the Preconcentrate

As part of a project undertaken for Etibank which is the owner of the deposit, the representative samples of Beylikahır ore deposit were taken from Devebağırtantepe and Küçükhöyüklütepe regions. The sampling was done with the help of geological engineers of the Mineral Exploration and Research Institute of Turkey (MTA). Then, the two samples were analysed semi-quantitatively by an optical spectrophotometer. Later, the rare earths were chemically analysed by an inductively coupled plasma (ICP) and CaF_2, $BaSO_4$, $CaCO_3$ analyses were done by wet chemical methods [110-112]. The chemical analysis of the samples showed that they were very similar in nature. The mineralogical studies undertaken on the two samples using an optical microscopy and X-ray diffraction (XRD) techniques also indicated that they were mineralogically similar. So, the two samples from Devebağırtantepe and Küçükhöyüklütepe regions were mixed in 1 to 2 ratio since the reserve of Küçükhöyüklütepe is twice that of Devebağırtantepe. In this way, the composite ore sample of Beylikahır rare earth deposit was prepared. The chemical analysis of the composite ore sample is given in Table 3.1.

The mineralogical analysis of the composite ore sample by XRD indicated the presence of fluorite (CaF_2), barite ($BaSO_4$), bastnasite ($LnFCO_3$) and mica. Investigations of the opaque and transparent minerals of the composite ore sample under an optical microscope and scanning electron microscope (SEM) showed the presence of fluorite, barite, bastnasite, manganese minerals (pyrolusite, psilomelane), hematite, calcite, quartz, biotite, muscovite, pyrite, limonite, etc. The grain size of fluorite was in the range of 35-3000 microns but the most commonly found size was 300-800 microns. On the otherhand, barite was present in the size range of 35-1200 microns, the commonly occurring size being 60-400 microns. The bastnasite mineral was present in Beylikahır composite ore as cement material between the fluorite and barite particles or as intimately associated with these minerals. The size of bastnasite was submicroscopic. The thorium content of the ore was mainly due to the presence of thoro-bastnasite and brockite ($CaTh(PO_4)H_2O$).

Table 3.1. The Complete Chemical Analysis of Composite Ore Sample*

Element or Compound	Weight % or ppm	Analytical Method Used
Ce	%3.00	ICP
La	%2.70	ICP
Nd	%0.55	ICP
Pr	%0.18	ICP
Sm	520 ppm	ICP
Gd	120 ppm	ICP
Eu	60 ppm	ICP
Tb	<25 ppm	ICP
Dy	60 ppm	ICP
Ho	20 ppm	ICP
Er	40 ppm	ICP
Tm	<10 ppm	ICP
Yb	25 ppm	ICP
Lu	<10 ppm	ICP
Y	300 ppm	ICP
$CaCO_3$	%2.80	Gravimetric
SiO_2	%1.30	Gravimetric
CaF_2	%52.47	Gravimetric
$BaSO_4$	%25.40	Gravimetric
Al_2O_3	%4.00	Gravimetric
Fe_2O_3	%3.00	AAS
ThO_2	%0.09	XRF
SrO	%0.60	XRF
MnO	%0.54	AAS
P_2O_5	%1.00	XRF
CO_2	%1.16	Volumetric
S	%3.60	Volumetric
Pb	%0.071	AAS
Sc	%0.004	Spectral**
Ag	%0.003	Spectral
Ti	%0.07	Spectral
V	%0.02	Spectral
Mg	%0.20	Spectral

* Total REE: %6.5, REO: %7.9, $LnFCO_3$: %10.2

** Optical Spectrophotometer

At the beginning of the mineral processing studies, the composite ore sample ground to –10 mesh(1.65mm) size was subjected to a sieve analysis, the results of which indicated that fluorite was concentrated above 65 mesh (0.210mm) size while barite content increased below that size. The REE were enriched considerably in sub-sieve sizes. So, the classical concentration methods mentioned in the literature were not applicable alone for the production of marketable bastnasite concentrate. Attrition scrubbing of the original composite ore, screening and desliming by cyclones was found to be the most promising method capable of concentrating the bastnasite. Therefore, the crushed ore was subjected to attrition scrubbing for 1 hour at a solid concentration of 50% by weight. After dilution and screening through 400 mesh (37 microns) screen, the screen undersize was passed through a series of hydrocyclones. A preconcentrate as cyclone overflow with 28%REO grade and 72.6% recovery was obtained for 1.65mm top feed size. The REO grade and recovery were found to be 23.5% and 77.5%, respectively, for 1 cm size feed material. On the otherhand, the beneficiation of fluorite and barite minerals was carried out by applying various physical concentration methods. The application of gravity separation method alone by using shaking tables produced fluorite and barite concentrates assaying 72.0%CaF_2 and 80.9%$BaSO_4$ with recoveries of 84.7% and 60.1%, respectively. Cleaning of gravity concentrates by flotation and magnetic separation methods upgraded the fluorite concentrate to 92.2% CaF_2 and barite concentrate to 90.0% $BaSO_4$ with recoveries of 45.4% and 49.6%, respectively [109].

3.4. Characterization of Bastnasite Preconcentrate

The physical, chemical and mineralogical characterization of bastnasite preconcenrate obtained by attrition scrubbing, screening and cycloning as mentioned above is summarized below. Hydrometallurgical studies within the scope of this thesis were planned and carried out with the preconcentrate having 23.5%REO which corresponded to 19.5%REE or 30.5% $LnFCO_3$.

3.4.1 Physical Characterization

The density of the bastnasite preconcentrate was measured to be 3.73g/cc by an air pycnometer and its bulk density was determined as 1.32g/cc. Particle size distribution analysis of preconcentrate was done by Malvern Master Sizer instrument in TÜBİTAK/ SAGE. The analysis results in as received form is given in Table 3.2. As it can be seen from the table, about 88 % of the sample was below 25 microns and the average particle size was calculated to be 8.3 microns. The bastnasite preconcentrate was used in the hydrometallurgical studies without futher size reduction due to its fine size.

Table 3.2 Particle Size Distribution Analysis of Preconcentrate

Range μm	Wt. %	Cumulative Wt. % Undersize	Cumulative Wt. % Oversize
0.50 - 1.32	0.70	0.70	99.30
1.32 - 1.60	2.78	3.48	96.52
1.60 - 1.95	4.28	7.76	92.24
1.95 - 2.38	4.97	12.74	87.26
2.38 - 2.90	4.99	17.73	82.27
2.90 - 3.53	4.76	22.49	77.51
3.53 - 4.30	4.80	27.29	72.71
4.30 - 5.24	5.44	32.73	67.27
5.24 - 6.39	6.65	39.38	60.62
6.39 - 7.78	7.91	47.29	52.71
7.78 - 9.48	8.58	55.87	44.13
9.48 - 11.55	8.60	64.47	35.53
11.55 - 14.08	7.89	72.36	27.64
14.08 - 17.55	6.59	78.95	21.05
17.55 - 20.09	5.14	84.09	15.91
20.09-25.46	3.98	88.07	11.93
25.46-31.01	3.29	91.37	8.63
31.01-37.79	2.83	94.20	5.80
37.79-46.03	2.34	96.54	3.46
46.03-56.09	1.74	98.28	1.72
56.09-68.33	1.07	99.34	0.66
68.33-83.26	0.50	99.84	0.16
83.26-101.44	0.16	100	0

3.4.2 Chemical Characterization

The semi-quantitative chemical analysis of preconcentrate was done first by using an optical spectrophotometer. The results of this analysis are given in Table 3.2.

Table 3.2. The Optical Spectrophotometric Analysis of Bastnasite Preconcentrate

Cu	%0.03	Ba	> %1
Mn	%0.2	Ca	> %10
Pb	%0.04	Mg	%0.3
Ti	%0.15	Sr	%0.3
V	%0.04	Fe	%3
Y	%0.04	Si	> %1
Ce	> %1	Al	> %1
La	> %1		

Table: 3.2. (Continued) The Elements that were not Detected and Their Detection Limits:

Co	%0.004	Sc	%0.004
Cr	%0.004	Zr	%0.02
Ga	%0.01	Cd	%0.1
Ge	%0.01	Ni	%0.004
Nb	%0.01	Ta	%0.1
Sn	%0.004	Tl	%0.01
Ag	%0.0004	B	%0.004
In	%0.01	As	%1
Bi	%0.004	Na	%0.2
W	%0.1	Li	%0.1
Zn	%0.1	P	%2
Sb	%0.1	Te	%0.4
Mo	%0.02		

Later, the complete chemical analysis of the bastnasite preconcentrate was carried out and the results obtained are summarized in Table 3.3 with the analytical methods used for the determination of each element or compound.

Table 3.3. The Complete Chemical Analysis of Bastnasite Preconcentrate*

Element or Compound	Weight % or ppm	Analytical Method Used
Ce	%8.32	ICP
La	%8.81	ICP
Nd	%1.60	ICP
Pr	%0.53	ICP
Sm	1790 ppm	ICP
Gd	300 ppm	ICP
Eu	160 ppm	ICP
Tb	<50 ppm	ICP
Dy	120 ppm	ICP
Ho	47 ppm	ICP
Er	85 ppm	ICP
Tm	24 ppm	ICP
Yb	75 ppm	ICP
Lu	10 ppm	ICP
Y	500 ppm	ICP
$CaCO_3$	%8.50	Gravimetric
SiO_2	%2.74	Gravimetric
CaF_2	%41.37	Gravimetric
$BaSO_4$	%10.69	Gravimetric
Al_2O_3	%2.83	Gravimetric
Fe_2O_3	%4.18	AAS
ThO_2	%0.26	XRF
SrO	%0.9	XRF
MnO	%0.34	AAS
P_2O_5	%1.20	XRF

* Total REE%: %19.5, REO: %23.5, $LnFCO_3$: % 30.5

3.4.3 Mineralogical Characterization

For the mineralogical characterization of the preconcentrate X-ray diffraction analysis, optical microscopy and scanning electron microscopy investigations were undertaken.

The X-ray diffraction analysis was performed by Regaku Geirflex X-ray diffractometer. The X-ray diffraction pattern obtained indicated the presence of fluorspar (CaF_2), barite ($BaSO_4$) and bastnasite ($LnFCO_3$). The diffraction pattern of the preconcentrate with the peaks of the mentioned phases can be seen in Figure 3.4.1.

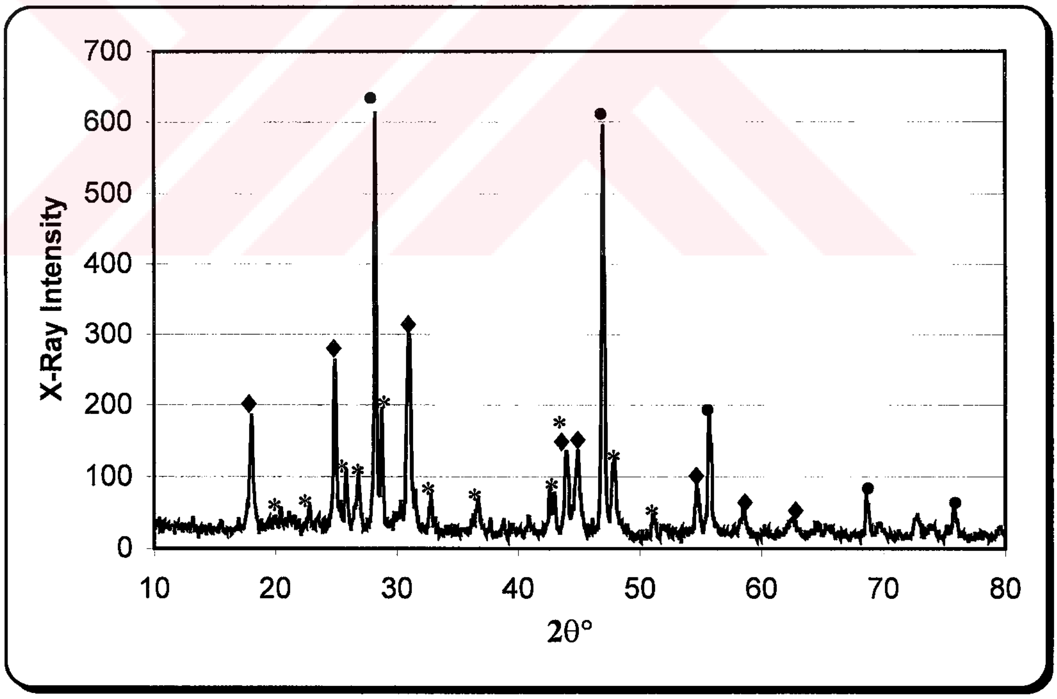


Figure 3.4.1. X-ray Diffraction Pattern of Bastnasite Preconcentrate; CaF_2:•, $LnFCO_3$:♦, $BaSO_4$:*

The mineralogical analysis using the Leitz-Orthoplan optical microscope indicated the presence of as main minerals fluorite, barite and thoro-bastnasite and small amounts of limonite ($2Fe_2O_3.3H_2O$), hematite (Fe_2O_3), anatase (TiO_2), rutile (TiO_2), psilomelane (H_4MnO_5), calcite ($CaCO_3$) and quartz (SiO_2). Also minor amounts of biotite and muscovite minerals were observed. The largest particle size of preconcentrate was measured as 40-50 microns in this microscope. Bastnasite was observed as a yellowish cloud and its size was very fine (1-2 microns). Thoro-bastnasite and clay minerals covered the other minerals, this caused a difficulty in the observation of other minerals. Photographs in Figures 3.4.2 – 3.4.6 show the main and minor constituents of the preconcentrate.

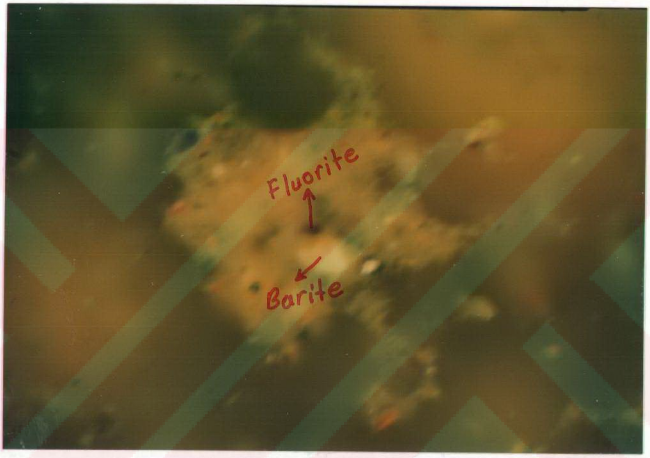


Figure 3.4.2. Optical Microscope Photograph of Bastnasite Preconcentrate; Fluorite, Barite and Thoro-Bastnasite (Yellowish Cloud is Thoro-bastnasite) (X250)

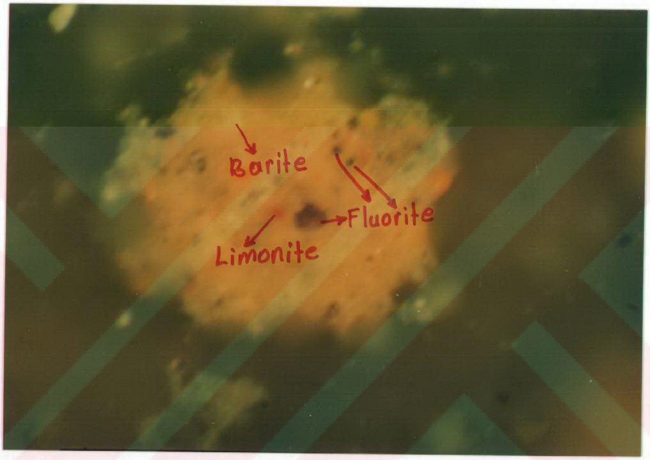


Figure 3.4.3. Optical Microscope Photograph of Bastnasite Preconcentrate; Fluorite, Barite and Limonite (X250)

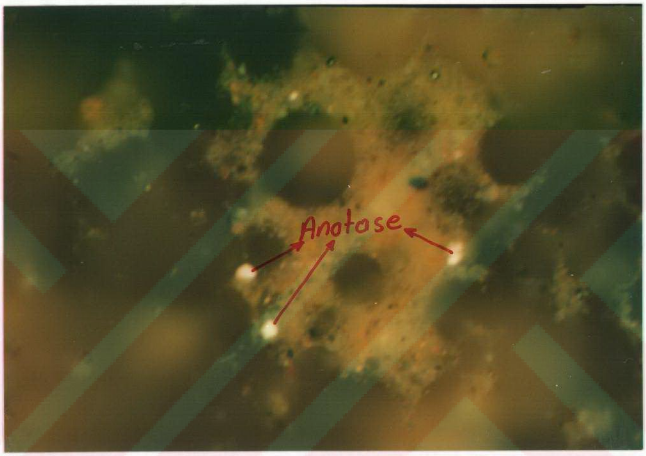


Figure 3.4.4. Optical Microscope Photograph of Bastnasite Preconcentrate; Anatase (X250)

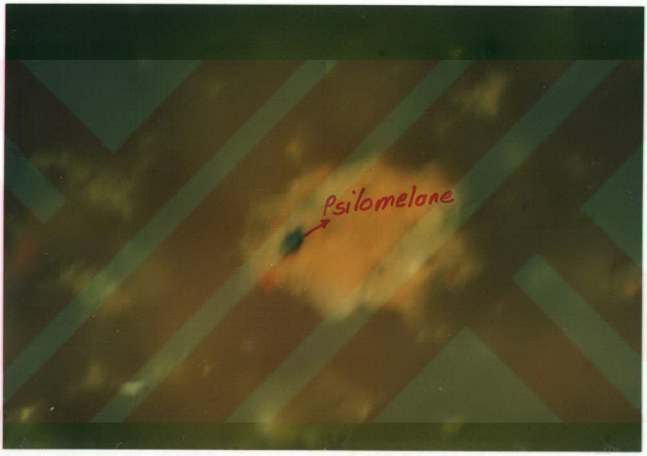


Figure 3.4.5. Optical Microscope Photograph of Bastnasite Preconcentrate; Psilomelane (X250)

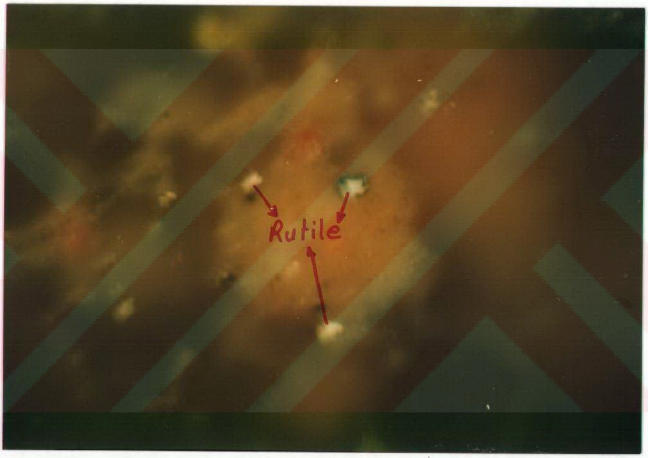


Figure 3.4.6. Optical Microscope Photograph of Bastnasite Preconcentrate; Rutile (X250)

SEM analysis confirmed the findings of X-ray diffraction and optical microscopy studies. SEM analysis was done by using JOEL ISM-6400 scanning electron microscope. The largest observed particle was about 40-50 microns as seen Figure 3.4.7. It may be mica or a clay mineral. It was composed of mainly Si, Mg, K, Al, Fe and O as given Figure 3.4.8. Photograph in Figure 3.4.9 shows a fluorite particle which is the largest particle in this photograph and it is about 20 microns in size. Its X-ray peaks as seen in Figure 3.4.10 showed that; it was composed of only Ca and F elements. General structure of preconcentrate is seen in photograph in Figure 3.4.11. X-ray analysis of this matrix phase as given Figure 3.4.12 showed the general composition of the preconcentrate which was composed of La, Ce, Ca, Si, Al, F, O, C and Fe. In photographs and Figures 3.4.13 to 16 a barite and an anatase minerals are seen, respectively with their X-ray peaks.

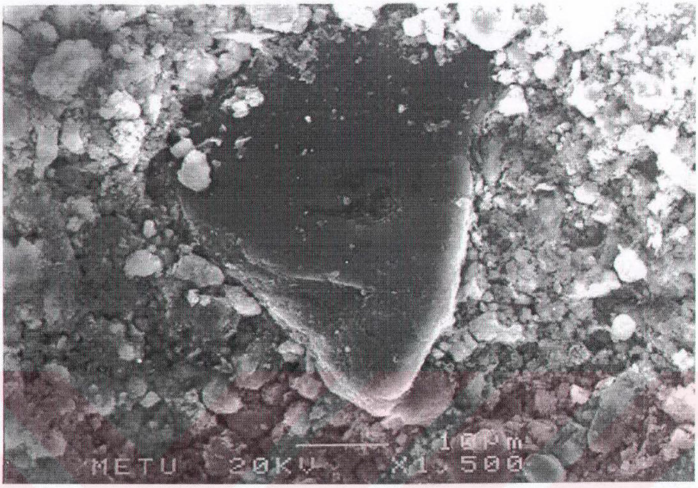


Figure 3.4.7. SEM Photograph of Bastnasite Preconcentrate: The Largest Particle A Clay Mineral

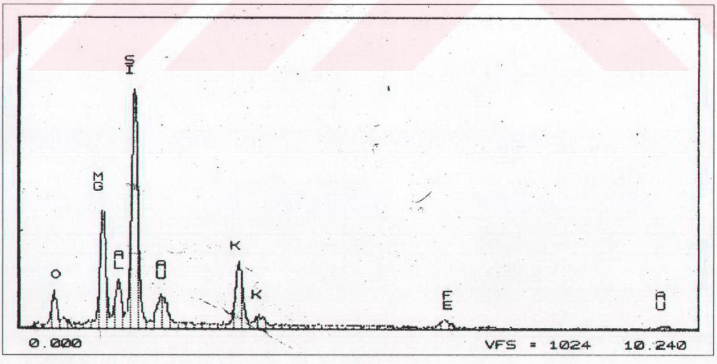


Figure 3.4.8. X-ray Diffraction Pattern of above Photograph

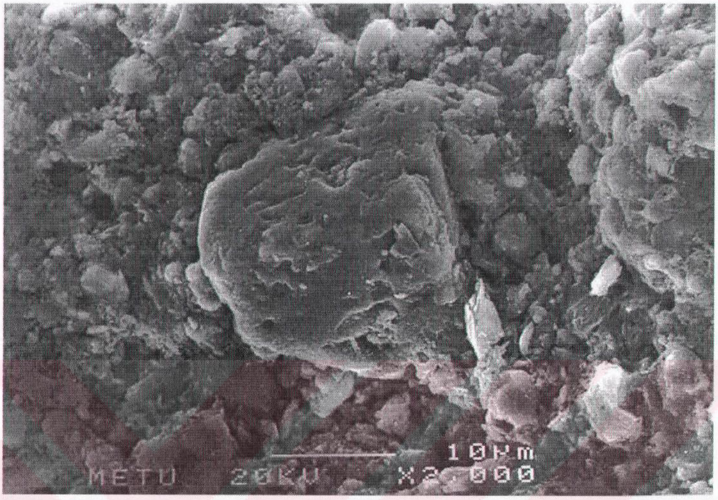


Figure 3.4.9. SEM Photograph of Bastnasite Preconcentrate: A Fluorite Particle

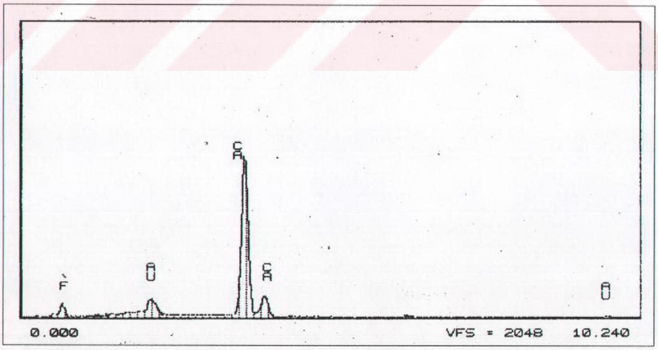


Figure 3.4.10. X-ray Diffraction Pattern of above Photograph

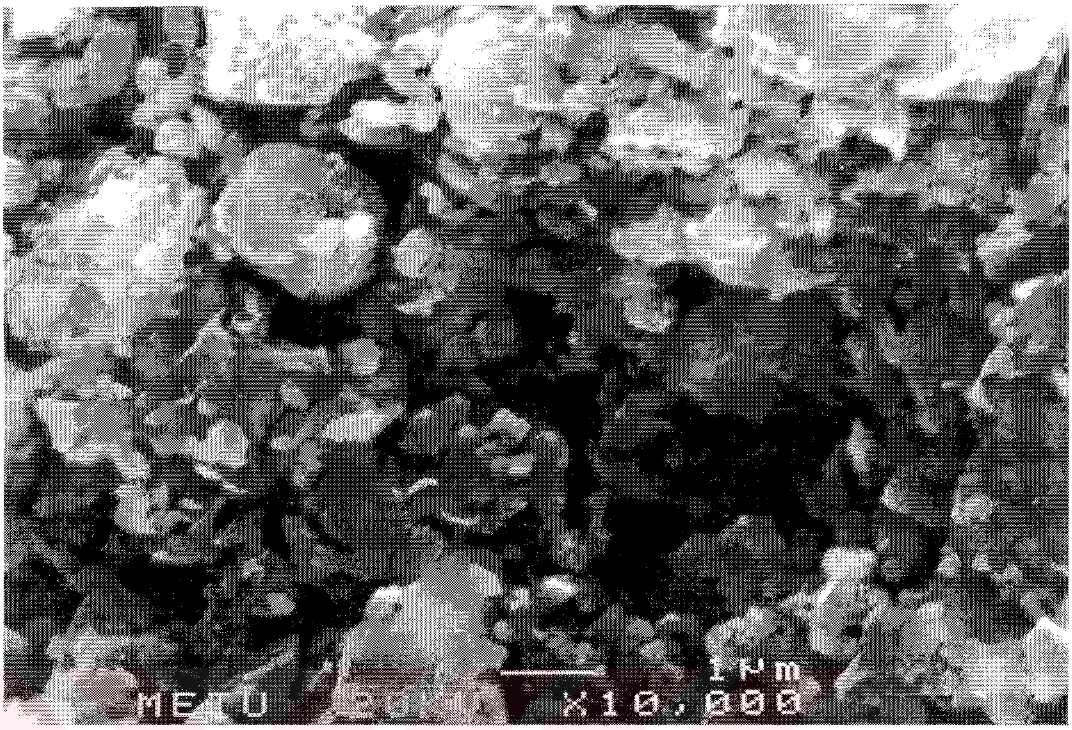


Figure 3.4.11. SEM Photograph of Bastnasite Preconcentrate: The Matrix Phase

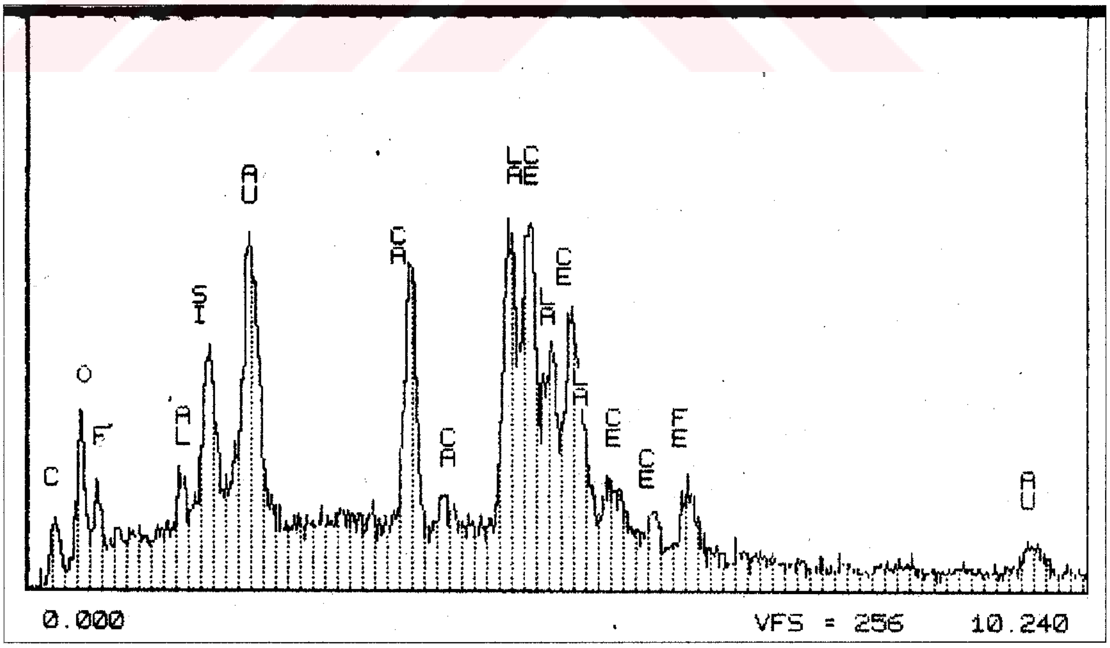


Figure 3.4.12. X-ray Diffraction Pattern of above Photograph

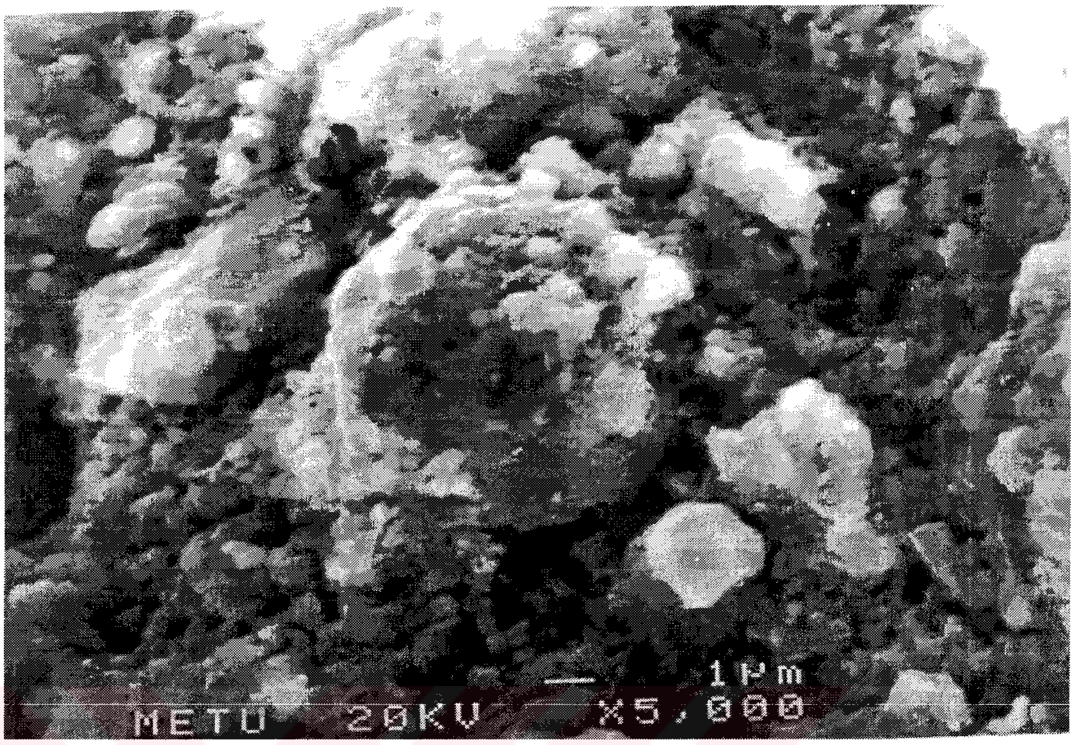


Figure 3.4.13. SEM Photograph of Bastnasite Preconcentrate: A Barite Particle

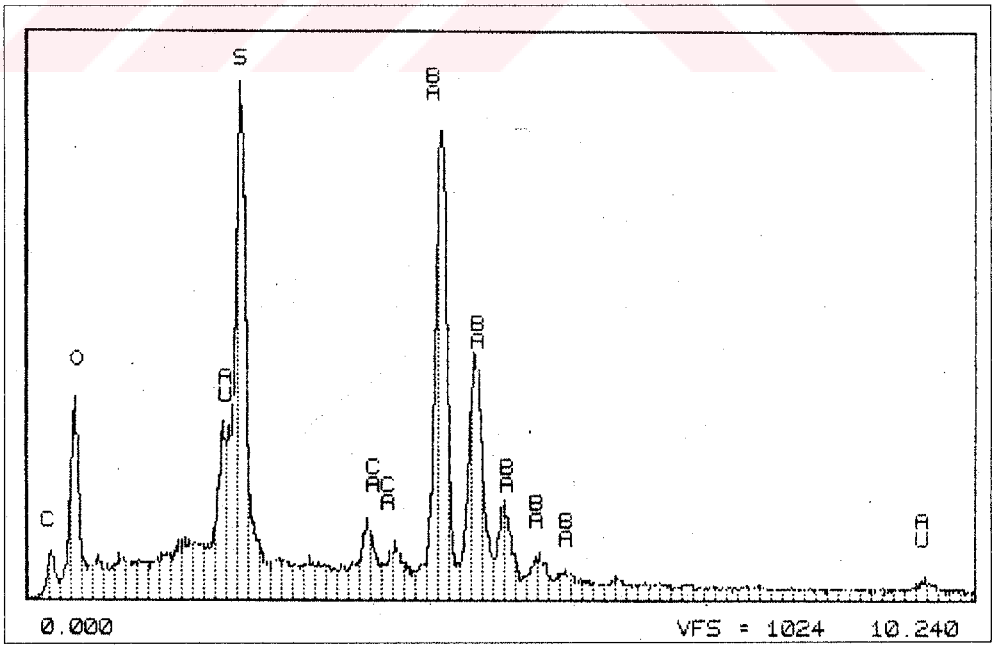


Figure 3.4.14. X-ray Diffraction Pattern of above Photograph

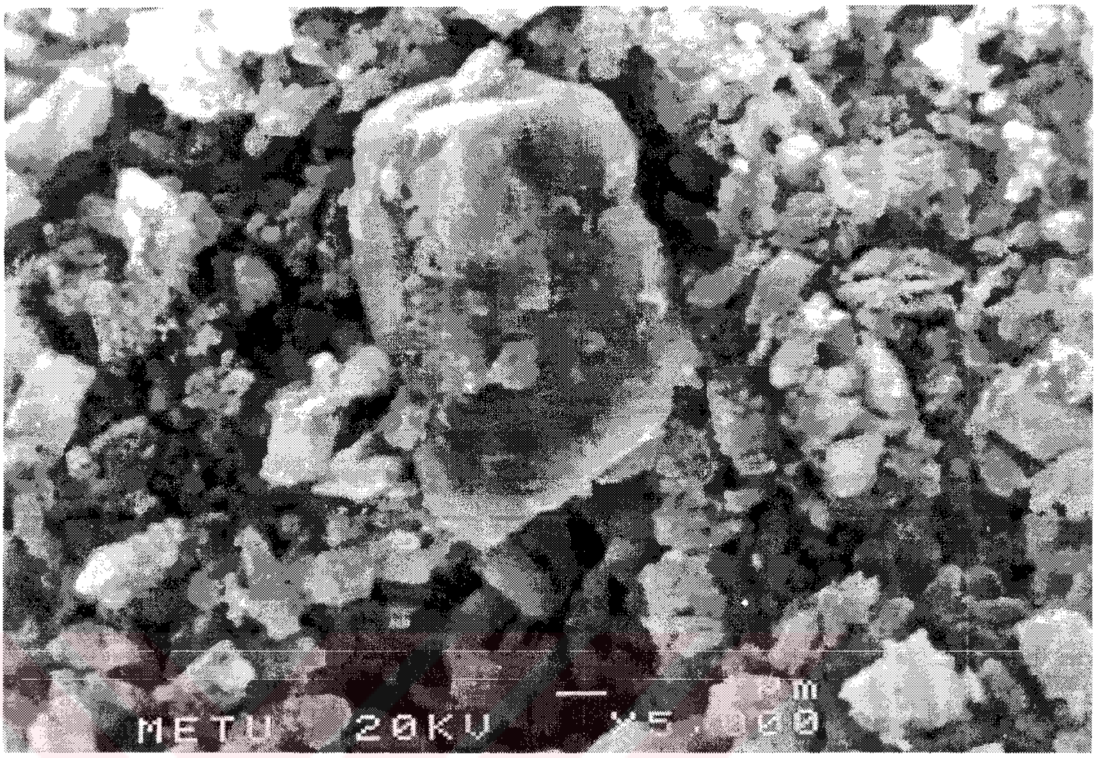


Figure 3.4.15. SEM Photograph of Bastnasite Preconcentrate: An Anatase Particle

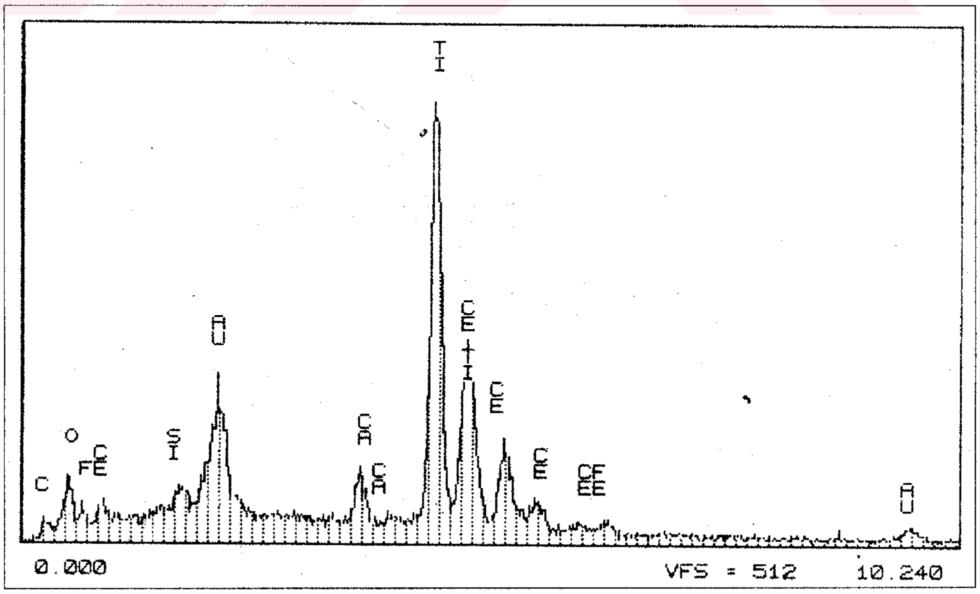


Figure 3.4.16. X-ray Diffraction Pattern of above Photograph

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1. Introduction

In this chapter, the experimental results obtained in the laboratory are given and the findings are discussed. In the hydrometallurgical extraction of rare earths from Beylikahır ore, the preconcentrate having 23.5% REO and a top size of 37 microns was used without further grinding. The complete chemical analysis of this preconcentrate was given in the previous chapter. Since this preconcentrate was low grade and not easily marketable, the conventional processes mentioned in Chapter 2 were not applicable. Previous studies and the information gathered from the literature indicated that the best way to recover the rare earths from the low grade Beylikahır preconcentrate was baking of the preconcentrate with concentrated sulphuric acid and subsequent water leaching [109]. So in this chapter, the experimental results of sulphuric acid baking, water leaching, precipitation of rare earths as double sulphate from pregnant leach solution with sodium sulphate, conversion of rare earth double sulphates to rare earth hydroxides with sodium hydroxide, drying of hydroxides and oxidation of Ce^{+3} to Ce^{+4}, hydrochloric acid leaching and separation of ceric oxide and separation of relatively heavier rare earths from light rare earths by solvent extraction are summarized.

4.2. Baking of Preconcentrate with Sulphuric Acid and Water Leaching

In connection with Beylikahır preconcentrate baking experiments, the stoichiometric requirement of sulphuric acid was calculated using the reactions given below:

$$2LnFCO_3 + 3H_2SO_4 = Ln_2(SO_4)_3 + 2HF + 2H_2CO_3 \quad (1)$$

$$CaCO_3 + H_2SO_4 = CaSO_4 + H_2CO_3 \quad (2)$$

$$CaF_2 + H_2SO_4 = CaSO_4 + 2HF \quad (3)$$

$$Fe_2O_3 + 3H_2SO_4 = Fe_2(SO_4)_3 + 3H_2O \quad (4)$$

$$MnO + H_2SO_4 = MnSO_4 + H_2O \quad (5)$$

The stoichiometric amount of concentrated sulphuric acid (98%) needed for the baking experiments was calculated to be 45.4 g H_2SO_4 per 50 g preconcentrate. Generally, the acid baking is applied to the treatment of monazite type rare earth ores or concentrates. But, several studies have been done in connection with acid baking of bastnasite type ores as well [80,81]. This method as mentioned before is also used for low grade (30%REO) bastnasite concentrates in China [50].

As stated before, the preconcentrate contains a substantial amount of CaF_2 which can be further processed to produce HF acid provided that its concentration is above a certain limit and the baking process is done at temperatures in excess of 200°C [113,114]. So the experimental route followed in baking was planned not only to convert bastnasite to water soluble sulphate but also to produce a marketable HF acid by the dissociation of 41.37 % CaF_2 that was present in the preconcentrate.

Samples weighing 50 g were mixed with calculated amount of concentrated H_2SO_4 in a Teflon beaker or porcelane capsule and a very fast exothermic reaction was observed causing formation of a hard mass after evolution of gases. The Teflon beaker was preferred at baking temperatures of 250°C or below. Then, the beaker or porcelain capsule was placed in a muffle furnace and the temperature was fixed at the desired level. A colour change was observed together with a weight loss as a result of baking. Finally, from the baked mass 40 g of sample was taken after grinding it to –1 mm for water leaching. The leaching experiments were carried out in a 400 cc beaker that was placed in a water bath for temperature control. The leaching experiments were done at 25°C for 2 hours at a solid to liquid ratio of 1/4 (g/cc) with the help of a mechanical stirrer at a constant stirring speed of 600 rpm. Among the experimental parameters investigated in baking were temperature, amount of sulphuric acid and duration of baking. Chemical analyses by ICP for the determination of leach recoveries were made by analyzing the rare earth concentrations of the leach residues that were also washed with distilled water after leaching.

4.2.1. Effect of Baking Temperature

In the first series of experiments, the effect of baking temperature on the recoveries of rare earth metals such as cerium and lanthanum was investigated. The other REE's were expected to behave in a similar manner to Ce and La. In these experiments, the amount of sulphuric acid added and the duration of baking were kept constant as the stoichiometric amount and 2 hours, respectively. As it can be seen from Table 4.2.1 and Figure 4.2.1, up to about 100°C of baking temperature the recoveries of rare earth metals were limited. Beyond 150°C of baking temperature, the recoveries of cerium and lanthanum reached a level of about 85-90% and there was little change up to 550°C. Since for the production of HF acid, the minimum temperature of baking should be 200°C, the optimum temperature of baking for the Beylikahır preconcentrate was chosen to be 200°C and kept constant in the following baking experiments.

Table 4.2.1. Effect of Baking Temperature on the Leach Recoveries of Ce and La

Experiment Code	Temperature, °C	Acid Amount, (gram)	Baking Duration (hour)	% La Leach Recovery	% Ce Leach Recovery
B1	**25**	45.4	2	65.7	55.1
B2	**50**	45.4	2	68.3	57.4
B3	**100**	45.4	2	69.5	59.3
B4	**150**	45.4	2	86.7	85.2
B5	**200**	45.4	2	89.1	85.3
B6	**250**	45.4	2	88.9	85.1
B7	**500**	45.4	2	89.8	85.3
B8	**550**	45.4	2	89.9	85.4

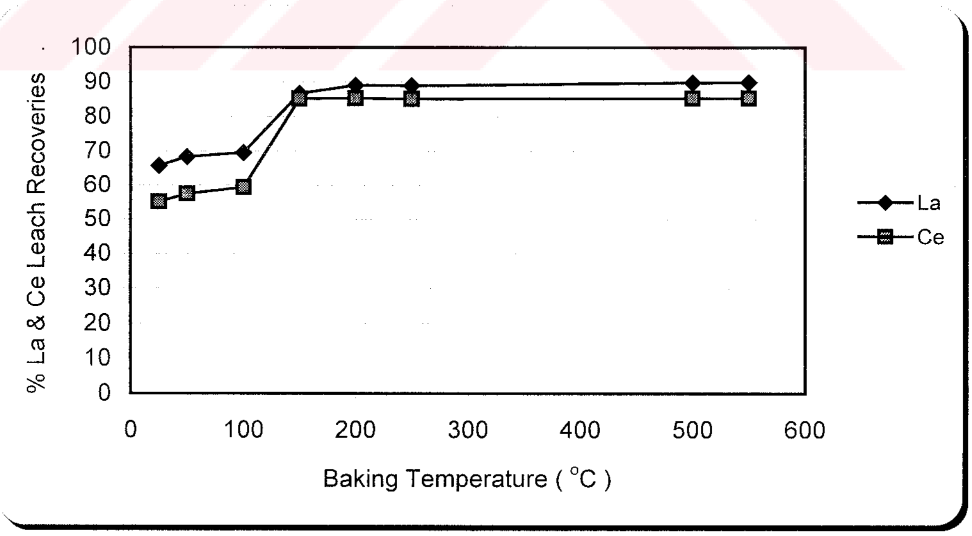


Figure 4.2.1. Effect of Baking Temperature on the Leach Recoveries of Ce and La

4.2.2. Effect of Acid Addition

In the second set of experiments, while keeping the baking temperature at 200°C and the baking duration at 2 hours, the amount of concentrated sulphuric acid added was varied in the range of 22.7 and 90.8 grams per 50 grams of preconcentrate. These acid additions corresponded to 1/2 and twice the calculated stoichiometric amount. The results of these second series of tests are given in Table 4.2.2 and Figure 4.2.2. As indicated by Figure 4.2.2, the minimum amount of sulphuric acid needed to obtain a rare earth recovery of the level of 85-90%, at least 45.4 grams of sulphuric acid (908 kg acid per ton of preconcentrate) was necessary which corresponded to the stoichiometric amount.

Table 4.2.2. Effect of Amount of Sulphuric Acid Added in Baking on the Leach Recoveries of Ce and La

Experiment Code	Temperature, °C	Acid Amount, (gram)	Baking Duration (hour)	% La Leach Recovery	% Ce Leach Recovery
B9	200	**22.7**	2	61.3	58.7
B10	200	**45.4**	2	89.1	85.3
B11	200	**68.1**	2	90.1	88.1
B12	200	**90.8**	2	92.2	89.3

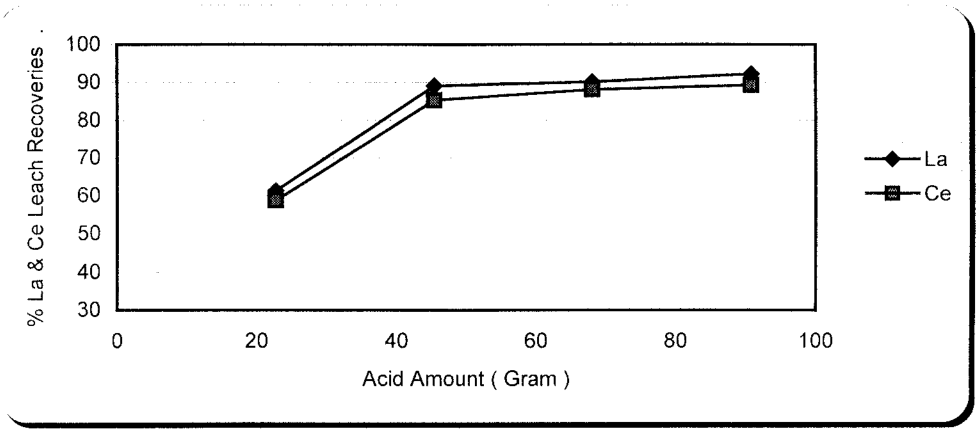


Figure 4.2.2. Effect of Amount of Sulphuric Acid Added in Baking on the Leach Recoveries of Ce and La

4.2.3. Effect of Baking Duration

In the last set of baking experiments, the duration of baking was optimized while keeping the baking temperature and the amount of acid added constant at 200°C and 45.4 g H_2SO_4 per 50 g preconcentrate, respectively. In these experiments, the baking duration was increased up to 24 hours and the results obtained are shown in Table 4.2.3 and Figure 4.2.3. From the figure, it can be seen that a baking duration of 2 hours was enough in order to obtain cerium and lanthanum leach recoveries of about 85% and 90%, respectively.

Table 4.2.3. Effect of Baking Duration on the Leach Recoveries of Ce and La

Experiment Code	Temperature, °C	Acid Amount, (gram)	Baking Duration (hour)	% La Leach Recovery	% Ce Leach Recovery
B13	200	45.4	½	76.1	77.5
B14	200	45.4	**1**	86.0	85.1
B15	200	45.4	**2**	89.1	85.3
B16	200	45.4	**3**	89.3	85.3
B17	200	45.4	**4**	89.0	85.4
B18	200	45.4	**6**	89.2	85.2
B19	200	45.4	**24**	89.1	85.3

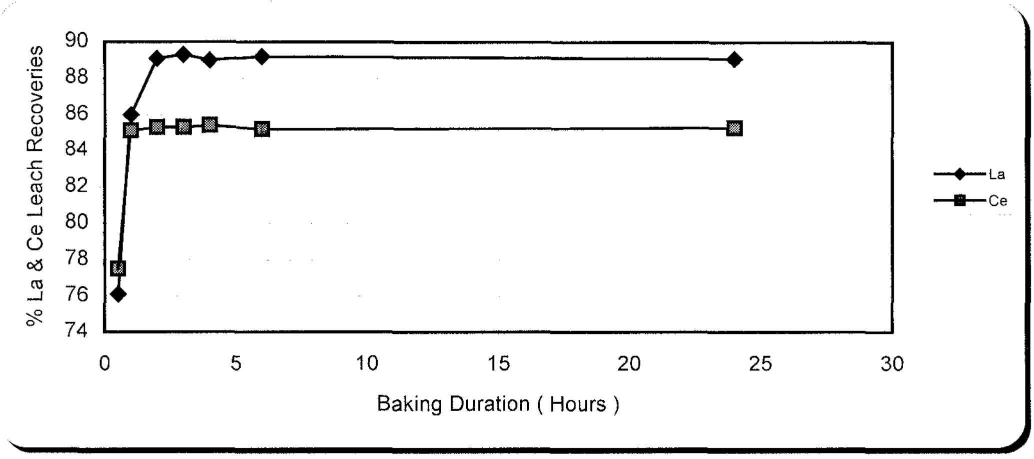


Figure 4.2.3. Effect of Baking Duration on the Leach Recoveries of Ce and La

So, the optimum conditions of baking for the Beylikahır preconcentrate was found to be 200°C baking temperature, 45.4 g H_2SO_4 per 50 g preconcentrate and 2 hours of baking duration. Under these conditions, 86% of the thorium present in the baked preconcentrate was leached, which was determined by means of XRF analysis. The pH of the pregnant leach solution obtained under the optimum conditions of baking was 2.6. XRD analysis of the leach residues indicated the presence of mainly gypsium, barite. The sulphuric acid baking and water leaching experiments carried out on the preconcentrate indicated that 85 to 90% of the REE's could be taken into leach solution as well as producing HF acid as by-product.

4.3. Optimization of Leaching Parameters

After the baking experiments of the preconcentrate, a baked preconcentrate stock was prepared under the optimum baking conditions for the leaching experiments, and then this stock was ground to -1 mm and homogenized. Then, the optimization of leaching parameters was done. The chemical analysis of the baked preconcentrate indicated that it had 5.73%La, 5.41%Ce, 1.04%Nd, 0.34%Pr, 1150 ppm Sm, 104 ppm Eu, 49 ppm Yb, 325 ppm Y, 16.0% Ca, 4.1%Ba, 1.95%Fe, 0.97%Al, 0.2%Mg, 0.17%Mn and 1500 ppm Th. The leaching experiments were carried out in a 400 cc beaker which was placed in a water bath for temperature control. In order to mix the solid and liquid a mechanical stirrer was used. The leaching experiments were conducted with distilled water.

4.3.1. Effect of Leaching Duration on the Leach Recoveries

Leach optimization experiments were started with the leaching duration. Leaching duration was varied between 1/2 to 4 hour while keeping leaching temperature, stirring speed and solid/liquid ratio constant at 25°C, 600 rpm, and 1/4, respectively. In these experiments, 40 grams of baked preconcentrate was leached with 160 cc distilled water and all of the results of these experiments are shown in Table 4.3.1 and Figure 4.3.1. As seen in Figure 4.3.1, half an hour was enough in order to extract the rare earth elements into leach solution. Above this leaching duration, the leach recoveries of REE's were not affected. As a result 1/2 hour was decided to be the optimum leaching duration.

Table 4.3.1. Effect of Leaching Duration on the Leach Recoveries of La and Ce

Experiment Code	Temperature, °C	S/L Ratio, g/cc	Leaching Duration, hr	Stirring Speed, rpm	% La Leach Recovery	% Ce Leach Recovery
L1	25	¼	½	600	88.9	85.1
L2	25	¼	**1**	600	89.3	85.2
L3	25	¼	**2**	600	89.1	85.3
L4	25	¼	**4**	600	89.4	85.2

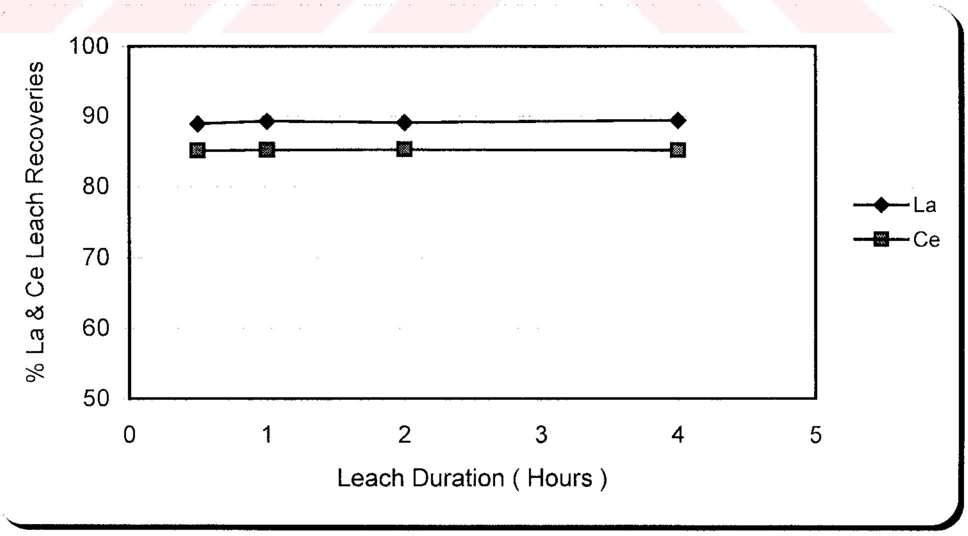


Figure 4.3.1. Effect of Leaching Duration on the Leach Recoveries of La and Ce

4.3.2. Effect of Leaching Temperature on the Leach Recoveries

The optimized second leaching parameter was leaching temperature. While keeping the leaching duration as 1/2 hour, solid-liquid ratio 1/4 and stirring speed 600 rpm constant, the leaching temperature was varied between 5 to 90°C. Results of these experiments showed that the recovery of REE's increased with decreasing leaching temperature as seen in Table 4.3.2 and Figure 4.3.2. Similar findings have been also reported in the literature [6]. The solubilities of sulfates of lanthanides are known to decrease with increasing temperature.

Table 4.3.2. Effect of Leaching Temperature on the Leach Recoveries of La and Ce

Experiment Code	Temperature, °C	S/L Ratio, g/cc	Leaching Duration, hr	Stirring Speed, rpm	% La Leach Recovery	% Ce Leach Recovery
L5	**5**	¼	½	600	92.8	89.0
L6	**25**	¼	½	600	88.9	85.1
L7	**50**	¼	½	600	86.9	85.1
L8	**75**	¼	½	600	86.9	83.2
L9	**90**	¼	½	600	75.2	71.5

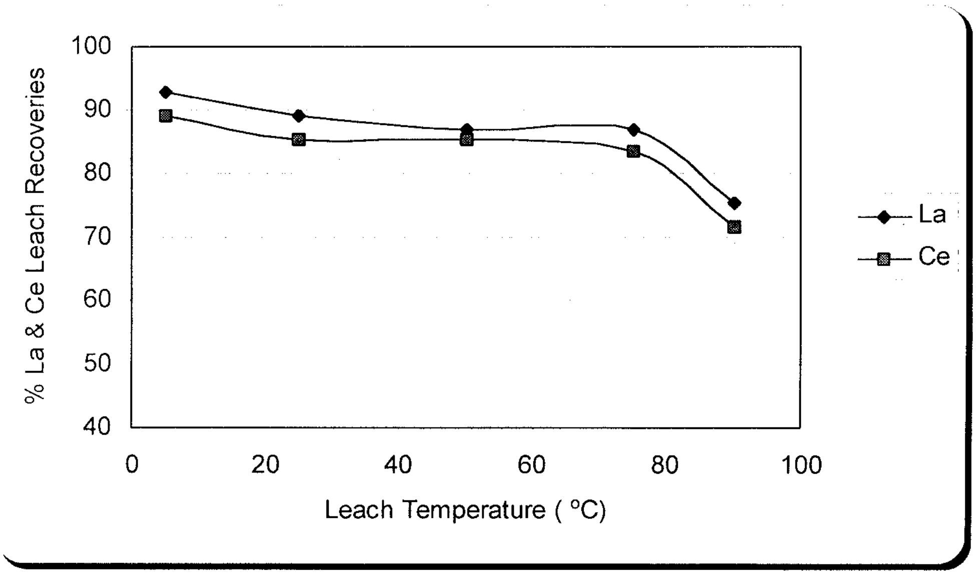


Figure 4.3.2. Effect of Leaching Temperature on the Leach Recoveries of La and Ce

4.3.3. Effect of Stirring Speed on the Leach Recoveries

In the third series of experiments, the effect of mechanical stirring speed on the recoveries of rare earth elements was investigated. In these experiments, the leaching temperature, duration of leaching and solid-liquid ratio were kept constant as 25°C, 1/2 hour and 1/4, respectively. As it can be seen from Table 4.3.3 and Figure 4.3.3, the leach recoveries of REE's were not influenced substantially by the variations in the stirring speed.

Table 4.3.3. Effect of Stirring Speed on the Leach Recoveries of La and Ce

Experiment Code	Temperature, °C	S/L Ratio, g/cc	Leaching Duration, hr	Stirring Speed, rpm	% La Leach Recovery	% Ce Leach Recovery
L10	25	¼	½	**200**	90.1	85.3
L11	25	¼	½	**400**	89.5	85.4
L12	25	¼	½	**600**	88.9	85.1
L13	25	¼	½	**800**	88.8	85.2

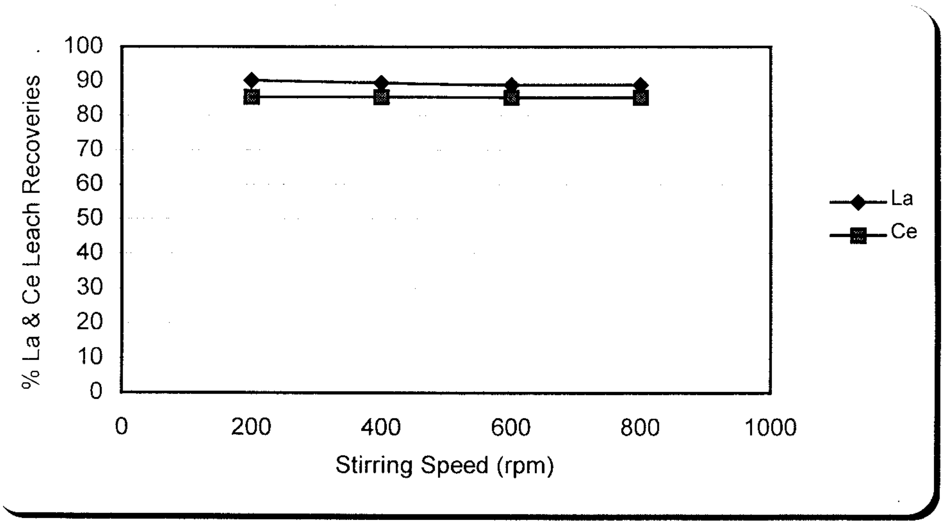


Figure 4.3.3. Effect of Stirring Speed on the Leach Recoveries of La and Ce.

4.3.4. Effect of Solid-Liquid Ratio on the Leach Recoveries

In the last series of leaching experiments, the effect of solid-liquid ratio on the leach recoveries of REE's was investigated. In these experiments, while the solid-liquid ratio was varied between 1/8 to 1/2, the other parameters were kept constant as follows; the leaching duration 1/2 hour , leaching temperature 25°C and stirring speed 600 rpm. The results of these experiments are given in Table 4.3.4 and Figure 4.3.4. As seen in this figure, the leach recoveries of La and Ce were not effected substantially from the changes in solid-liquid ratio.

Table 4.3.4. Effect of Solid-Liquid Ratio on the Leach Recoveries of La and Ce

Experiment Code	Temperature, °C	S/L Ratio, g/cc	Leaching Duration, hr	Stirring Speed, rpm	% La Leach Recovery	% Ce Leach Recovery
L14	25	**1/8**	½	600	89.3	87.0
L15	25	**2/8**	½	600	88.9	85.1
L16	25	**3/8**	½	600	86.2	85.0
L17	25	**4/8**	½	600	87.4	85.3

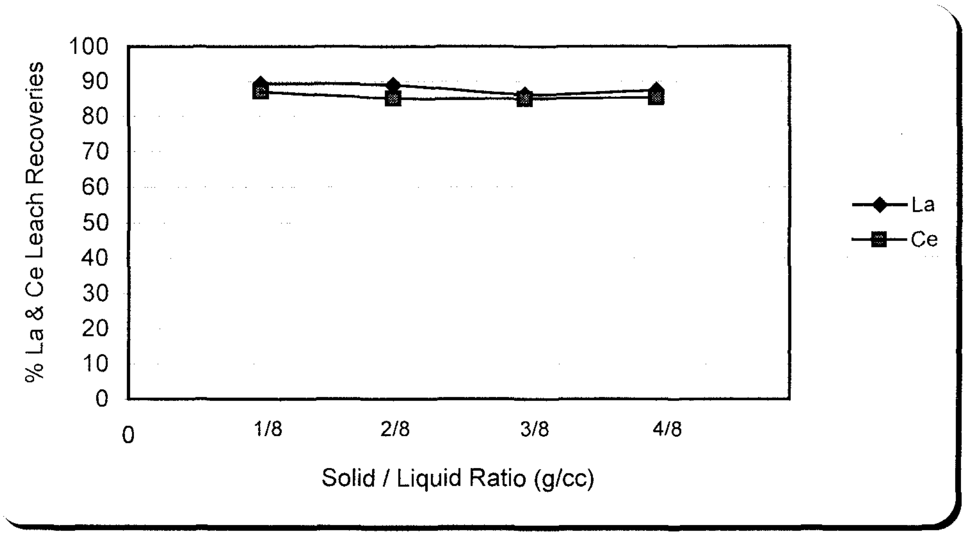


Figure 4.3.4. Effect of Solid-Liquid Ratio on the Leach Recoveries of La and Ce

4.3.5. Effect of H_2SO_4 or H_2O_2 Addition to Leach Solution on the Leach Recoveries

In an additional series of experiments, the effect of H_2SO_4 or H_2O_2 addition to leach solution on the leach recoveries of La & Ce was investigated. In these experiments, the leaching variables were kept constant as; the leaching duration 1/2 hour, leaching temperature 25°C, stirring speed 600 rpm and solid-liquid ratio 1/4. The results are given in Table 4.3.5.

Table 4.3.5. Effect of H_2SO_4 or H_2O_2 Addition to Leach Solution on the Leach Recoveries of La & Ce

H_2SO_4 Amount (cc.)	H_2O_2 Amount (cc.)	% La Leach Recovery	% Ce Leach Recovery
-	-	88.9	85.1
1.6	-	91.1	86.1
3.2	-	91.3	86.6
-	1.0	90.0	85.9
-	2.0	89.5	85.3

As seen from Table 4.3.5, the addition of H_2SO_4 or H_2O_2 did not affect the leach recoveries of La and Ce so much. But, the addition of H_2O_2 oxidized the Ce from Ce^{+3} to Ce^{+4}. This property may be used in the separation of Ce from other REE's. Therefore, the addition of H_2O_2 may be useful.

As a result, the optimum leaching parameters were chosen to be as; the leaching duration of half an hour and leaching temperature of 25°C due to easier control. Leach recoveries of the rare earth elements were affected very little by changes in stirring speed and solid-liquid ratio. Also distilled water without any additions of H_2SO_4 or H_2O_2 was decided to be the leachant.

4.4. Optimization of Precipitation Parameters

First of all, a pregnant leach solution stock was produced under the optimum baking and leaching conditions and this solution was used in the precipitation experiments. The chemical analysis of the stock solution, which was done using ICP, showed that it contained 12519 ppm La, 11380 ppm Ce, 2280 ppm Nd, 750 ppm Pr, 250 ppm Sm, 23 ppm Eu, 10 ppm Yb, 65 ppm Y, 420 ppm Mg, 3710 ppm Fe, 1665 ppm Al, 610 ppm Ca, 360 ppm Mn and 1 ppm Ba. Also 310 ppm Th was determined in this solution, the analysis of which was done at TAEK by XRF. On the other hand, the chemical analysis of the leach residue showed that there was 1.11%La, 1.55%Ce, 0.21%Nd, 0.07%Pr, 310 ppm Sm, 22 ppm Eu, 10 ppm Yb, 70 ppm Y, 32.1%Ca, 8.4%Ba, 3.7%SiO_2, 0.48%Fe, 0.60%Al, 0.05%Mg, 0.06%Mn and 482 ppm Th. The XRD analysis of the leach residue indicated that it was mainly made of gypsium ($CaSO_4$) and barite.

The calculated amount of pure solid sodium sulfate (Na_2SO_4) was mixed with 50 cc of pregnant leach solution in the precipitation experiments. The mixing was done in a three-necked balloon with a condenser and a temperature controllable hot plate with magnetic stirrer. Added Na_2SO_4 amount, precipitation temperature and precipitation duration were investigated as the precipitation parameters. The precipitate was washed with hot 2% Na_2SO_4 solution and dried at 105°C. The filtrate, which was obtained after precipitation, was analyzed by ICP and the precipitation recoveries were calculated. The following reaction was assumed for the precipitation of rare earth elements and the stoichiometric amount of sodium sulfate was calculated by using this reaction [3]:

$$Ln_2(SO_4)_3 + Na_2SO_4 + 2H_2O = Na_2SO_4.Ln_2(SO_4)_3.2H_2O \qquad (6)$$

The results of rare earth double sulfate precipitation experiments have been summarized in the following sections.

4.4.1. Effect of Na_2SO_4 Amount on the Precipitation Recovery

In the first series experiments, the amount of sodium sulfate added was varied in the range of 1 to 3 times of the stoichiometric ratio. In these experiments, the precipitation duration and precipitation temperature were kept constant as 90 minutes and 90°C, respectively. The results of these experiments are given in Table 4.4.1 and Figure 4.4.1. The lanthanum precipitation recovery increased from 96.1% to 98.2%, when Na_2SO_4 amount added was changed from 1 (0.68 g) to 1.25(0.85 g) times of the stoichiometric amount. Also, the cerium precipitation recovery increased from 93.1% to 96.5%. The precipitation recoveries of Y and Yb were maximum 76.2% and 85.3%, respectively in the same range.

As seen in Figure 4.4.1, an important increase in the La, Ce, Y and Yb precipitation recoveries was not observed above 1.25 times of the stoichiometric Na_2SO_4 addition. On the other hand, the amount of thorium in the precipitate also increased with the increasing amount of Na_2SO_4 addition. For example; when the added Na_2SO_4 amount was 1.25 times of the stoichiometric ratio, thorium precipitation recovery was only 30.2%. But when the amount of Na_2SO_4 added was increased to 3 times of the stoichiometric amount 64.3% of thorium in the pregnant leach solution was precipitated. Similar findings have been reported in the literature that the precipitation of thorium increases with the increasing amount of sodium sulfate addition [5]. Therefore, 1.25 times of the stoichiometric Na_2SO_4 amount was chosen as the optimum addition.

Table 4.4.1. Effect of Na_2SO_4 Amount on the Precipitation Recovery of Rare Earths

Experiment Code	Temperature, °C	Na_2SO_4 Amount*	Precipitation Duration, min	% La Precipitation Recovery	% Ce Precipitation Recovery	% Y Precipitation Recovery	% Yb Precipitation Recovery
P1	90	**1.00**	90	96.1	93.1	70.9	84.2
P2	90	**1.25**	90	98.2	96.5	76.2	85.3
P3	90	**1.50**	90	98.7	97.8	76.9	85.2
P4	90	**2.00**	90	99.5	98.6	78.1	85.4
P5	90	**3.00**	90	99.9	99.9	80.1	87.1

* with respect to the stoichiometric amount, i.e. Added Na_2SO_4 / Stoichiometric Na_2SO_4

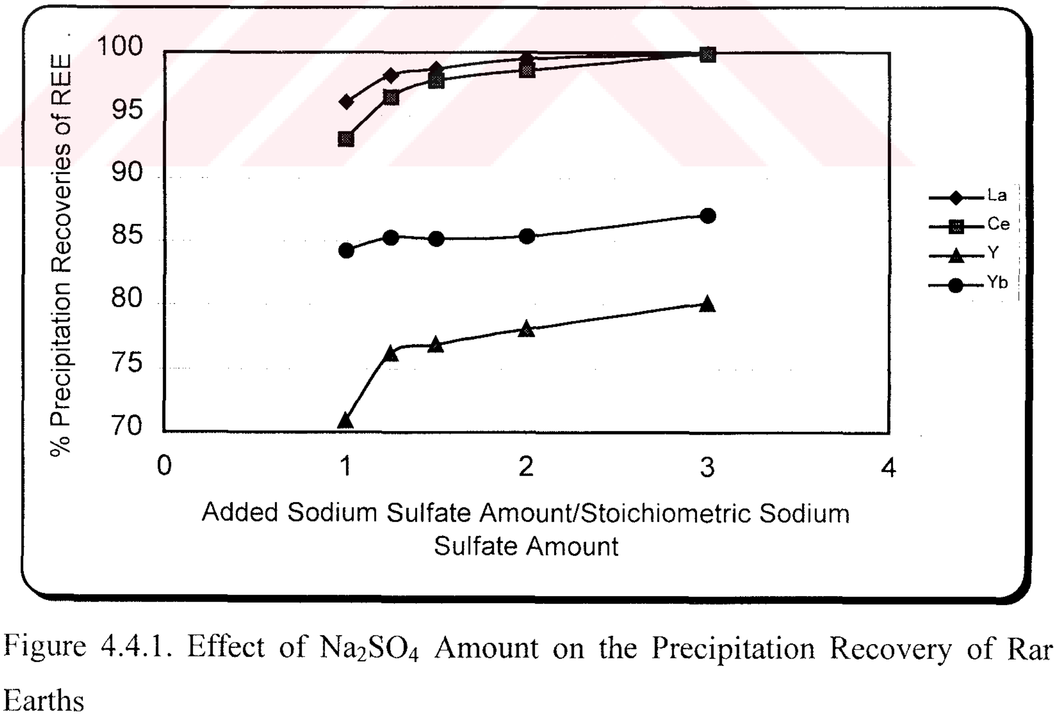


Figure 4.4.1. Effect of Na_2SO_4 Amount on the Precipitation Recovery of Rare Earths

4.4.2. Effect of Precipitation Temperature on the Precipitation Recovery

The second optimized precipitation parameter was precipitation temperature. While keeping constant, the precipitation duration as 90 minutes and Na_2SO_4 addition as 1.25 times of the stoichiometrically calculated in these experiments, the precipitation temperature was changed between 25°C and 90°C. Precipitation recoveries of rare earth metals were a little low below 50°C as seen in Table 4.4.2 and Figure 4.4.2. But the increase in the precipitation recoveries above 50°C were not so much. Also an increase in thorium precipitation and contamination of REE precipitate was observed with the increasing temperature. For example; only 6% of Th in the pregnant leach solution was precipitated with REE's at 25°C. When the precipitation temperature was increased to 90°C thorium precipitation recovery was also increased to 30.2%. Therefore, the optimum precipitation temperature was chosen as 50°C. According to the literature, as the precipitation temperature increases the precipitation of thorium and heavier rare earths are promoted [5].

Table 4.4.2. Effect of Precipitation Temperature on the Precipitation Recovery of Rare Earths

Experiment Code	Temperature, °C	Na_2SO_4 Amount	Precipitation Duration, min	% La Precipitation Recovery	% Ce Precipitation Recovery	% Y Precipitation Recovery	% Yb Precipitation Recovery
P6	**25**	1.25	90	89.7	81.1	72.3	77.9
P7	**50**	1.25	90	97.3	94.2	75.2	82.1
P8	**75**	1.25	90	97.9	96.0	76.1	84.6
P9	**90**	1.25	90	98.2	96.5	76.2	85.3

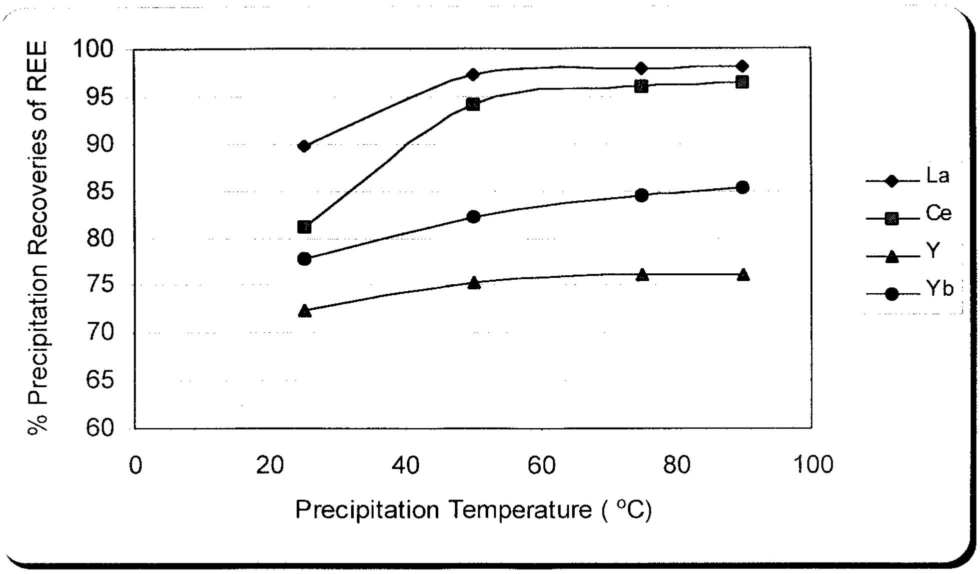


Figure 4.4.2. Effect of Precipitation Temperature on the Precipitation Recovery of Rare Earths

4.4.3. Effect of Precipitation Duration on the Precipitation Recovery

In the last two series of precipitation experiments, the effect of precipitation duration on the precipitation recoveries of rare earth elements were researched at two different temperatures. Precipitation temperature of 50°C and Na_2SO_4 addition of 1.25 times of the stoichiometrically calculated were kept constant while precipitation duration was varying from 5 to 180 minutes in the first series of experiments. As shown Table 4.4.3 and Figure 4.4.3, very high La and Ce precipitation recoveries were obtainable in a very short time (like 5 minutes). The increase in the precipitation recovery of La was about 5% when the duration was increased from 5 to 60 minutes. Also, the precipitation of impurity elements like Ca, Fe, Al and Mg was increased with increasing duration of precipitation as seen in Table 4.4.4 and Figure 4.4.4. This resulted in an increase in the impurity content of the rare earth double sulfate precipitates. Therefore, at a relatively low temperature and in a short duration of precipitation, it was easier to produce a cleaner REE precipitate.

Table 4.4.3. Effect of Precipitation Duration on the Precipitation Recovery of REE at 50°C

Experiment Code	Temperature, °C	Na_2SO_4 Amount	Precipitation Duration, min	% La Precipitation Recovery	% Ce Precipitation Recovery	% Y Precipitation Recovery	% Yb Precipitation Recovery
P10	50	1.25	**5**	91.1	92.3	70.0	80.0
P11	50	1.25	**60**	96.5	93.4	73.0	81.0
P7	50	1.25	**90**	97.3	94.2	75.2	82.1
P12	50	1.25	**180**	97.5	95.9	76.0	83.0

Table 4.4.4. Effect of Precipitation Duration on the Precipitation of Impurities at 50°C

Experiment Code	Temperature °C	Na_2SO_4 Amount	Precipitation Duration, min	%Ca Precipitation	%Fe Precipitation	%Al Precipitation	%Mg Precipitation
P10	50	1.25	**5**	61.1	10.2	10.2	0.5
P11	50	1.25	**60**	63.9	24.2	20.0	14.7
P12	50	1.25	**180**	66.5	29.3	27.4	18.7

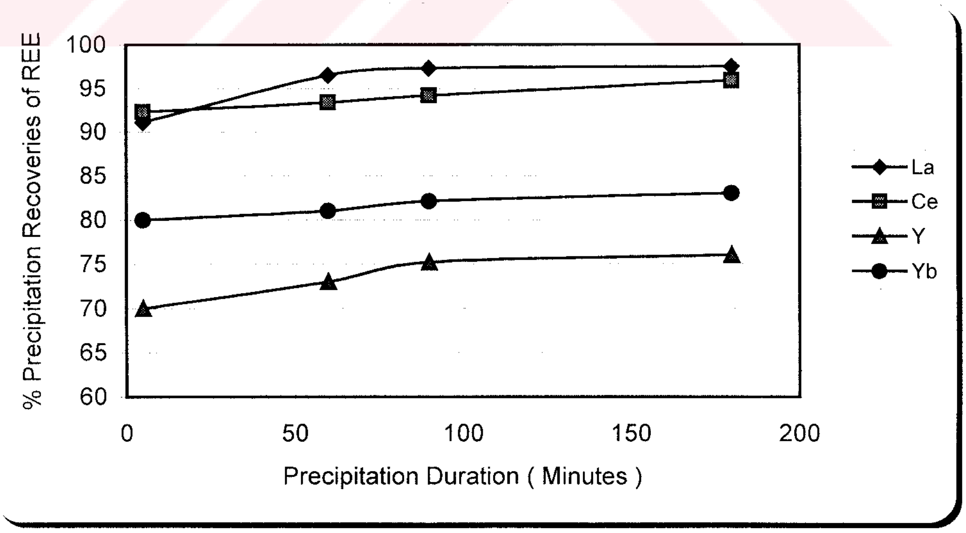


Figure 4.4.3. Effect of Precipitation Duration on the Precipitation Recovery of REE at 50°C

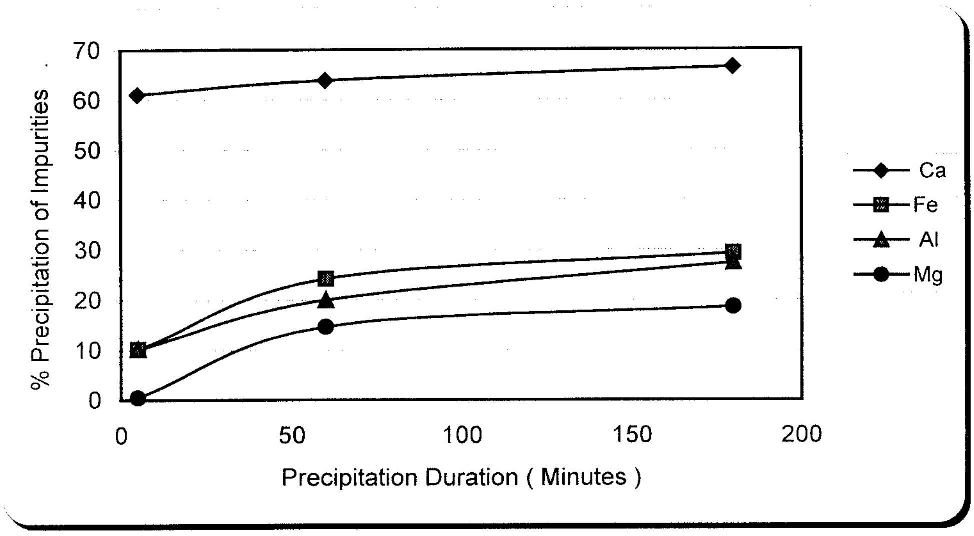


Figure 4.4.4. Effect of Precipitation Duration on the Precipitation of Impurities at 50°C

At the last series of experiments, the effect of precipitation duration at 90°C on the precipitation recoveries of lanthanides and other metals were studied. As seen in Table 4.4.5 and Figure 4.4.5, the precipitation recoveries of lanthanides were not affected so much from the precipitation duration at high temperatures. However, the precipitation of impurity metals such as Fe, Mg, Al was decreased or that of Ca was increased a little with the increasing precipitation duration as shown in Table 4.4.6 and Figure 4.4.6. At the same time, the thorium content of the rare earth metals precipitated as a double sulphate salt increased with the increasing precipitation duration. For example; when the precipitation duration was 5 minutes, 23.7 % of Th in the pregnant leach solution was precipitated, but when the precipitation duration was increased to 90 minutes, the precipitation recovery of thorium was 30.2%. Therefore, in a short duration of precipitation at 50°C and with 1.25 times of the stoichiometric Na_2SO_4 addition, it is expected to produce the rare earth double sulfate salt as precipitate of optimum concentration.

In this way, a fair degree of decontamination of the precipitate from impurities such as Fe, Al and Mg is possible.

Table 4.4.5. Effect of Precipitation Duration on the Precipitation Recovery of REE at 90°C

Experiment Code	Temperature, °C	Na_2SO_4 Amount	Precipitation Duration, min	% La Precipitation Recovery	% Ce Precipitation Recovery	% Y Precipitation Recovery	% Yb Precipitation Recovery
P13	90	1.25	**5**	97.5	96.4	75.5	85.0
P14	90	1.25	**60**	98.1	96.5	76.0	85.1
P9	90	1.25	**90**	98.2	96.5	76.2	85.3
P15	90	1.25	**180**	99.2	98.3	76.6	85.4

Table 4.4.6. Effect of Precipitation Duration on the Precipitation of Impurities at 90°C

Experiment Code	Temperature, °C	Na_2SO_4 Amount	Precipitation Duration, min	%Ca Precipitation	%Fe Precipitation	%Al Precipitation	%Mg Precipitation
P13	90	1.25	**5**	56.1	28.2	27.1	17.9
P14	90	1.25	**60**	62.8	25.1	25.3	14.8
P15	90	1.25	**180**	61.9	22.8	21.9	11.2

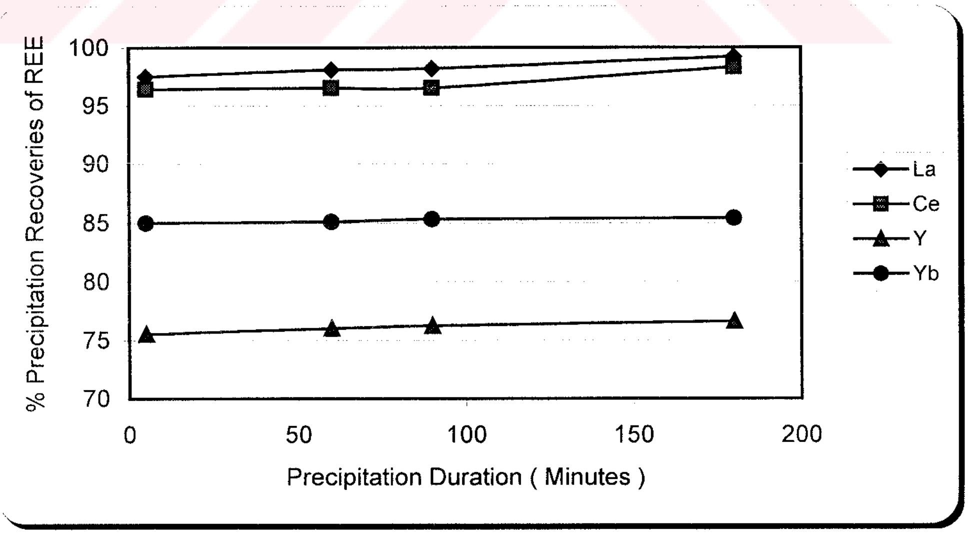


Figure 4.4.5. Effect of Precipitation Duration on the Precipitation Recovery of REE at 90°C

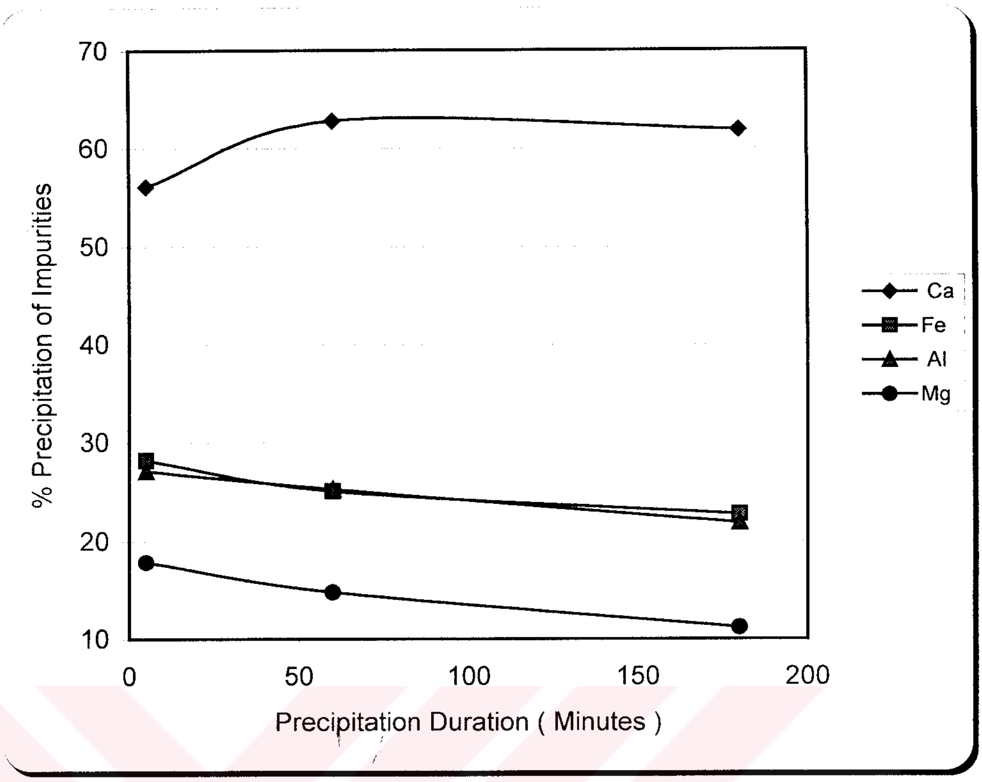


Figure 4.4.6. Effect of Precipitation Duration on the Precipitation of Impurities at 90°C

After that, a rare earth double sulfate salt ($Na_2SO_4.Ln_2(SO_4)_3.2H_2O$) was precipitated from the pregnant leach solution and a stock of this precipitate was obtained. In order to produce this stock, 1.25 times of the stoichiometric ratio solid sodium sulfate was added to the pregnant leach solution at 50°C and this mixture was stirred for 5 minutes. The precipitated rare earth double sulfate salt was washed with hot 2% Na_2SO_4 solution and dried at 105°C. The chemical analysis of this rare earth double sulfate salt stock, which was done by ICP, showed that, it contained 17.33% La, 15.64 % Ce, 3.15% Nd, 1.10% Pr, 0.31% Sm, 320 ppm Eu, 111 ppm Yb, 210 ppm Y, 75 ppm Mg, 136 ppm Mn, 1023 ppm Fe, 1100 ppm Al, 4231 ppm Ca and 1 ppm Ba. The stock of this precipitate was used in the conversion of rare earth double sulfate to rare earth hydroxide by sodium hydroxide experiments.

4.5. Conversion of Rare Earth Double Sulfate to Rare Earth Hydroxide by Sodium Hydroxide

In this part, the conversion of rare earth double sulfate, which was obtained by using the optimum baking, leaching and precipitation parameters, to rare earth hydroxide by sodium hydroxide was investigated.

In the conversion experiments, the following reaction was used for the conversion of rare earth double sulfate salt to rare earth hydroxide:

$$Na_2SO_4.Ln_2(SO_4)_3.2H_2O + 6NaOH = 2Ln(OH)_3 + 4Na_2SO_4 + 2H_2O \qquad (7)$$

The stoichiometric sodium hydroxide amount was calculated by using this reaction. The calculated amount of pure sodium hydroxide was mixed with 50 cc of distilled water and this solution was heated to the boiling temperature (98°C) in order to obtain a granular rare earth hydroxide. Then the calculated amount rare earth double sulfate salt from the prepared stock was added into this solution. The mixing was done in a three-necked balloon with a condenser and a temperature controllable hot plate with magnetic stirrer.

As the hydroxide conversion parameters; the NaOH amount to be added and conversion duration were studied. In these experiments, $Ln(OH)_3$ precipitate separated by filtration was washed with hot distilled water and then dried at room temperature. The obtained $Ln(OH)_3$ precipitate and filtrate from the experiments were analysed by ICP and by wet chemical techniques for sulphate, so the percent conversion of REE to hydroxide and transfer of other metals to the precipitate were calculated. Also XRD studies of the produced rare earth hydroxides were done and percent conversions to hydroxide were determined from the analyses results.

4.5.1. Effect of NaOH Amount on the Conversion

In the first series of conversion experiments, the amount of sodium hydroxide added was varied between 1/2 to 3 times of the stoichiometric ratio. In these experiments, the conversion temperature and duration were kept constant as 98°C (boiling point) and 30 minutes, respectively. Sulfate analyses of the produced rare earth hydroxides were done and percent conversions to hydroxide were calculated from the analyses results. These data are given in Table 4.5.1 and Figure 4.5.1.

As seen in Figure 4.5.1, as the added NaOH amount was increased to 1.1 times of the stoichiometric ratio, the conversion percentage of REE to hydroxide increased to 98%. But, above this stoichiometric ratio (1.61 gram NaOH / 5 gram rare earth double sulfate salt) with further additions of NaOH, the increases in percent conversion were less than 1%. Therefore, it was decided that 1.1 times of the stoichiometric NaOH amount was enough for conversion of REE double sulfate to hydroxide.

Table 4.5.1. Effect of Sodium Hydroxide Amount on the Conversion of Rare Earth Double Sulfate Salt to Rare Earth Hydroxide

Experiment Code	Conversion Duration, Min.	Temperature °C	NaOH Amount *	% Conversion to Hydroxide
C1	30	98	**3/4**	76.1
C2	30	98	**1.0**	92.1
C3	30	98	**1.1**	98.3
C4	30	98	**1.25**	98.6
C5	30	98	**1.5**	98.6
C6	30	98	**2**	99.0
C7	30	98	**3**	99.0

*Added NaOH amount/Stoichiometric amount

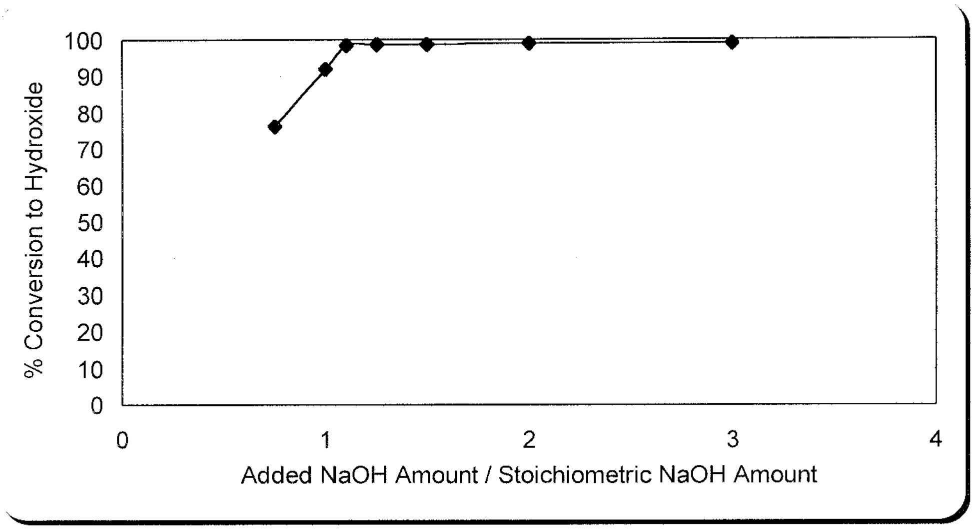


Figure 4.5.1. Effect of Sodium Hydroxide Amount on the Conversion of Rare Earth Double Sulfate Salt to Rare Earth Hydroxide

Also, the chemical analyses of each hydroxide precipitate and filtrate were done by ICP. The aim of these analyses was to determine whether the REE and other metals (impurities) ended-up in the filtrate or precipitate during conversion. The results of these analyses are given in Tables 4.5.2 and 4.5.3.

Table 4.5.2. Effect of NaOH Amount on the Transfer of REE to Hydroxide in Conversion

Experiment Code	NaOH Amount wrt Stoichiometric	Conversion Duration (min.)	% Transfer of REE to Hydroxide			
			La	Ce	Yb	Y
C1	**3/4**	30	100	100	100	98
C2	**1.0**	30	100	100	100	99
C3	**1.1**	30	100	100	100	99
C4	**1.25**	30	100	100	100	100
C5	**1.5**	30	100	100	100	100
C6	**2**	30	100	100	100	100
C7	**3**	30	100	100	100	100

Table 4.5.3. Effect of NaOH Amount on the Transfer of the Other Metals to Hydroxide in Conversion

Experiment Code	NaOH Amount wrt Stoichiometric	Conversion Duration (min.)	% Transfer of Impurities to Hydroxide		
			Al	Mg	Fe
C1	**3/4**	30	80	100	100
C2	**1.0**	30	85	100	100
C3	**1.1**	30	90	100	100
C4	**1.25**	30	100	100	100
C5	**1.5**	30	100	100	100
C6	**2**	30	100	100	100
C7	**3**	30	100	100	100

As seen from these tables, almost all of the lanthanides, iron and magnesium reported to the precipitates. Only some part of the aluminium in the rare earth double sulfate salt did not report to the precipitate when NaOH used was below the stoichiometric amount. As a result, during the conversion to hydroxide, the elimination of the impurities was almost impossible. Almost all of the impurities in rare earth double sulfate salt were transferred to rare earth hydroxide precipitate.

XRD diagrams of rare earth double sulfate salt and rare earth hydroxides are given in Figure 4.5.2., 4.5.3. and 4.5.4. Figure 4.5.2 shows the XRD diagram of the rare earth double sulphate before conversion. Figure 4.5.3 is the XRD diagram of the hydroxide that was obtained by the addition of 3/4 times stoichiometric NaOH amount. The XRD diagram of the hydroxide produced by the addition of 1.1 times stoichiometric NaOH is shown in Figure 4.5.4.

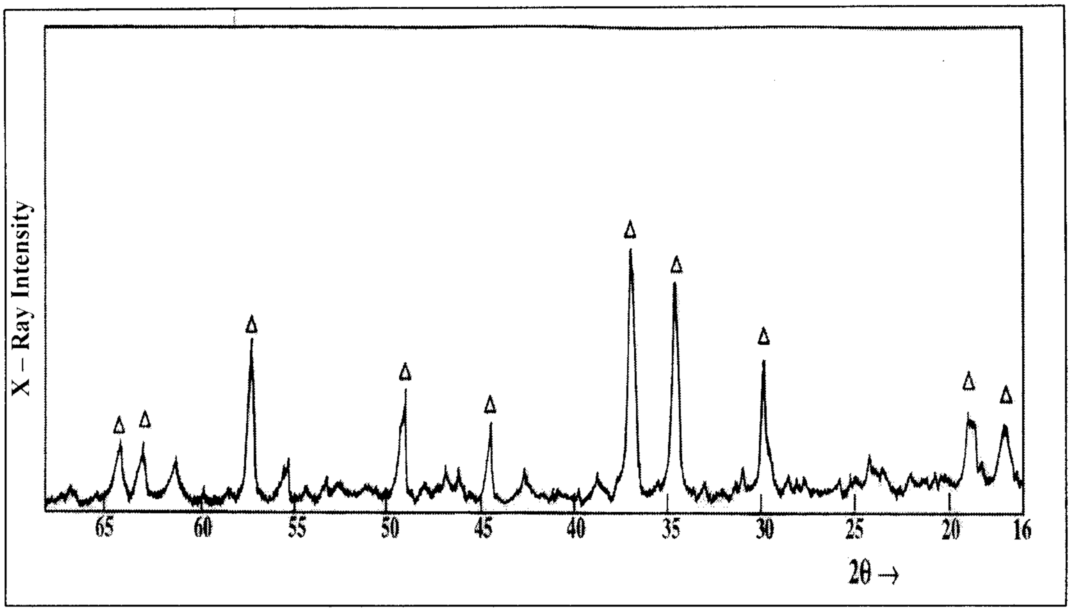


Figure 4.5.2. XRD Diagram of Rare Earth Double Sulfate Stock,

Δ ; $Ln_2(SO_4)_3.Na_2SO_4.2H_2O$

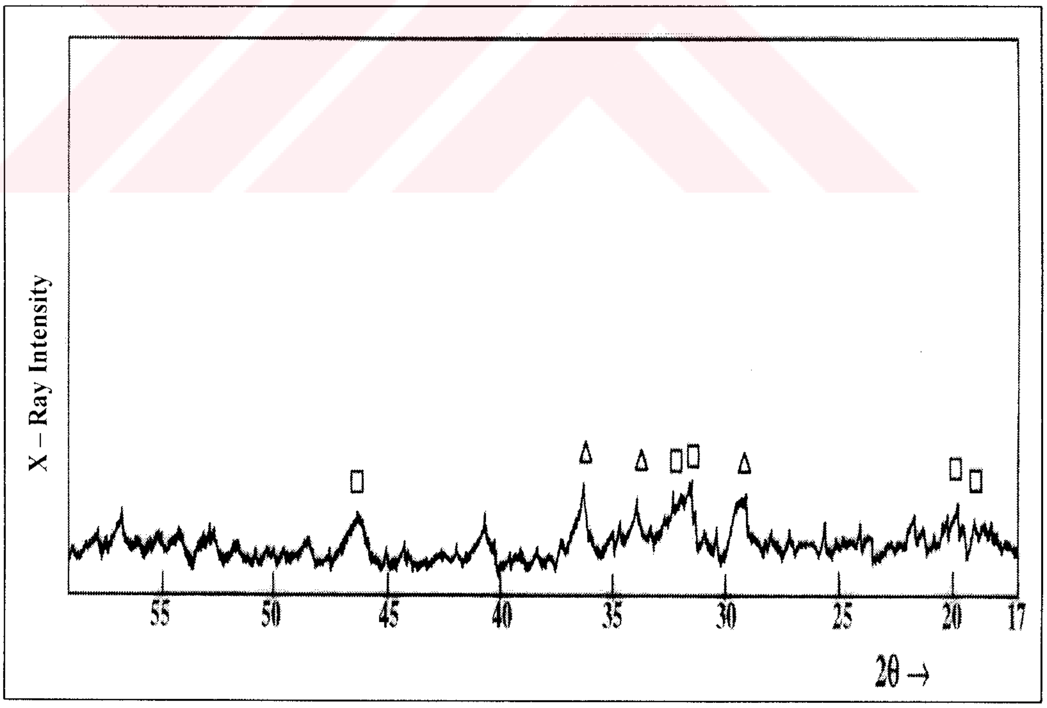


Figure 4.5.3. XRD Diagram of Rare Earth Hydroxide Produced by 3/4 Times Stoichiometric NaOH Addition, Δ ; $Ln_2(SO_4)_3.Na_2SO_4.2H_2O$, □ ; $Ln(OH)_3$

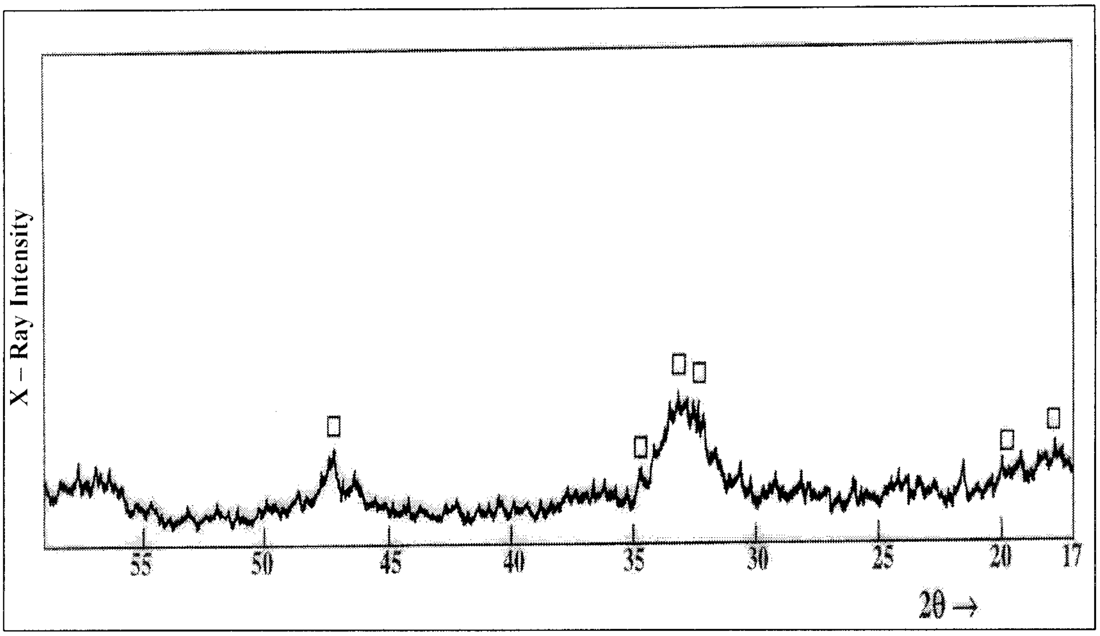


Figure 4.5.4. XRD Diagram of Rare Earth Hydroxide Produced by 1.1 Times Stoichiometric NaOH Addition □ ; $Ln(OH)_3$

As seen from these XRD analyses, when sodium hydroxide used was below 1.1 times of the stoichiometric amount, the conversion to hydroxide was not complete.

4.5.2. Effect of Duration on the Conversion

The second conversion parameter investigated was duration. While keeping constant the NaOH addition at 1.1 times of the stoichiometric amount, the conversion duration was changed between 5 to 180 minutes. Also the conversion temperature was kept constant as 98°C. Chemical analysis of the obtained precipitates and filtrates were carried out by ICP, sulfate analyses of them were also done by wet chemical analysis method and conversion ratios controlled by XRD. Percent conversion to hydroxide based on sulfate analysis results are given in Table 4.5.4 and Figure 4.5.5. As seen from the figure, during conversion 98%

of the rare earth double sulfate salt was converted to rare earth hydroxide in 5 minutes. Increases in conversion duration up to 180 minutes caused only 0.5% increase in the amount of conversion. The product obtained was granular i.e., not gelatinous, and it was easily filtered. The filtrate with a pH value of 12.7 contained substantial amount of sodium sulfate which could be recovered by crystallization and recycled.

Table 4.5.4. Effect of Conversion Duration on the Conversion of Rare Earth Double Sulfate Salt to Rare Earth Hydroxide

Experiment Code	Conversion Duration, Min.	Temperature °C	NaOH Amount	% Conversion to Hydroxide
C8	**5**	98	1.1	98.2
C9	**30**	98	1.1	98.3
C10	**60**	98	1.1	98.2
C11	**120**	98	1.1	98.6
C12	**180**	98	1.1	98.6

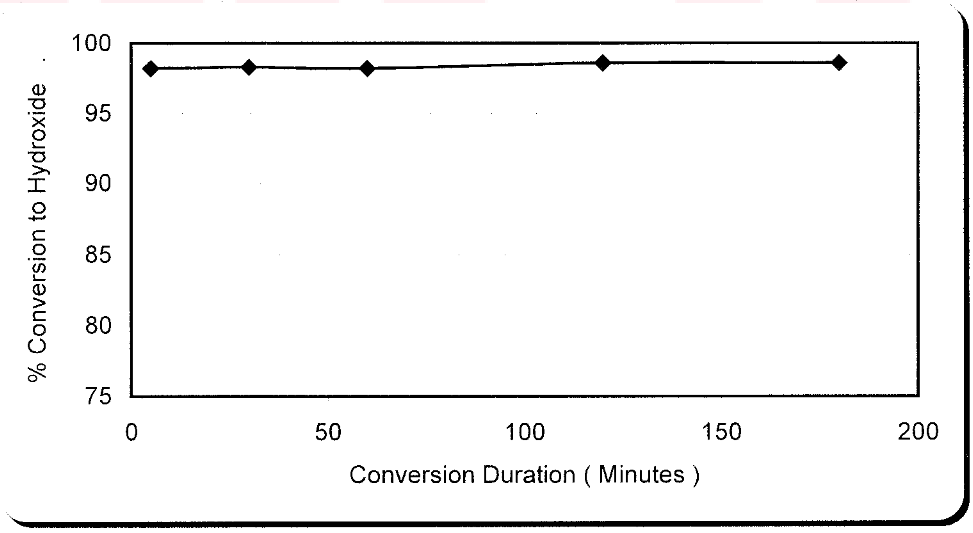


Figure 4.5.5. Effect of Conversion Duration on the Conversion of Rare Earth Double Sulfate Salt to Rare Earth Hydroxide

According to ICP analysis result, almost all of the rare earth elements in the rare earth double sulfate salt passed into the hydroxide precipitate as shown in Table 4.5.5. XRD diagram of hydroxide, which was produced in 5 minutes, is given in Figure 4.5.6. As indicated in the figure, 5 minutes was enough for the conversion of the rare earth double sulfate salt to rare earth hydroxide.

Table 4.5.5. Effect of Conversion Duration on the Transfer of REE to Hydroxide in the Conversion of Lanthanides

Experiment Code	NaOH Amount wrt Stoichiometric	Conversion Duration (min.)	% Transfer of REE to Precipitate			
			La	Ce	Yb	Y
C8	1.1	**5**	100	100	100	99
C9	1.1	**30**	100	100	100	100
C10	1.1	**60**	100	100	100	100
C11	1.1	**120**	100	100	100	100
C12	1.1	**180**	100	100	100	100

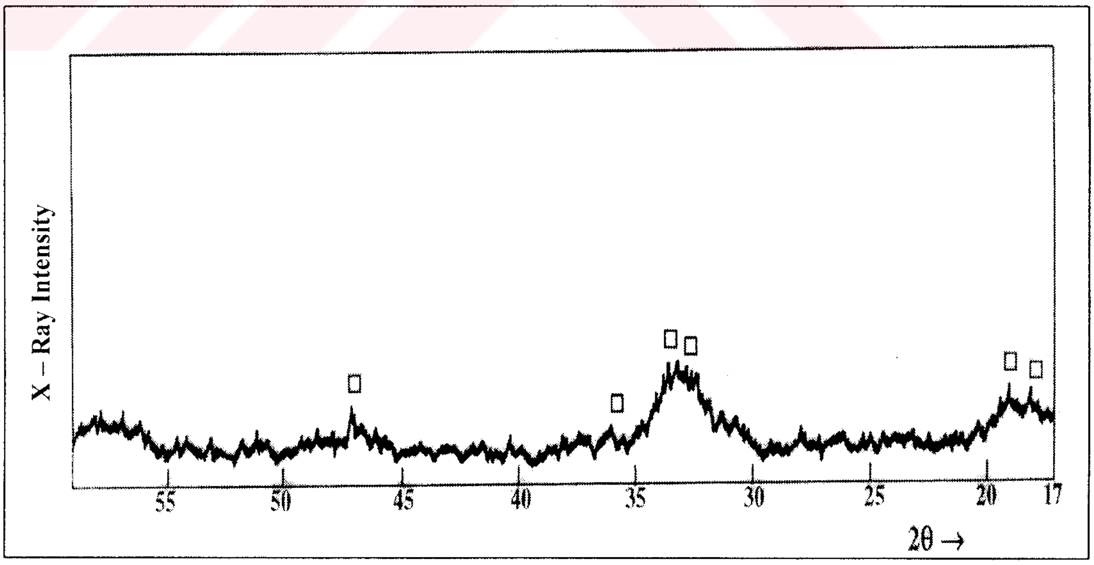


Figure 4.5.6. XRD Diagram of Rare Earth Hydroxide which was Produced in 5 Minutes, □ Ln(OH)$_3$

Finally, two experiments were done to observe the effect of temperature of wash water on the $Ln(OH)_3$ precipitate. In these experiments, two-hydroxide precipitates which were produced under the same conditions, i.e. the optimum conditions, were washed with hot (90°C) and cold (25°C) water. The chemical analyses of the wash waters were done by ICP and the results obtained are given in Table 4.5.6. As seen from the table, the solubility of rare earth hydroxide in cold water was more than in hot water, therefore it was decided that the rare earth hydroxide precipitate should be washed with hot water.

Table 4.5.6. Effect of Hot and Cold Wash Water on the Rare Earth Hydroxide Precipitate

Wash water	La (mg/l)	Ce(mg/l)	% La Solubilized	% Ce Solubilized
Hot	0.029	1.692	≅0	0.0038
Cold	0.053	1.918	0.0012	0.0448

After the production of rare earth double sulfate salt at the optimum precipitation parameters, this salt stock was converted to rare earth hydroxide at the optimum conversion conditions. The conversion parameters; 1.1 times stoichiometric amount NaOH, 98°C conversion temperature and 5 minutes conversion duration were determined as the optimum conversion parameters for 98% conversion, as given in detail in the previous part. The analysis of the rare earth hydroxide showed that it contained 33.9%La, 30.1%Ce, 5.9%Nd, 2.2%Pr, 0.61%Sm, 650 ppm Eu, 220 ppm Yb, 370 ppm Y, 1887 ppm Fe, 1775 ppm Al, 142 ppm Mg and 265 ppm Mn. This produced $Ln(OH)_3$ stock was dried and oxidised in a muffle furnace at 150°C and for 6 hours, as a result Ce^{3+} in the stock was oxidised to Ce^{4+} (CeO_2). So that CeO_2 (ceric oxide) formed would not be dissolved by HCl during the following selective leaching process, therefore a high grade CeO_2 concentrate could be obtained after acid leaching [42]. Commercial separations involving the oxidation to the tetravalent state are limited to the removal of cerium after oxidation.

4.6. Hydrochloric Acid Leaching of Rare Earth Hydroxide

In the leaching experiments of dried and oxidised rare earth hydroxide, 1 gram sample was taken from the stock and it was placed in 15 cc of HCl solution. So the rare earth metals except Ce were subjected to selective leaching. The leaching experiments were carried out in a 50 cc beaker. It was closed with a plastic cork and four holes were drilled through this cork, and then a pH meter electrode, a thermometer, a glass pipe and a small condenser were placed through these holes. During the leaching process, the temperature of solution was kept constant and acid was added through the glass pipe to keep the pH of solution constant. A magnetic stirrer was placed into the beaker for mixing. This 50 cc beaker was placed into another 500 cc beaker which was used as a hot water bath, because it was filled with water and placed on to a hot plate with temperature controller. The larger beaker also had a magnetic stirrer, so that temperature variations were minimised. The acid amount (pH), leaching duration and temperature were studied as the leaching parameters. After the experiments, the insoluble solid precipitate (CeO_2 concentrate) was filtered and removed from liquid phase. The obtained pregnant leach solution and solid precipitate were analysed by ICP and the leach recoveries of rare earth metals were calculated from these analyses results. The following reaction has taken place during the hydrochloric acid leaching experiments:

$$Ln(OH)_3+3HCl = Ln^{3+} + 3H_2O + 3Cl^- \quad (8)$$

In this reaction Ln symbolizes all lanthanides other than cerium. The results of hydrochloric acid leaching experiments for various parameters are summarized below.

4.6.1. Effect of Acid Amount (pH) on the Leach Recovery

In the first series of experiments, to put rare earth hydroxides into leach solution, the pH of solution was changed between 0.5 and 3.0. In these experiments, the leaching duration and temperature were kept constant as 3 hours and 75°C, respectively. Leach solutions obtained from these experiments were analysed by ICP and the leach recoveries, which were obtained from these analysis results, are given in Table 4.6.1. and presented graphically in Figure 4.6.1. As seen in Figure 4.6.1, with increasing added acid amount, the leach recoveries of lanthanum and cerium increased.

Table 4.6.1. Effect of HCl Amount (pH) on the Leach Recoveries of Ce and La

Experiment No	Duration, Hours	Temperature, °C	pH	% La Recovery	% Ce Recovery
A1	3	75	**0.5**	83.6	7.9
A2	3	75	**1**	81.2	7.3
A3	3	75	**2**	80.8	6.1
A4	3	75	**3**	80.9	4.0

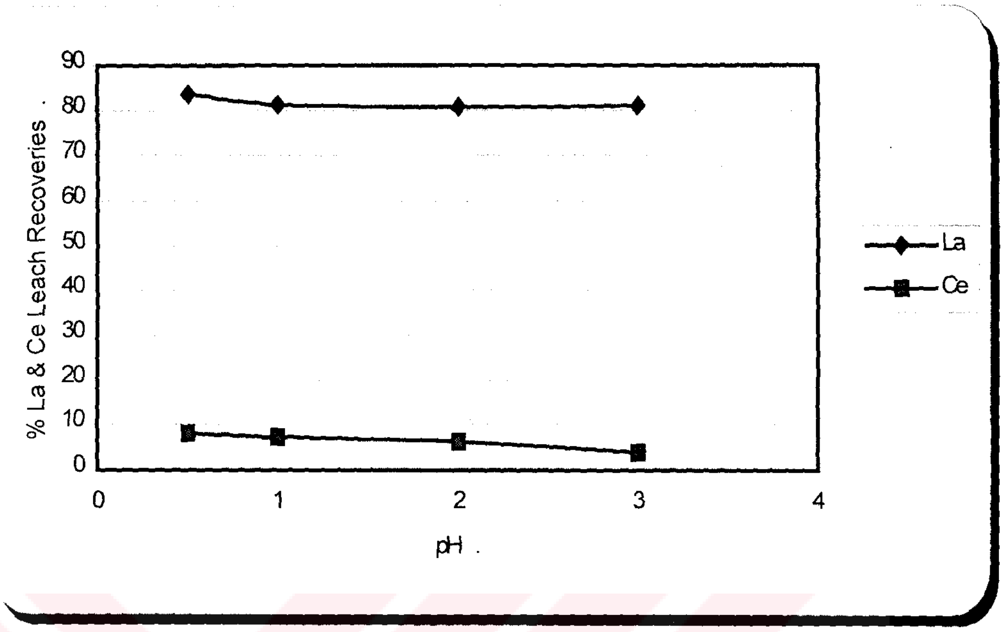


Figure 4.6.1. Effect of HCl Amount (pH) on the Leach Recoveries of Ce and La

The leach recovery of La at pH 3 was 80.9% whereas the same recovery at pH 0.5 was 83.6%, which corresponded to an increase of 2.7% with increasing HCl concentration. At the same time, when the pH of solution was decreased from 3.0 to 0.5, the leaching of CeO_2 increased from 4.0% to 7.9%, which meant that, Ce lost from CeO_2 concentrate to the pregnant leach solution increased with increasing acid amount. Therefore, 0.001 M HCl (pH 3) concentration was suitable for leaching of $Ln(OH)_3$. Also this low acid concentration was suitable for the next step which was solvent extraction (SX). Since the extraction and separation of rare earth metals by SX at high acid concentration is very difficult compared to low acid concentration. Therefore, the leaching with HCl solution at pH 3 was more suitable than the others.

4.6.2. Effect of Leaching Temperature on the Leach Recovery

The second parameter optimised was leaching temperature. While keeping constant the solution pH at 3 and leaching duration at 3 hours, the leaching temperature was changed between 25 to 90°C. The analysis of pregnant leach solution and solid residue were done by ICP as before. The leach recoveries of rare earth metals which were calculated from these analyses results are given in tabulated form in Table 4.6.2 and graphically in Figure 4.6.2. As seen from Figure 4.6.2, the dissolution of lanthanum increased with increasing leaching temperature up to 75°C, but increases in leach recovery was very little above this temperature. However, when the leaching of Ce from the dried and oxidised rare earth hydroxide was observed from the same figure, there was not any significant change with increasing temperature because CeO_2 is a very stable oxide and it may dissolve only at high acid concentrations. As a result, the optimum acid leaching temperature was chosen as 75°C.

Table 4.6.2. Effect of HCl Leaching Temperature on the Leach Recoveries of Ce and La

Experiment No	Duration, Hours	Temperature, °C	pH	% La Recovery	% Ce Recovery
A5	3	**25**	3	60.4	4.5
A6	3	**50**	3	65.9	4.1
A7	3	**75**	3	80.9	4.0
A8	3	**90**	3	81.2	4.3

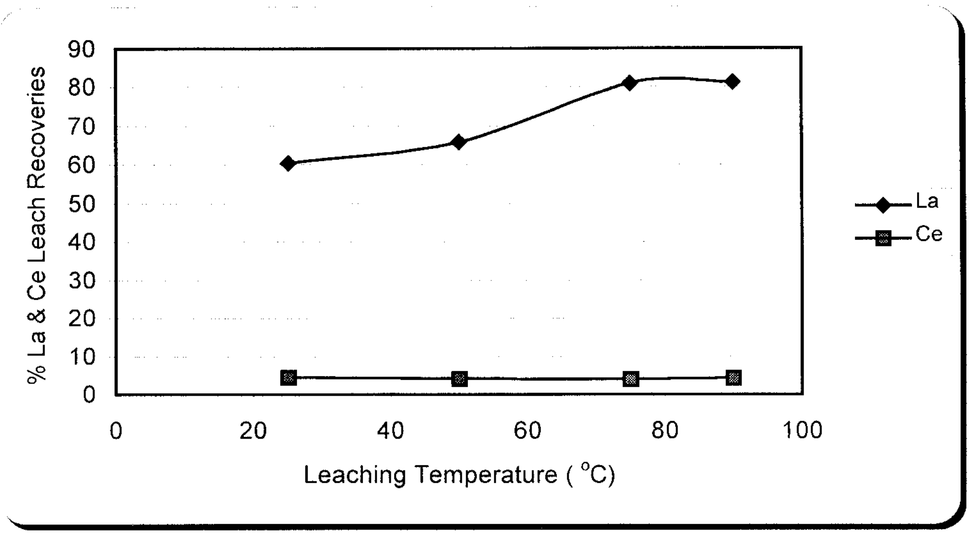


Figure 4.6.2. Effect of HCl Leaching Temperature on the Leach Recoveries of Ce and La

4.6.3. Effect of Leaching Duration on the Leach Recovery

In the last series of experiments, the leaching duration of dried and oxidised rare earth hydroxide was researched and the duration was changed between 1 to 6 hours. In the leaching experiments, the leaching temperature and acid concentration were kept constant as 75°C and pH at 3, respectively. The results of these experiments are presented in Table 4.6.3 and Figure 4.6.3. As shown in this figure, the leach recovery of La increased with increasing leaching duration, but beyond 5 hours no significant change was observed in the leach recovery. On the other hand, the leach recovery of Ce was not affected from the leaching duration as seen in Figure 4.6.3. As a result, 5 hours of leaching duration could be selected as the optimum.

Table 4.6.3. Effect of HCl Leaching Duration on the Leach Recoveries of Ce and La

Experiment No	Duration, Hours	Temperature, °C	pH	% La Recovery	% Ce Recovery
A9	**1**	75	3	74.7	5.2
A10	**2**	75	3	79.9	4.0
A11	**3**	75	3	80.9	4.0
A12	**5**	75	3	85.7	4.8
A13	**6**	75	3	86.0	4.7

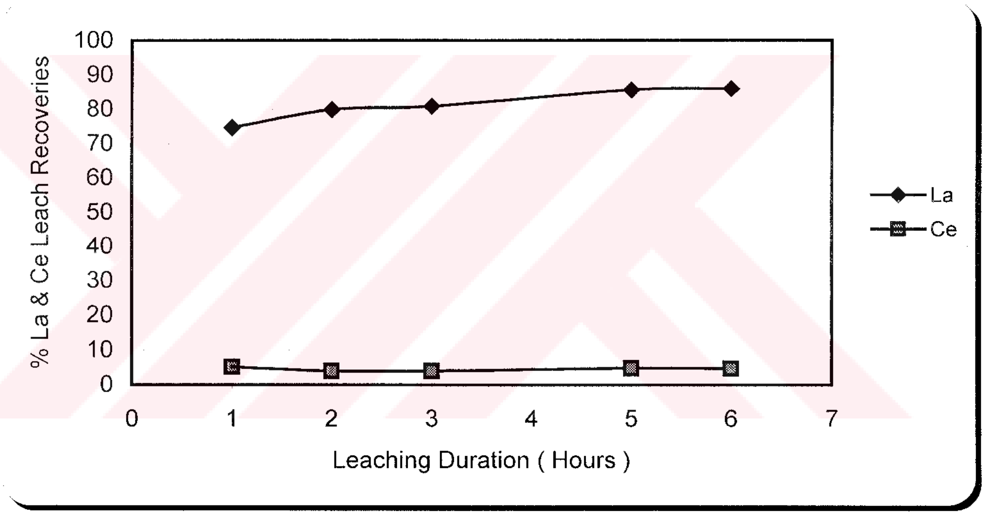


Figure 4.6.3. Effect of HCl Leaching Duration on the Leach Recoveries of Ce and La

After selective leaching of rare earth hydroxide stock, a high-grade ceric oxide concentrate containing 86.4%CeO_2 and 7.8%La_2O_3 was obtained. In addition, dissolved hydroxides yielded a chloride type pregnant leach solution containing 16990 ppm La, 2090 ppm Ce, 698 ppm Pr, 1734 ppm Nd, 29 ppm Sm, 11 ppm Eu, 20 ppm Y, when leaching was done at the optimum leaching conditions with HCl at 75^{o}C leaching temperature, 5 hours of leaching duration at pH 3 or higher.

4.7. Solvent Extraction of Rare Earths from Beylikahır Preconcentrate

In the solvent extraction (SX) experiments of rare earth elements from above aqueous leach solution PC-88A (2-ethylhexyl hydrogen 2-ethylhexyl phosphonate) which is the recommended reagent for rare earth elements SX, was used as organic phase.

The organic phase was diluted with kerosene in order to obtain a 1 molar PC-88A (molecular weight: 306.4). In each SX experiment, 15cc of aqueous phase was mixed at room temperature with a known volume of organic phase in a 50 cc beaker. The mixing was done using a hot plate with a magnetic stirrer. After mixing the organic and aqueous phases for a fixed duration, the mixture was placed in a separation funnel. After the completion of the disengagement of the two phases, the aqueous phase was separated and filtered through a filter paper. Later, it was analysed by ICP for La and Eu. In the solvent extraction experiments, La (atomic number 57, ionic radius 1.04 °A) was chosen to represent the light rare earths elements and Eu (atomic number 63, ionic radius 0.96 °A) to represent the relatively heavier rare earth elements. After completion of the analysis of the aqueous phase, the % extraction recovery of each element as well as separation factor were calculated assuming that the analysis of the stock solution used in extraction experiments was constant. The extraction reaction is given below:

$$Ln^{+3} + 3(HG_2)_{(org)} = Ln(G_2)_{3(org)} + 3H^{+} \qquad (9)$$

where, Ln represents the lanthanides and HG_2 the organic reagent. As stated before, several investigations have shown that the extractability of PC-88A increased with the increasing atomic number of REE or decreasing ionic radius. Thus, the relative extractability of Eu was more than La [44, 47].

When, a component, say Ln_A (Eu in this work) is distributed between the two phases and will have a distribution coefficient (D_A), measured at equilibrium:

D_A= (Concentration of A in organic phase)/(Concentration of A in aqueous phase)

For two components, Ln_A (Eu in this work) and Ln_B (La in this work), both distributed between the organic and aqueous phases, a separation factor can be defined as:

$$\beta^{B}_{A} = D_A / D_B \qquad (10)$$

The closer this factor approaches "1" the more difficult it will be to separate those two elements.

4.7.1. Effect of Mixing Duration on the Solvent Extraction Recovery

In the first series of solvent extraction experiments, in order to extract Eu to the organic phase in preference to La, the duration of mixing was varied between 5 and 60 minutes. In these experiments, the organic to aqueous ratio (O/A) (vol/vol) and initial pH of aqueous phase were kept constant as 1/1 and 3.15, respectively. From the analysis of the aqueous phase after extraction, the La and Eu extraction percentages to PC-88A and Eu-La separation factor were calculated as given in Table 4.7.1 and plotted in Figures 4.7.1 and 4.7.2. As seen from the figures, the solvent extraction recoveries of Eu and La increased with increasing mixing duration. The increase was substantial for shorter durations. However, from Figure 4.7.2, it can be noticed that the separation factor of Eu and La reached to a maximum point at 15 minutes.

Table 4.7.1. Effect of Mixing Duration on the Solvent Extraction Recoveries and the Separation Factor at pH 3.15

Experiment Code	Duration, min.	O/A ratio	Volume of Aqueous, cc	Initial pH	% La SX Recovery	% Eu SX Recovery	β^{Eu}_{La}
SX1	**5**	1/1	15	3.15	9.6	74.5	29.1
SX2	**10**	1/1	15	3.15	15.0	76.2	31.7
SX3	**15**	1/1	15	3.15	16.0	87.3	72.4
SX4	**30**	1/1	15	3.15	39.1	89.1	11.8
SX5	**60**	1/1	15	3.15	38.2	89.1	14.2

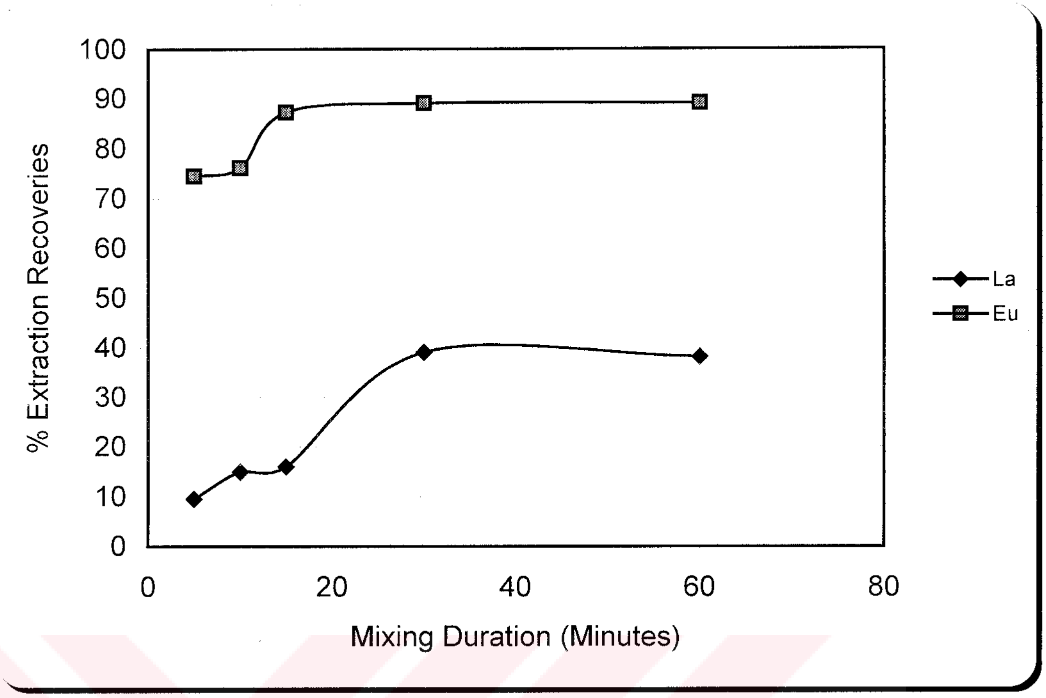


Figure 4.7.1. Effect of Mixing Duration on the Solvent Extraction Recoveries

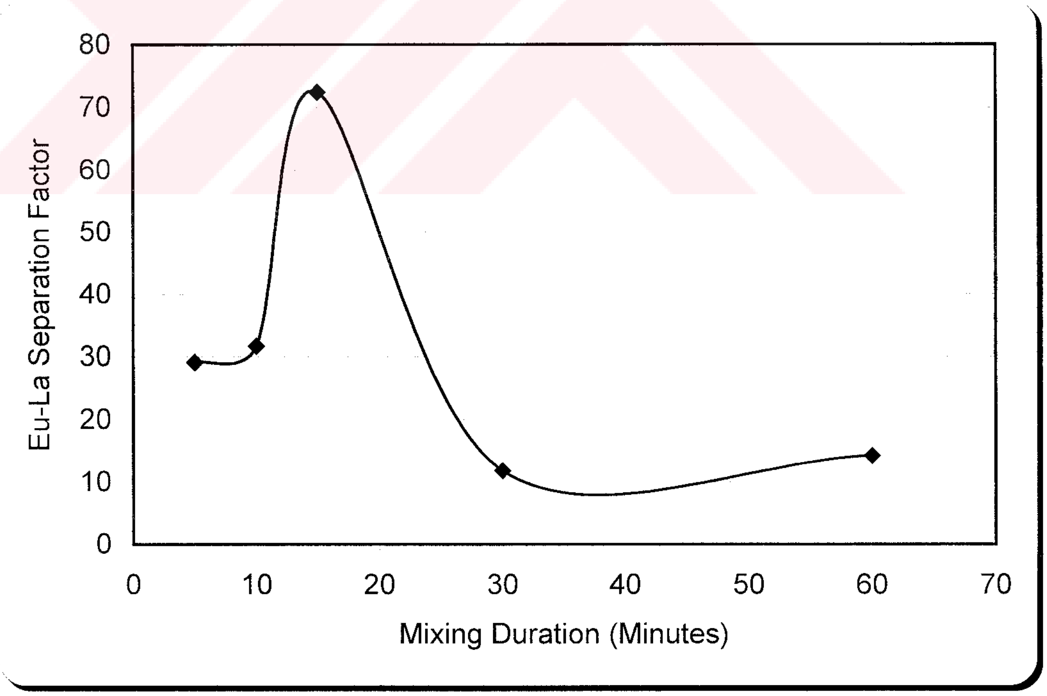


Figure 4.7.2. Effect of Mixing Duration on Separation Factor at pH 3.15

Therefore, for better separation of europium from lanthanum the optimum duration of mixing in SX was chosen to be 15 minutes. At longer contact times, the transfer of La ions to the organic phase continued thus resulting in lower separation factors. So shorter mixing times limited the La transfer to the organic phase to some degree. Too short an extraction duration was not also desirable. In the solvent extraction experiments, there was no third phase formation so a modifier was not needed and the disengagement time was less than 15 minutes.

4.7.2. Effect of O/A Ratio on the Solvent Extraction Recovery

The second solvent extraction parameter that was optimised in the course of this research was O/A ratio. While keeping constant the mixing duration at 30 minutes and initial pH of the aqueous phase at 3.15, the O/A ratio was varied between 1/2 and 3/2. The results obtained are given in Table 4.7.2 and Figures 4.7.3 and 4.7.4. As seen from Figure 4.7.3, the amounts of La and Eu extracted to the organic phase increased slightly with increasing O/A ratio. On the other hand, better separation between La and Eu was obtained for O/A ratios more than 1/1 as clearly seen from Figure 4.7.4. Therefore, the optimum O/A ratio was decided to be 1/1 for economical reasons.

Table 4.7.2. Effect of O/A Ratio on the Solvent Extraction Recovery

Experiment Code	Duration, min.	O/A ratio	Volume of Aqueous, cc	Initial pH	% La SX Recovery	% Eu SX Recovery	β_{La}^{Eu}
SX6	30	½	15	3.15	35.3	83.6	9.4
SX7	30	¾	15	3.15	37.6	85.5	9.8
SX8	30	**1/1**	15	3.15	40.9	89.1	11.8
SX9	30	**3/2**	15	3.15	41.9	90.0	12.5

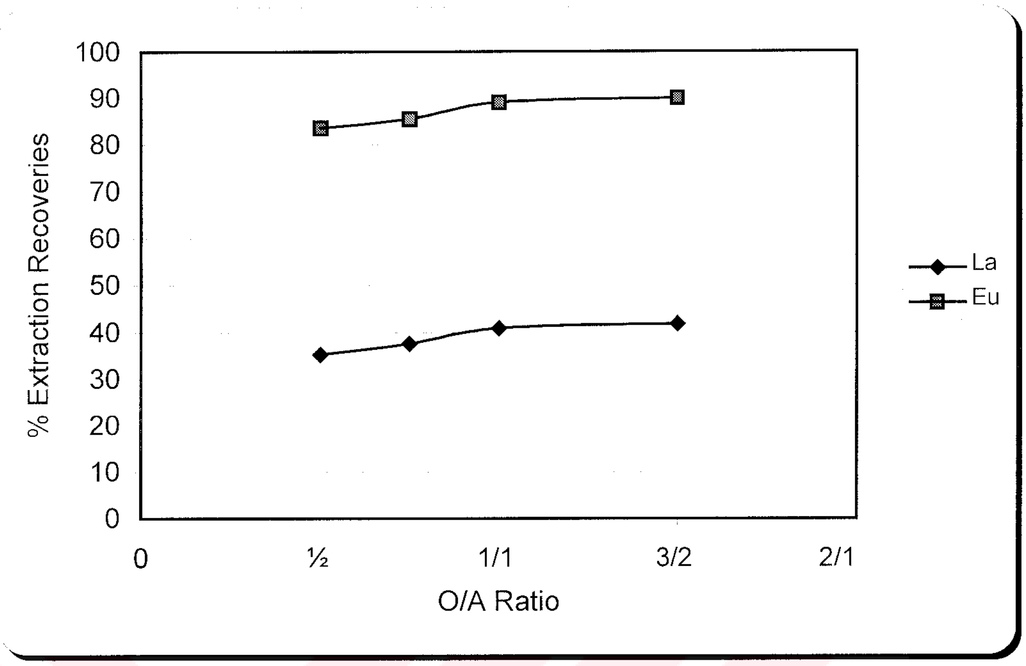


Figure 4.7.3. Effect of O/A Ratio on the Solvent Extraction Recoveries

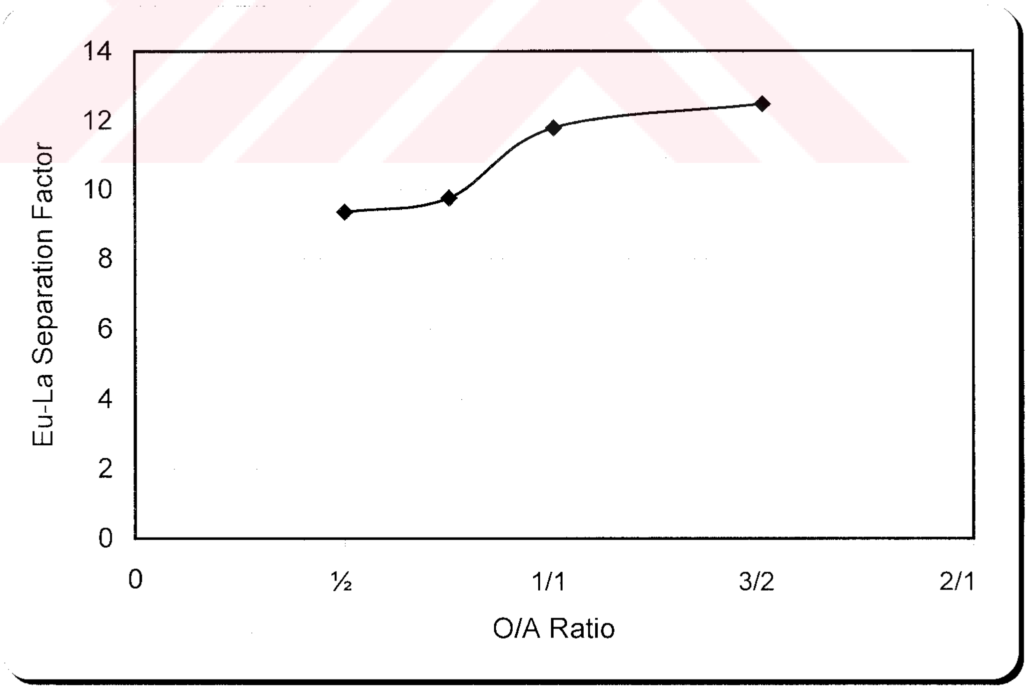


Figure 4.7.4. Effect of O/A Ratio on Separation Factor

4.7.3. Effect of Initial pH of the Aqueous Phase on the Solvent Extraction Recovery

In the third series of solvent extraction experiments, the effect of initial pH of aqueous phase was investigated. For this purpose, the initial pH of aqueous phase was varied in the range of 0 and 4. For the pH adjustment, HCl acid and NaOH solutions were used. The duration of mixing and O/A ratio were kept constant as 30 minutes and 1/1, respectively in these experiments. The results of experiments are given in Table 4.7.3 and Figures 4.7.5 and 4.7.6. As seen from Figure 4.7.5, the extraction of Eu to the organic phase increased with increasing pH whereas the extraction of La decreased slightly in the same range. In the pH range studied, the highest separation of Eu from La was obtained at pH 4. Due to the precipitation reactions, it was not possible to increase the pH beyond 4.

Table 4.7.3 Effect of Initial pH of the Aqueous Phase on the Solvent Extraction Recovery

Experiment Code	Duration, min.	O/A ratio	Volume of Aqueous, cc	Initial pH	% La SX Recovery	% Eu SX Recovery	β^{Eu}_{La}
SX10	30	1/1	15	**0**	47.7	21.8	0.3
SX11	30	1/1	15	**1**	40.7	65.5	2.8
SX12	30	1/1	15	**2**	41.2	88.2	10.7
SX13	30	1/1	15	**3**	40.9	89.1	11.8
SX14	30	1/1	15	**4**	40.6	92.7	18.7

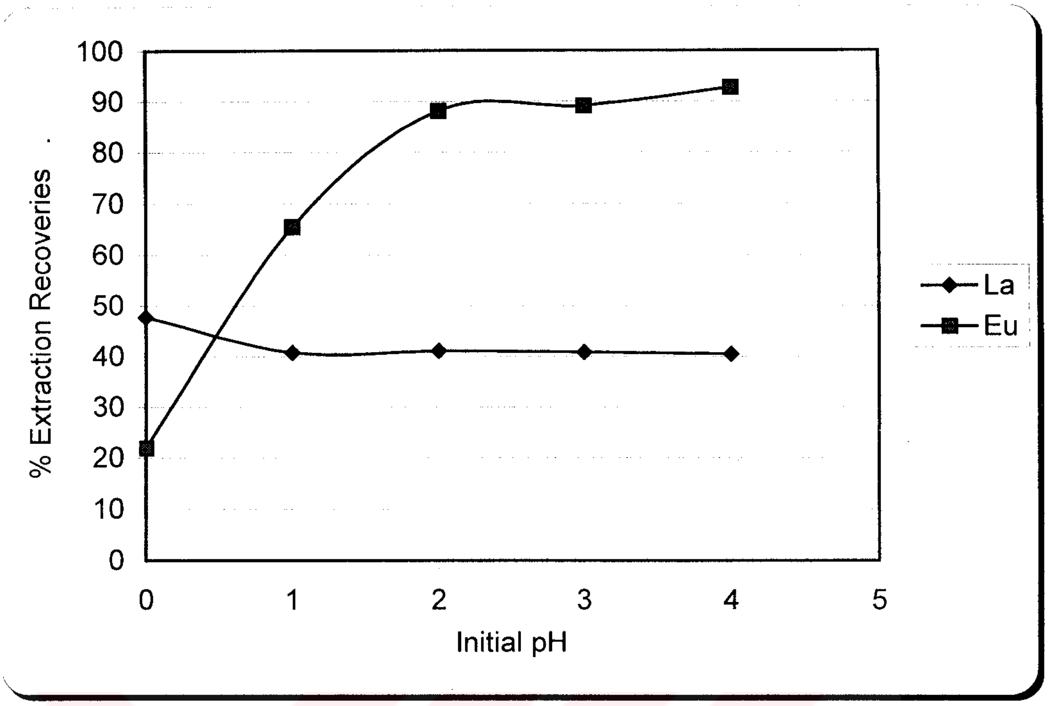


Figure 4.7.5. Effect of Initial pH of the Aqueous Phase on the Solvent Extraction Recoveries

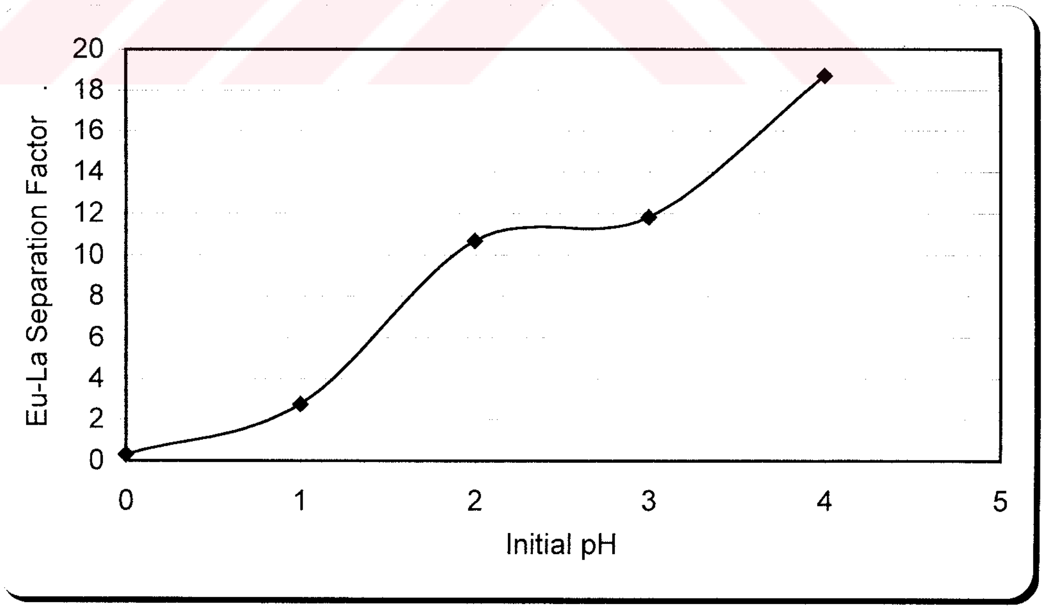


Figure 4.7.6. Effect of Initial pH of the Aqueous Phase on Separation Factor

4.7.4. Effect of Initial Feed Concentration

In the last series of SX experiments, the effect of initial feed concentration on the extraction and separation of Eu and La was researched. In order to do these experiments, pregnant leach solutions with higher REE's concentrations were prepared by leaching higher amounts of the dried and oxidized rare earth hydroxide in HCl. The results of these experiments are summarized in Table 4.7.4. As it can be seen from the table, as the rare earth metal concentration increased in the SX feed solution, the percentages of La and Eu extracted to the organic phase decreased in general. There was also a decrease in the separation factor. These findings indicated that the aqueous phase obtained under the optimum conditions stated above should be used in solvent extraction directly without further concentration operation.

Table 4.7.4. Effect of Initial Feed Concentration on REE Extraction

Initial feed concentration		Duration, min.	O/A ratio	Vol. of Aq. cc.	Initial pH	Final pH	% La SX Recovery	% Eu SX Recovery	β^{Eu}_{La}
La (mg/l)	**Eu (mg/l)**								
16990	**11**	30	1/1	15	2	1.25	43.2	89.1	10.8
34900	**30**	30	1/1	15	2	1.07	30.4	73.3	6.3
64900	**57**	30	1/1	15	2	0.79	37.7	71.2	4.1

4.7.5. Solvent Extraction of Rare Earths from Beylikahır Preconcentrate at pH 4

Finally in the solvent extraction experiments at pH 4, in order to extract Eu to the organic phase in preference to La, the duration of mixing was varied between 10 and 60 minutes. In these experiments, the organic to aqueous ratio (O/A) (vol/vol) and initial pH of aqueous phase were kept constant as 1/1 and 4, respectively. From the analysis of the aqueous phase after extraction, the La and Eu extraction percentages to PC-88A and Eu-La separation factor were calculated and presented numerically in Table 4.7.5 and plotted in Figures 4.7.7 and 4.7.8. As seen from the figures, the solvent extraction recoveries of La and Eu increased with increasing mixing duration. The increase was substantial for shorter durations. But when we look at the second figure, it can be noticed that the separation factor of Eu and La reached to a maximum point at 15 minutes. Therefore, for better separation of europium from lanthanium, the optimum duration of mixing in SX should be limited to 15 minutes at initial pH of 4.

For the stripping of REE's from the loaded organic phase strong HCl solution has to be used. Some initial stripping tests in the laboratory indicated that it was possible to strip Eu from the loaded organic with 5 M HCl solution.

Table 4.7.5. Effect of Mixing Duration on the Solvent Extraction Recoveries of REE at pH 4

Experiment Code	Duration, min.	O/A Ratio	Vol. of Aq., cc	Initial pH	Final pH	% La SX Recovery	% Eu SX Recovery	β^{Eu}_{La}
T1	**10**	1/1	15	4	1.40	15.7	76.8	32.7
T2	**15**	1/1	15	4	1.39	18.3	89.8	81.3
T3	**20**	1/1	15	4	1.38	25.5	91.2	34.0
T4	**25**	1/1	15	4	1.39	35.1	92.7	23.2
T5	**30**	1/1	15	4	1.38	39.1	90.8	15.4
T6	**60**	1/1	15	4	1.38	40.2	91.8	14.3

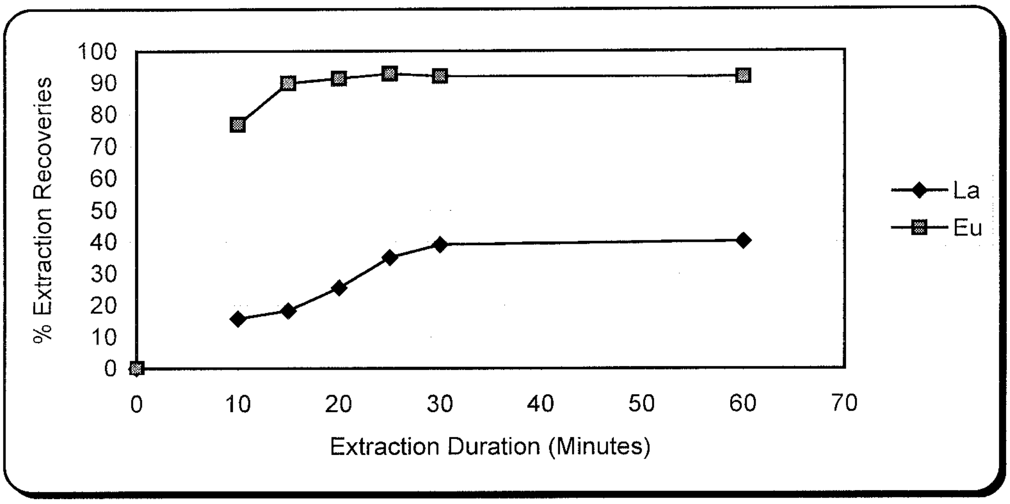


Figure 4.7.7. Effect of Mixing Duration on the Solvent Extraction Recoveries

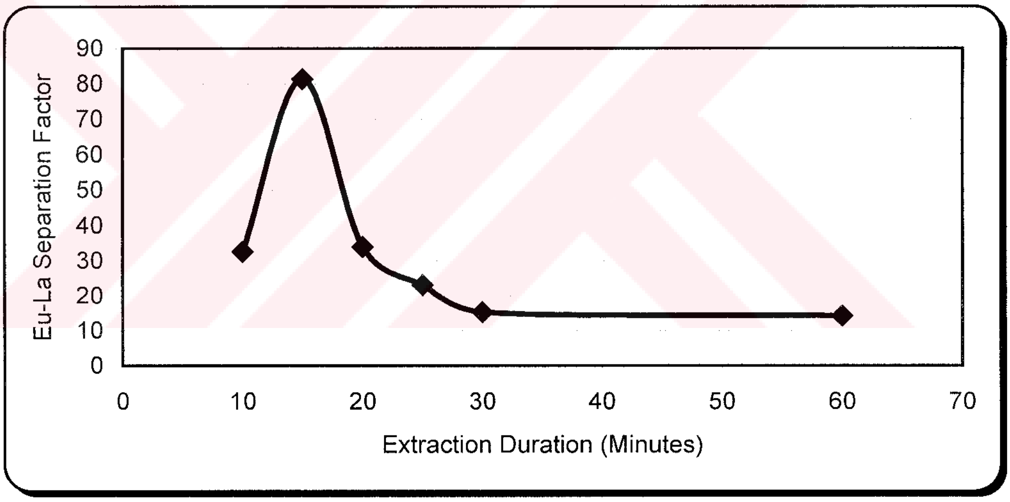


Figure 4.7.8. Effect of Mixing Duration on Separation Factor at pH 4

In summary, initial solvent extraction experiments in the laboratory indicated that relatively heavier REE's could be separated from light rare earths by solvent extraction using PC-88A as the organic extractant. But for complete separation of REE's the SX steps has to be repeated many times. In fact, in the industrial operations the use of mixer settler solvent extraction systems having 700 to 1000 stages are very common.

CHATER 5

CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

Hydrometallurgical studies within the scope of this thesis were planned and carried out with the preconcentrate having 23.5%REO which corresponded to 19.5%REE or 30.5% $LnFCO_3$ and a top size of 37 microns. The preconcentrate obtained from Beylikahır ore by attrition scrubbing, screening and cycloning was used in the hydrometallurgical studies without further size reduction due to its fine size. The preconcentrate also contained 41.37% CaF_2, 10.69% $BaSO_4$, 8.50% $CaCO_3$, 2.74% SiO_2, 4.18% Fe_2O_3, etc. The mineralogical analysis using X-ray diffraction, optical microscope and scanning electron microscope indicated the presence of fluorspar (CaF_2), barite ($BaSO_4$) and bastnasite ($LnFCO_3$) and small amounts of limonite ($2Fe_2O_3.3H_2O$), hematite (Fe_2O_3), anatase (TiO_2), psilomelane (H_4MnO_5), calcite ($CaCO_3$), quartz (SiO_2). Also minor amounts of biotite and muscovite were observed.

The sulphuric acid baking experiments were then optimized and optimum conditions were determined as follows:

1. 200°C baking temperature
2. 45.4 g H_2SO_4 per 50 g preconcentrate
3. 2 hours of baking duration

Under these optimum conditions, the amount of thorium leached from the preconcentrate was determined to be 86% by means of XRF analysis. The pH of the pregnant leach solution obtained under the optimum conditions of baking was

2.6. XRD analysis of the leach residues indicated the presence of mainly gypsium, barite, etc. The sulphuric acid baking and water leaching experiments carried out on the preconcentrate indicated that 85 to 90% of the REE's could be taken into leach solution as well as producing HF acid as by-product.

After the optimization of baking conditions of preconcentrate, the leaching of baked preconcentrate with distilled water was optimized. The optimum leaching parameters were determined to be as; the leaching duration of half an hour and leaching temperature of 25°C due to easier control. Leach recoveries of the rare earth elements were effected very little by changes in stirring speed and solid-liquid ratio. Also distilled water without any additions of H_2SO_4 or H_2O_2 was decided to be the best leachant.

After the optimization of the leaching of baked preconcentrate with water, the optimization of precipitation parameters were done and the optimum conditions were determined for the precipitation of rare earth double sulfate salt with sodium sulfate as follows :

1. 5 minutes precipitation duration.
2. 50°C precipitation temperature.
3. 1.25 times of the stoichiometric Na_2SO_4 amount.

In this way, a fair degree of decontamination of the precipitate from impurities such as Th, Fe, Al and Mg was possible.

And then, the experiments of conversion of rare earth double sulfate to rare earth hydroxide by sodium hydroxide were carried out and the optimum conditions were determined as follows:

1. NaOH addition 1.1 times of the stoichiometric NaOH amount
2. Conversion duration 5 minutes

The solubility of rare earth hydroxide in cold water was more than in hot water, therefore it was decided that the rare earth hydroxide precipitate obtained should be washed with hot water.

After the conversion experiments, the optimum parameters of hydrochloric acid leaching of dried and oxidized rare earth hydroxide were determined as follows:

1. Acid amount; at pH 3
2. Leaching temperature of 75°C
3. Leaching duration of 5 hours

After the experiments, the insoluble solid precipitate (CeO_2 concentrate) was filtered and removed from liquid phase. Also, these experiments show that; the solid precipitate, which was obtained at the optimum leaching conditions, contained 86.4% CeO_2.

Finally, the solvent extraction parameters were optimized. The optimum conditions were determined as follows:

1. Mixing duration of 15 minutes
2. Organic / Aqueous (O/A) ratio of 1/1
3. Initial pH of feed solution 4

As a result, it was shown that relatively heavier and light rare earth elements could be separated from each other by using 1M PC 88-A organic reagent in kerosene at room temperature.

Future work proposed is as follows

i) Acid baking of the preconcentrate should be done in such manner that HF and other gases that form as a result of reactions could be collected and utilized.

ii) Na_2SO_4 formed as a result of conversion of rare earth double sulfate salt to rare earth hydroxide should be recovered by crystallisation.

iii) Using PC-88A as the organic reagent, the solvent extraction experiments should be continued for the complete separation of REE's of economical importance. Scrubbing and stripping of REE's from the loaded organic phase should be also investigated. As the final step, the separated REE's could be precipitated as hydroxide, carbonate or oxalate.

iv) Pilot plant testing of the proposed flowsheet should be done in order to obtain data for a continuously operating system. Later, a feasibility study should be completed for investment purposes.

v) Possibility of production of thorium from the preconcentrate should be investigated. Also, the environmental problems caused by thorium contamination of barite and fluorite concentrates need to be studied.

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Package Programs	MsOffice, CMS

Projects

1998-2003	"Production of Rare Earth Metals and Thorium as Byproduct",(DPT Project) Prof. Dr. Yavuz Topkaya, Prof. Dr. İshak Karakaya, METU, Ankara-TURKEY
1998	"Thermoset & Thermoplastic Materials in Composite Products", Assoc. Prof. Dr. Cevdet Kaynak, METU, Ankara-TURKEY
1997	"Fiber Reinforced Composite Glass & Glass-Ceramics", Assoc. Prof. Dr. Abdullah Öztürk, METU, Ankara-TURKEY
1996-1997	"Production of Germanium from Çinkur Copper Cake", Prof. Dr. Yavuz Topkaya, METU, Ankara-TURKEY
1994	Graduation Project, "Materials in Nuclear Power Stations", Prof. Dr. Ö. Tarık Oğurtanı, METU, Ankara-TURKEY

Training

1995	ISO 9000 Quality Assurance System Course by TSE, Ankara-Turkey
1995	Assessor/Lead Assessor Course by CTA,Ireland

Publications

1. Recovery of Rare Earths from a Bastnaesite Preconcentrate, TMS'2000, Nashville, Tennessee, USA, Rare Earths and Actinides: Science Technology and Applications IV, 2000, p.11-16, (Edited by: R.G. Bautista)

2. Nadir Toprak Elementlerinin Beylikahır Bastnasit Önkonsantresinden Metalurjik Kazanımı, 10th International Metallurgy and Materials Congress, İstanbul, Proceeding of the Conference: 24-28.May.2000, Vol.1, p.93-100.

3. Metallurgical Treatment of a Turkish Rare Earth Ore, 7th. International Conference on Mining, Petroleum and Metallurgical Engineering (MPM'7-2001), Assuit, Egypt, Proceedings of Conference, Volume II, 10-12. February, 2001, p.22-27.

4. Hydrometallurgical Treatment of a Rare Earth Preconcentrate, VI. Southern Hemisphere Meeting on Mineral Technology (VI SHMMT-2001), Rio de Janeiro, Brazil, Proceedings of the Conference, Vol.2, 27.May-1.June.2001, p.395-399.

5. Hydrometallurgical Treatment of a Rare Earth Preconcentrate, 23rd. Rare Earth Research Conference, University of California, Davis, USA, Program and Abstracts: 13-18. July.2002, Poster Paper, p.162.