OPTIMIZATION OF CONDITIONS OF METALLOTHERMIC REDUCTION OF RARE EARTH PRECONCENTRATES

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ABSTRACT

THE OPTIMIZATION OF CONDITIONS OF METALLOTHERMIC REDUCTION OF RARE EARTH PRECONCENTRATES

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Rare earth ferrosilicon alloy is an important additive for ferrous metallurgy. It is mainly used to control the detrimental effects of sulfur in steel and to modify graphite structures in cast iron. The aim of this study was to optimize the conditions for the production of rare earth ferrosilicon alloy by metallothermic reduction process using a preconcentrate prepared from a bastnasite type of ore present in the Beylikahır-Eskişehir region of Turkey.

In this study, the rare earth preconcentrate was reduced by aluminum together with ferrosilicon and rare earth ferrosilicon alloys were produced. The optimum conditions of reduction, which are time, temperature, reducer amounts and the basicity of the slag phase, were investigated by smelting in an induction furnace. At the end of the study, a rare earth ferrosilicon alloy containing 39.3 % rare earths, 37.5 % silicon, 19.3 % iron and 3.9 % aluminum was produced under the optimum conditions determined with 57.7 % rare earth metal recovery.

Key words: Rare earth ferrosilicon, bastnasite, metallothermic reduction

ÖZ

NADİR TOPRAK METALLERİ ÖN KONSANTRELERİNİN METALOTERMİK YÖNTEMLE İNDİRGENMESİ İŞLEMİNDE KOŞULLARIN OPTİMİZASYONU

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Nadir toprak metalleri-demir-silisyum alaşımı demir-çelik metalurjisinde önemli bir katkı malzemesidir. Temel olarak kükürtün çelik içerisindeki zararlı etkilerinin kontrolunü sağlamak ve dökme demir içindeki grafit yapılarının şeklini kontrol etmek için kullanılmaktadır. Bu çalışmanın amacı, Türkiye'nin Beylikahır-Eskişehir yöresinde bulunan bastnasit cevherinden hazırlanan ön konsantre kullanılarak nadir toprak metalleri-demir-silisyum alaşımlarının metalotermik indirgeme yöntemiyle üretilmesi ve en uygun üretim koşullarının saptanmasıdır.

Çalışma süresince, nadir toprak metalleri ön konsantresi aluminyum ve ferrosilisyum kullanılarak indirgenmiş ve nadir toprak metalleri-demir-silisyum alaşımları üretilmiştir. İndirgenme için en uygun koşullar, süre, sıcaklık, indirgeyici miktarları ve curufun baziklik oranı, indüksiyon fırını kullanılarak gerçekleştirilen ergitme işlemleri vasıtasıyla bulunmaya çalışılmıştır. Çalışmanın sonunda bulunan en uygun koşullarda, ağırlıkça % 39.3 nadir toprak metalleri, % 37.5 silisyum, % 19.3 demir ve % 3.9 aluminyum içeren nadir toprak metalleri-demir-silisyum alaşımı % 57.7 nadir toprak metalleri eldesiyle üretilmiştir.

Anahtar kelimeler: Nadir toprak metalleri-demir-silisyum alaşımı, bastnasit, metalotermik indirgeme

To My Parents;
Münire and İsmail YILMAZ

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CHAPTER 1

INTRODUCTION

The rare earth elements consist of 17 chemically similar elements which are scandium, yttrium and the lanthanides. Although about 250 rare earth containing minerals are known, three of them which are bastnasite, monazite and xenotime are the main sources of the rare earths. The rare earth ore beds in Turkey which contain bastnasite type rare earth mineral are found in the Beylikahır-Eskişehir region.

The rare earths as metals, alloys or compounds have found use in many different application areas. Especially rare earth ferrosilicon alloy is utilized in steelmaking industry for deoxidation and desulfurization of steel and modification of sulfide inclusions in steel. Also it is used as an additive for cast iron to increase the tensile strength of grey cast iron. In both cases, the addition of rare earth ferrosilicon alloy increases the properties of the product.

Rare earth ferrosilicon alloy, the typical analysis of which consists of about 30% of each of its major constituents, is produced by two different reduction methods; carbothermic reduction and metallothermic reduction. Metallothermic reduction method gives a higher rare earth recovery and a better grade than carbothermic reduction method.

Optimization of the conditions of rare earth ferrosilicon alloy production by metallothermic reduction method using the rare earth preconcentrate produced from the ore taken from Beylikahır-Eskişehir region of Turkey was the main aim of this study.

CHAPTER 2

LITERATURE SURVEY

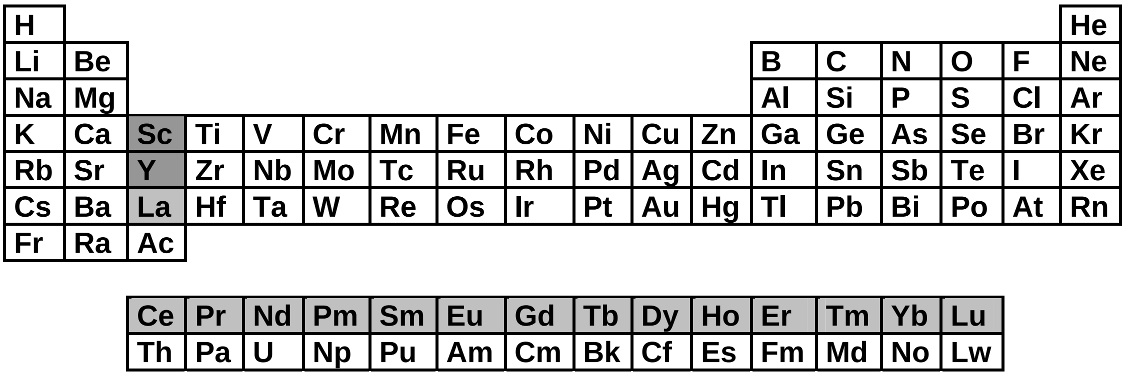
2.1. Rare Earth Elements

2.1.1. Place of the Rare Earths in the Periodic Table

The term “rare earths” (symbolized as RE or REE) denotes the group of 17 chemically similar metallic elements, including scandium, yttrium, and the lanthanides. The lanthanide (Ln) group comprises 14 elements which have atomic numbers ranging from 58 (cerium) to 71 (lutetium) which are located in 6th row of the periodic table following lanthanum, and whose properties resemble those of lanthanum. For this reason lanthanum is also included in the group and responsible for the name “lanthanides” (e.g., resembling lanthanum). Moreover, scandium and yttrium, which belong to group III, are almost always present together with the lanthanides in minerals and have similar properties with lanthanides. Except promethium, all of the rare earths occur in nature [1,5]. The place of the rare earth elements in the periodic table is shown in Figure 2.1.

2.1.2. Some Properties and Applications of the Rare Earths

All the rare earths are typical transition metals, with high lustre and electrical conductivity. They are silver, silver-white or grey in colour and in their metallic form they are soft and ductile. Chemically, REE are strong reducing agents and their compounds are generally ionic. Most of the rare earth elements are trivalent, with europium also having a valance of +2 and cerium also having a valance of +4. In air, the rare earths tend to tarnish rapidly forming rare earth oxides (REO). Because of their chemical similarity, it is exceedingly difficult to separate them from each other and they behave as a single chemical entity. All the rare earths are paramagnetic, except Gd, Dy and Ho, which have ferromagnetic properties [1,2,3].



H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lw

Figure 2.1. Periodic table showing rare earth elements (light shaded) and scandium, yttrium (highlighted)

The rare earths, used as metals, alloys and chemical compounds, have an ever growing variety of applications in the modern technology; Ferrous and nonferrous metallurgy, production of glass and ceramics, the chemical industry, production of permanent magnets, nuclear applications and many more. They still have other potential uses, the number of which increases as the properties of lanthanides, their alloys and compounds become known [1,5]. Some of the important properties of the rare earths are given in Table 2.1.

The largest single application of rare earths is in the manufacture of rare earth containing zeolite cracking catalysts required in the petroleum refining process since about 35 % of REE are used as catalysts. REE’s are also included in catalytic converters which are used to control vehicle exhaust emissions in automobiles [2,5].

Rare earths are used extensively in glass and ceramics industry. They find use as decolourising agents, glass-polishing compounds, UV absorbers and antibrowning agents, glass and ceramic colourising agents, activators in laser glasses. They are also used as additives to structural ceramics such as stabilized zirconia and in optical lenses and glasses [1,2].

Table 2.1. Some of the important properties of the rare earth elements [2]

Element	***Symbol***	***Atomic no.***	***Atomic wt.***	***Density (g/cm^3)***	***Valence***	***Melting point (^oC)***	***Boiling point (^oC)***
Lanthanum	La	57	138.9	6.15	3	918	3464
Cerium	Ce	58	140.12	6.77	3,4	789	3443
Praseodymium	Pr	59	140.98	6.44	3	931	3520
Neodymium	Nd	60	144.24	7.01	3	1021	3074
Promethium	Pm	61	145	7.26	3	1042	3000
Samarium	Sm	62	150.4	7.52	3	1074	1794
Europium	Eu	63	151.96	5.2	3,2	822	1527
Gadolinium	Gd	64	157.25	7.9	3	1313	3273
Terbium	Tb	65	158.93	8.23	3	1356	3230
Dysprosium	Dy	66	162.5	8.55	3	1412	2567
Holmium	Ho	67	164.93	8.8	3	1474	2700
Erbium	Er	68	167.26	9.1	3	1529	2868
Thulium	Tm	69	168.93	9.34	3	1545	1950
Ytterbium	Yb	70	173.04	7	3	819	1196
Lutetium	Lu	71	174.97	9.84	3	1663	3402
Scandium	Sc	21	44.96	3	3	1541	2836
Yttrium	Y	39	88.91	4.47	3	1522	3338

Rare earth elements, notably cerium and mischmetal (Ce+La+Nd), have also been used as minor alloying additives for controlling shape of inclusions in cast iron and steel. The addition of rare earth metals to various aluminum, titanium and magnesium alloys increases their properties as in the ferrous metallurgy such as high-temperature and creep strength [1,5,7].

Apart from the applications mentioned, rare earths are also utilized in permanent magnets, lighter flints, nuclear technology, electronics, rechargeable batteries and many others number of which is growing day by day.

2.1.3. Abundance and Resources of the Rare Earths

"Rare" earth elements is a historical misnomer; persistence of the term reflects unfamiliarity rather than true rarity. In terms of inherent abundance in the earth's crust, the rare earths are not rare because the total rare earths abundance (220 ppm) is more than that of even carbon (200 ppm), and several rare earth elements are more abundant than many better known metals. The most common rare earths are La, Ce and Nd. Rare earths with odd atomic numbers are less abundant than their immediate neighbors with even atomic numbers. These facts are presented in Figures 2.2. and 2.3 [1,5,8].

Rare earth elements are classified into two groups: The light or cerium subgroup comprising the first seven elements whose atomic numbers are from 57 to 63 (La, Ce, Pr, Nd, Pm, Sm, Eu) and the heavy or yttrium subgroup comprising the elements with atomic numbers from 64 to 71 (Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y). Despite its low atomic weight yttrium is categorized with the heavy REE because its properties are closer to those of the heavier REE than to the lighter group [2,4].

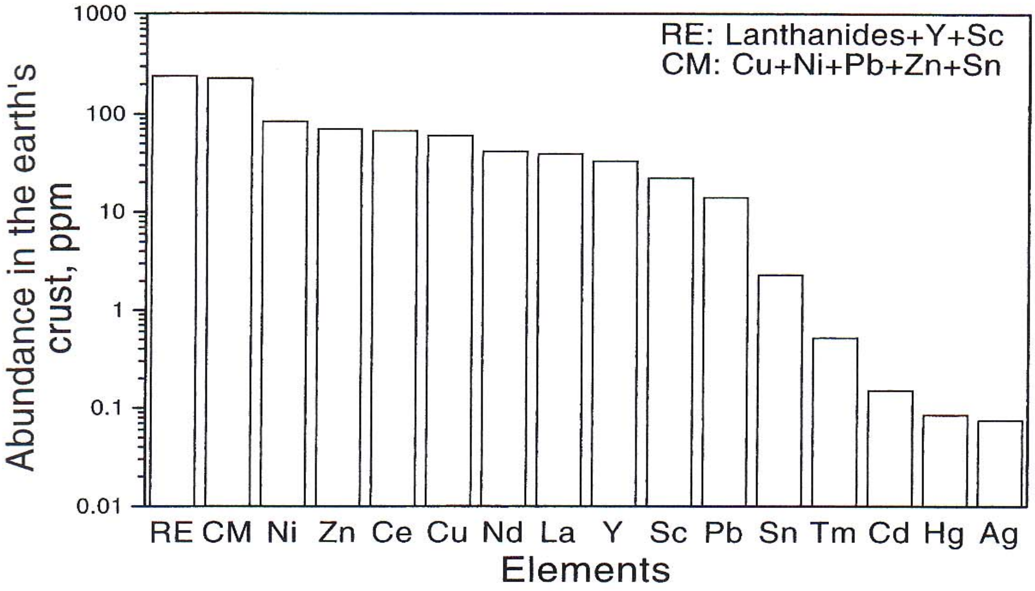


Figure 2.2. Abundance of rare earths and certain common elements in the earth's crust [5]

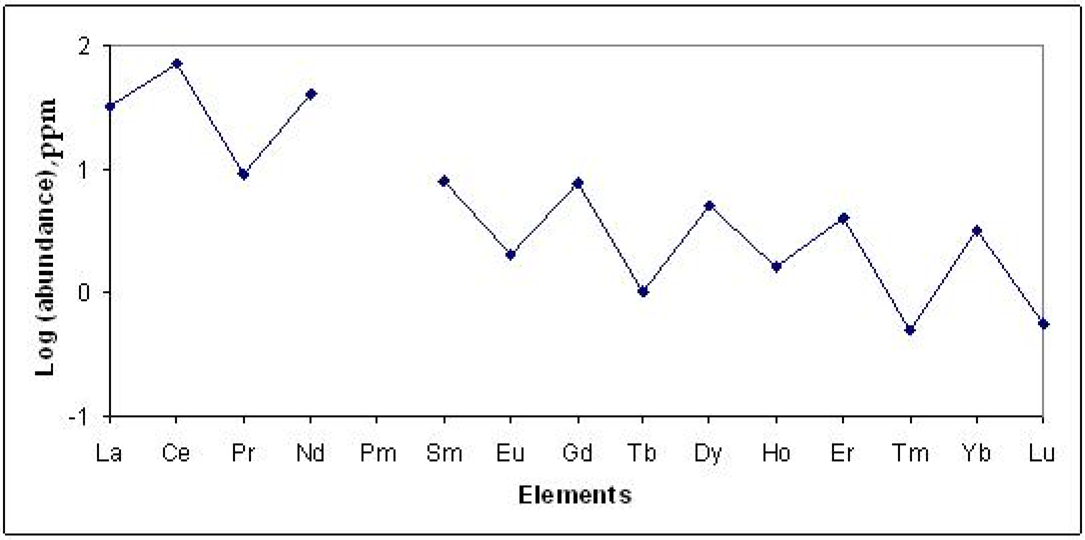


Figure 2.3. Individual abundances of rare earths [1]

Although more than 250 rare earth containing minerals are known, about 95 % of the rare earths occur in only three minerals; bastnasite, monazite and xenotime. Some properties of the minerals are shown in Table 2.2.

Table 2.2. Some of the important rare earth minerals [5]

Mineral	***Formula***	***Rare earth content (%)***	***Other constituents (%)***
Bastnasite	$(Ce,La,Pr)(CO_3)F$	Ce_2O_3 36.9-40.5; $(La, Pr,...)_2O_3$ 36.3-36.6	CO_2 19.8-20.2 F 6.2-8.5
Euxanite	$(Y,Ce,Ca,U,Th)(Ti,Nb,Ta)_2O_6$	$(Y,Er)_2O_3$ 18.2-27.7 $(Ce,La,...)_2O_3$ 16-30	TiO_2 16-30; Nb_2O_5 4.3-47.4; Ta_2O_5 1.3-23; ThO_2 1-5; UO_2 0.4-12
Fergusonite	$(Y,Sr,Ce,U)(Nb,Ta,Ti)O_4$	Y_2O_3 31-42; $(Ce,La,...)_2O_3$ 0.9-6; Er_2O_3 0-14	$(Nb,Ta)_2O_5$ 46-57.5; ThO_2 1-3.4; UO_2 1.2-6; TiO_2 0-6; also ZrO_2, SnO_2, WO_3
Gadolinite	$(Y,Ce)_2FeBe_2Si_2O_{10}$	Y_2O_3 30.7-46.5 ; $(Ce,La,...)_2O_3$ 16-30	FeO 10-13.7; SiO_2 23-24.5; ThO_2 0.3-0.4; BeO 9-10.2; also Ca, Mg
Loparite	$(Na,Ca,Ce,Sr)_2(Ti,Ta,Nb)_2O_6$	$(Ce,La,...)_2O_3$ 32-34	TiO_2 39.2-40; $(Nb,Ta)_2$ 8-11; CaO 4.2-5.2; Na_2O 7.8-9; also Sr, K, Si, Th
Monazite	$(Ce,La,...)PO_4$	$(Ce,La,...)_2O_3$ 32-34	P_2O_5 22-31.5; ThO_2 4-12; U 0.1-0.3; ZrO_2 0 to 7; SiO_2 0 to 6
Orthite	$(Ca,Ce)_2(Al,Fe)_3Si_3O_{12}$ [O,OH]	Ce_2O_3 0-6; La_2O_3 0-7; Y_2O_3; 0-8	BeO 3.8; also ThO_2
Parisite	$Ca(Ce,La,...)_2(CO_3)F_2$	Ce_2O_3 26-31; $(La,Nd,...)_2O_3$ 27.3-30.4; Y 8	CaO 10.4-11.4; CO_2 23-24.5; F 6-7
Xenotime	YPO_4	Y_2O_3 52-62	ThO_2, UO_2 up to 5; ZrO_2 3; SnO, SiO_2 9
Yttrocerite	$(Ca,Y,Ce,Er)F_2\text{-}3H_2O$	Ce 8.5-11.5; Y 14.3-37.7	Ca 19.7-32.7; F 37.7-41.6

2.1.3.1. Bastnasite

The mineral bastnasite is a fluorocarbonate of the cerium group rare earth metals with an ideal formula of $LnFCO_3$ or (Ce, La,…)FCO_3 and hardly contains any thorium. The specific gravity of bastnasite is 4.9-5.2, its hardness is 4-4.5 and it is yellow to brown in colour. Bastnasite occurs as veins or dissemination in a complex of carbonate-silicate rocks, in quartz veins, fluorite-bearing veins and quartzite [5,6]. Bastnasite ore is generally treated by conventional mineral processing technology, that is, communition followed by froth flotation [9].

Bastnasite has been identified in various locations on several continents. The two most important deposits of rare earths are found in Bayan Obo in China (800 million metric tons; 6 % REO) and at Mountain Pass, California in the US (3.3 million metric tons; 7.7 % REO) [5,10]. Rare earth ore beds in Turkey are situated in the Beylikahır-Eskişehir region, and are consisted of bastnasite type rare earth mineral.

2.1.3.2. Monazite

The mineral monazite is a phosphate, mainly of the cerium group rare earths and thorium. It is a red, brown or yellow, translucent mineral which is generally denoted by (Ce,La,Th,Y)PO_4. Its specific gravity is 4.9-5.3 and the hardness 5-5.5. The mineral is very inert and resistant to water attack. Monazite is found in many geological environment. It occurs as an accessory mineral in acidic igneous rocks, in metamorphic rocks, and in certain vein deposits. Due to its chemical stability it also develops into detrital mineral in placer deposits and beach sands [5].

Some and the most important sources of monazite are beach placers. Beach sand deposits also contain other heavy minerals such as ilmenite, rutile and zircon. The primary monazite deposits have been useful as rare earth resources in a few instances and some of them are in South Africa, US, China, Australia and India [5].

2.1.3.3. Xenotime

Xenotime is a yttrium phosphate mineral whose chemical formula is YPO_4. It contains about 67 % REO, mostly of the heavier elements. Xenotime is typically translucent to opaque (rarely transparent) in shades of brown to brownish yellow, but also reddish to greenish brown and gray. Its specific gravity is 4.4-5.1.

The most important deposits of xenotime are in Malaysia, Australia, Indonesia, Thailand, China and Brazil [5].

2.2. Mischmetal

Mischmetal is a mixture of the rare earth metals and varies in composition, depending on the material that is reduced. Its typical composition includes approximately 45-50 % Ce, 22-25 % La, 14-17 % Nd, 5-8 % Pr, 2-3 % Sm, 0.2-0.5 % Fe and small amounts of other rare earth metals and tracers which are mainly Al, C, O, N. Large-scale commercial production of mischmetal is presently limited to the electrolysis of fused anhydrous chlorides [11].

The most common use of mischmetal is in the "flint" ignition device of many lighters and torches. Also it is utilized in cast iron and steel technology to improve the quality of product [11].

2.3. Rare Earth Ferrosilicon

2.3.1. Definition

Rare earth ferrosilicon is an alloy which mainly consists of, as the name regards, mixed rare earth metals, iron and silicon. The alloy is the most extensively used form of rare earths in cast iron and steel making technology. Typical analysis of some of the commercial rare earth ferrosilicon alloys are given in Table 2.3. Production of rare earth ferrosilicon is the main concern of this thesis study.

Table 2.3. Typical analysis of some commercial rare earth ferrosilicon alloys (wt.%)

CODE	*REE*	*Si (Max.)*	*Mn (max.)*	*Ca (max.)*	*Ti (max.)*	*Fe*
FeSiRE23	21.0 -- <24.0	44.0	3.0	5.0	3.0	Balance
FeSiRE26	24.0 -- <27.0	43.0	3.0	5.0	3.0	
FeSiRE29	27.0 -- <30.0	42.0	3.0	5.0	3.0	
FeSiRE32-A	30.0 --< 33.0	40.0	3.0	4.0	3.0	
FeSiRE32-B	30.0 -- <33.0	40.0	3.0	4.0	1.0	
FeSiRE35-A	33.0 -- <36.0	39.0	3.0	4.0	3.0	
FeSiRE35-B	33.0 -- <36.0	39.0	3.0	4.0	1.0	
FeSiRE38	36.0 -- <39.0	38.0	3.0	3.0	2.0	
FeSiRE41	39.0 -- <42.0	37.0	3.0	3.0	2.0	

2.3.2. Applications

2.3.2.1. In Steelmaking

The rare earth metals form extremely stable sulfides and oxysulfides. Sulfide, oxide and silicate inclusions present in steel can be soft enough at hot working temperatures to deform into long stringers oriented parallel to the hot rolling direction and they act as infinitely sharp internal notches or crack initiators. The rare earths, especially cerium, appear to combine with the sulfide inclusions that are invariably present in steel to form particles with a more rounded morphology that is less likely to promote cracking, instead of elongated stringers. Thus, addition of rare earths, in their rare earth ferrosilicon or mischmetal form which are found more economical than their elemental forms, results in the improvement of toughness and formability of the steel [7,12]. Because of the sulfur and oxygen affinity of rare earths, rare earth addition into steel must be done after deoxidizing and desulfurizing treatment to increase their function of controlling the shape of sulfide inclusions [4].

The rare earth sulfide inclusions that form after rare earth treatment of steel are harder and have a higher melting range than inclusions they replace. Unlikely to other oxide, sulfide and oxysulfide inclusions, the rare earth sulfide inclusions do not deform during hot working and remain globular. This fact is especially important in carbon and HSLA steels for automotive applications [13,14].

2.3.2.2. In Casting

A typical microstructure of gray cast iron consists of a large fraction of graphite flakes that behave as notches or cracks, reducing both ductility and toughness. The mechanical properties depend on the volume fraction and shape of the dispersed graphite, and the properties of the matrix. On the other hand, nodular iron has properties similar to mild steel and is essentially a ductile cast iron. Nodular iron results when the graphite flakes in cast iron are converted to nodules. The addition of mischmetal or rare earth ferrosilicon into cast iron melt causes the graphite to separate into a nodular form. As the nodules do not form points of stress concentration, the mechanical properties of the product are markedly improved [15, 16]. Table 2.4. shows plane strain fracture toughness of pearlitic gray cast iron with respect to graphite structure.

Table 2.4. Plane strain fracture toughness of pearlitic gray cast iron [16]

Graphite Structure	K_{IC} ***(MPa*** $m^{1/2}$***)***	
	Experimental	***Theoretical***
Lamellar	28.1	23.0
Nodular	57.3	58.0
Steel Matrix	~70.0	~70.0

In the manufacture of nodular iron, rare earths are added as mischmetal or rare earth ferrosilicon and not as pure rare earth metals, mainly due to cost consideration. The rare earth elements cleanse the metal of elements that prohibit spherical graphite growth, and the compounds they then form provide heterogeneous substrates for graphite nucleation. Its good physical and foundry properties have made nodular iron, so that rare earth ferrosilicon, attractive engineering material, particularly in the automotive industry [5].

2.3.3. Production Methods of Rare Earth Ferrosilicon Alloy

2.3.3.1. Carbothermic Reduction

Carbothermic reduction process makes use of carbon to extract metal values from rare earth metal sources. Reduction process is carried out in a submerged arc furnace using carbon electrodes, since temperatures in excess of 1930 ˚C are required, according to the general reaction;

$$\text{Metal Oxide} + \text{Carbon} = \text{Metal} + \text{CO} \tag{1}$$

Rare earth metal source required to produce a rare earth ferrosilicon alloy by carbothermic reduction may be rare earth metal oxides, carbonates, phosphates, silicates, fluorocarbonates. Compounds in the form of ore or ore concentrates of the rare earth metals can be used as well as relatively pure materials. However, commercially available rare earth metal compounds are generally in the form of fine powders which are difficult to add to a reduction furnace without loss of the metal values due to dusting. Therefore, it is desirable to agglomerate the fine rare earth metal compounds prior to the carbothermic reduction [17].

Silica, iron and carbon which are required for the carbothermic reduction process may be supplied in any conventional form. For example, sand or quartz may be used as a source of silica, and carbon may be supplied as coal, coke or combinations of several carbonaceous materials. Iron, for economic reasons, is supplied in the form of steel scrap, although any sources of iron could be used in the process [17].

Carbon required for the reduction of rare earth metal oxides, other metal oxides and silica must be in excess of the stoichiometric amount. The amount of carbon required for the carbothermic reduction process varies from 10 % to 50 % in excess of the stoichiometric amount depending on the specific furnace conditions employed in the process. Using excessive amount of carbon serves to secure complete reduction of the silica used in the reduction process. This has a beneficial effect that the formation of rare earth metal carbides is suppressed since silicon favors the production of rare earth metal silicides rather than rare earth metal carbides [17].

2.3.3.2. Metallothermic Reduction

2.3.3.2.1. Metallothermic Reduction with Ca-Si

As Sump [18] stated in 1966, a rare earth metal silicon alloy can be produced by reducing the rare earth source with Ca-Si that contains preferably 30 % calcium. In his method, a mixture of rare earth source, calcium silicide as the reducing agent and silica as a fluxing agent is melted in a graphite crucible in an electric arc furnace.

The rare earth compounds which can be reduced by the process of this invention may be rare earth oxides, carbonates, phosphates, silicates and fluorocarbonates. Compounds in the form of ores or ore concentrates of the rare earths can be utilized as well as relatively pure materials such as cerium oxide or mixed cerium lanthanum oxide [18].

It is also very important that silica be present in the reaction mixture since it serves a two-fold purpose; first, silica avoids the catastrophic attack upon the graphite crucible by the highly reactive rare earth metals, secondly, separation and the removal of the alloy from other products are simplified by using silica. The amount of silica varies from 3 % to 15 %, but a preferred amount is about 10 % based on the combined weight of rare earth compound and reducing metal [18].

Because of the high melting temperatures of the rare earth compounds, the reduction must be carried out in an electric arc furnace with graphite electrodes. Especially at high temperatures, it is very possible for rare earths to react with graphite crucible, therefore, conventional electric furnaces which provide heat through the walls of the crucible can not be utilized for this process. Further, Sump utilized “cold-wall” graphite crucibles in his study to prevent the reaction between the crucible and the mixture [18].

In a test carried out by Sump et al. [18], a mixture of 4.53 kg rare earth oxide, 6.8 kg Ca-Si (30 % calcium) and 1.13 kg SiO_2 was charged into an electric arc furnace using graphite electrodes with a “cold-wall” graphite crucible. The furnace was operated as a direct current arc at 1400 amperes and 35 volts for 50 minutes. The alloy was cast into molds after the reduction. Ingot alloy recovery was 7.25 kg per run. The entire melting and casting operations were conducted in the absence of a protective atmosphere. The total rare earth content of the product alloy was 42.5 % by weight. It also contained 51 % Si, 4.6 % Ca and 1.9 % Fe.

2.3.3.2.2. Metallothermic Reduction with Ca-Si and CaC_2

As Bungart and Kallenbach [19] stated in their studies, an improved process for producing master alloys of the rare earth metals and silicon which is devoid of technical difficulties and which yields a product containing 40 % or more of rare earth metals could be accomplished by this type of reduction. The technique depends on the conditions that the silicon starting or base alloy should contain between about 5 % and 40 % by weight calcium, a portion of the calcium-silicon base alloy should be replaced by a predetermined quantity of calcium carbide and the mixture of calcium-silicon alloy and calcium carbide should be reacted with a predetermined quantity of rare earth metal oxides or salts at an elevated temperature.

According to this study the process needs a reaction mixture containing preferably between 35 % and 50 % by weight rare earth metal oxides or equivalent amount of rare earth metal salts, between 25 % and 62.5 % by weight of a calcium-silicon alloy which contains between about 5 % and 40 % by weight calcium and between about 2.5 % and 25 % by weight calcium carbide. This mixture is heated to a temperature within the range of 1200 ˚C to 1800 ˚C to have an effective reduction and to form the desired master alloy product. Consequently the master alloy obtained is separated from the secondary products of the reaction. Also the reaction is carried out in the presence of a flux which absorbs these sluggy reaction products and contains one or more chlorides or fluorides of the alkaline earth metals and preferentially added to the reaction mixture in an amount such that the overall mixture contained from about 5 % to 20 % by weight of said flux [19].

A three coordinate diagram which was found by Walter Bungardt and Rudolf Kallenbach is given in Figure 2.4. It is shown in this diagram that the relative proportions of the rare earth oxides, calcium silicon alloy and calcium carbide in the reaction mixture should be somewhere inside the area which is defined by the points A, B, C and D. The area defined by the points A’, B’, C’ and D’ which is also plotted on the mentioned diagram indicates a particularly more advantageous area for this constituents to fall. The actual values of these points are given in Table 2.5 [19].

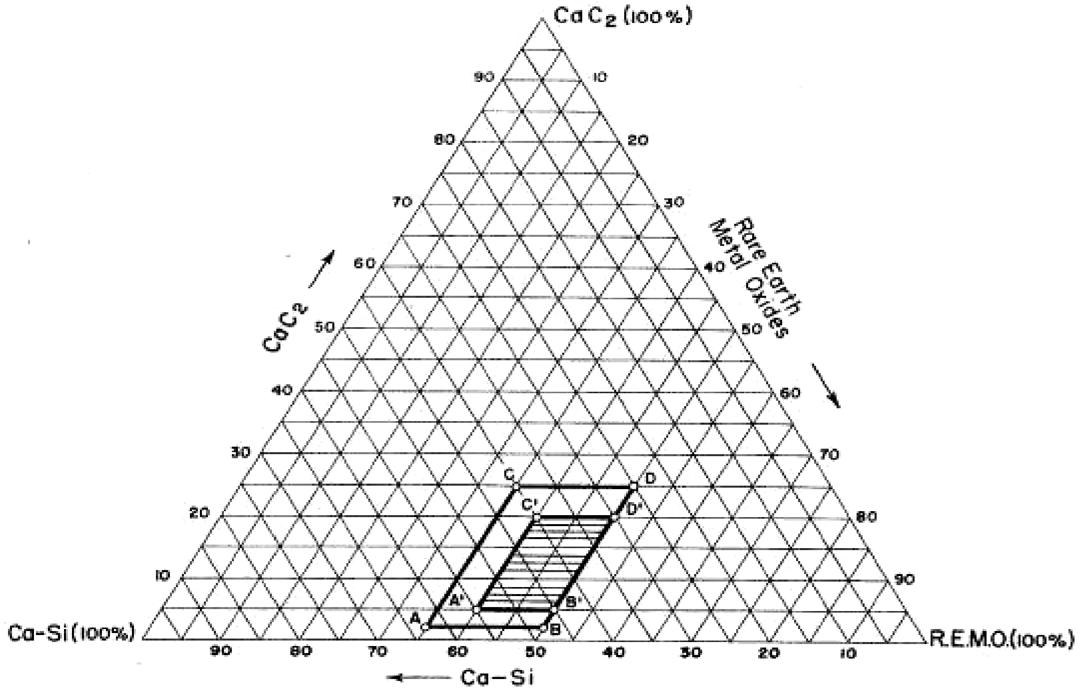


Figure 2.4. Three coordinate diagram invented by Kallenbach and Bungardt [19]

Table 2.5. Actual values of points in Figure 2.4. [19]

	RE-metal oxides (wt.%)	***Ca-Si Alloy (wt.%)***	***CaC_2 (wt.%)***
A	35	62.5	2.5
B	50	47.5	2.5
C	35	40	25
D	50	25	25
A’	40	55	5
B’	50	45	5
C’	40	40	20
D’	50	30	20

In one of the examples given by Bungart et al. [19] a reaction mixture which consisted of 24 grams of commercial mixed rare earth metal oxides, 27 grams of a commercial calcium silicon alloy (64.3 % Si, 27.3 % Ca, 3.8 % Fe), 9 grams of commercial calcium carbide (80 % CaC_2) and 15 grams of commercial calcium fluoride as a flux was prepared. Reaction was carried out in a graphite crucible at about 1550 °C and then a 30 grams weighed metal product which contained 54.6 % mischmetal, 30.9 % silicon, 5.7 % calcium and other impurities was obtained. The recovery was approximately 83 %.

2.3.3.2.3. Metallothermic Reduction with a Metal Silicide or Silicon in an ESR Furnace

This modified technique was found by Herchenroeder [20] in 1976 and it relates to methods of making reactive metal silicide (including rare earth silicide) and particularly to methods of making master alloys of lanthanum and silicon, and of other reactive metals and silicon in an ESR (electro-slag refining) furnace.

In prior methods a mixture of rare earth oxides and metal silicides was heated to promote a reaction to form metal oxide slag and a rare earth-silicon alloy. Calcium carbide and iron were added to improve the reaction. However, these methods were not satisfactory for producing lanthanum-silicon alloy with any degree of efficiency and economy. If reactants are simply blended and heated to a temperature to cause a reaction between the reactive metal oxides and silicon but not to cause a fluid slag the resulting alloy is intermingled with the slag product and need an ore dressing operation to recover the alloy. If mixture is heated to a slag forming temperature there are reactions with the normal reaction vessels such as carbon or ceramics which is undesirable. Herchenroeder suggested a method that a rare earth silicon alloy which was clearly separated from the slag components could be provided without need for further cleaning operations and which could be used directly as an additive in metal making operation [20].

A nonreactable water cooled crucible which was usually constructed of copper was used in mentioned technique to avoid contamination of the product alloy. Because of the intensity of ESR furnace the slags are relatively controllable and the process is efficient.

Preferentially, Herchenroeder [20] fed a mixture of rare earth metal oxide and metal silicide or silicon into a slag pool formed between a non-consumable electrode and the base of a water cooled crucible to form a pool of rare earth metal silicon alloy covered with slag, raising the electrode as the molten bath rises in the container, to allow the alloy to solidify beneath the slag and then separate the slag and rare earth metal silicon alloy.

Flux materials such as fluorspar could be added to maintain the slag in fluid condition throughout the process. Rare earth metal concentrations of the product alloy obtained from this operation were generally above 50% [20].

In an example for this method given by Herchenroeder, 18.14 kg of La_2O_3 was blended with 16.3 kg of Ca-Si (35% Ca, 65% Si) and 2.1 kg of CaF_2. A 1.13 kg starting pad was placed in the bottom of a 20.3 cm diameter water cooled copper crucible of an ESR furnace, equipped with a 15.2 cm diameter graphite electrode. 2.3 kg of CaF_2 and 64 grams of Ca-Si alloy were used to form a starting fluid pool into which the blend was fed. At the end of the test 28 kg of alloy was recovered which contained 52.89 % lanthanum, 5.37 % calcium, and 32.7 % silicon [20].

2.3.3.2.4. Metallothermic Reduction with Al and Fe-Si

2.3.3.2.4.1. A Brief Explanation

The main purpose of investigating the production of rare earth ferrosilicon alloy by the metallothermic reduction with aluminum and Fe-Si is to obtain a better grade alloy and higher recoveries than achieved by the carbothermic and other reduction methods. In this reduction process, rare earth oxides are reduced in the presence of Al and Fe-Si in a suitable furnace to achieve a temperature high enough to melt both metal and slag phases. Main aim of this thesis is based on this type of reduction process and the optimization of the conditions of the production of rare earth ferrosilicon alloy by this reduction method will be investigated.

2.3.3.2.4.2 Amount of Components to be Charged

Metallothermic reduction with Al and FeSi is represented by Reaction 2 which is given below and charge calculations of the components are made with respect to this reaction;

$$3RE_2O_3 + 15Si + 2Al = 6RESi_2 + 3SiO_2 + Al_2O_3 \tag{2}$$

In order to begin the calculation the content of the rare earth metal oxides or other compounds of rare earth metals in the source is determined. Taking the average molecular weight of rare earth metals as it is found in nature as being 140, the rare earth metal oxide if such ores are used, is thus calculated to have a molecular weight of about 328. If the percentage of rare earth metal in the ore is known moles of RE_2O_3 can be easily calculated. According to Morrice et al. [21] rare earth metal sources can be oxides, carbonates and fluorocarbonates as well as other compounds. Further, Mitchell et al. indicated in their study that if carbonates, fluorocarbonates or silicates are used as the sources of rare earth metals, the oxides of rare earths would immediately form under the reaction conditions [23].

After calculating the moles of the rare earth oxide that will be reduced, needed silicon content can be determined according to the reaction stoichiometry. The moles of silicon must be five times of the moles of rare earth oxide. But since silicon is added in the form of ferrosilicon, the weight percentage of silicon in the ferrosilicon must be known to calculate the amount of ferrosilicon that will be charged. Likewise, the moles of aluminum which will enter the reaction must be 2/3 times of the moles of rare earth oxide [21]. Beside this, it was seen by the previous researchers that the stoichiometric amounts of aluminum and ferrosilicon were not enough to achieve the highest recovery. Excessive amounts of silicon up to 120% and aluminum up to 700% are utilized for the reduction process reasons of which will be explained later.

The amount of slag can be calculated with the known silica and alumina amounts. However, it is an important fact that some of the aluminum enters the alloy product instead of the slag [22]. Fluxing agents such as CaO, CaF_2 or MgO can be added into the charge according to desired properties of the slag such as melting point, viscosity or basicity to enhance the reaction thermochemistry.

2.3.3.2.4.3 The Effect of Aluminum and Ferrosilicon

Aluminum and ferrosilicon have the most important effect on the main reduction reaction when they are added as reductants. Although they are both given as reductants, most of the reduction is accomplished by aluminum, and ferrosilicon has a role in the reduction reaction as an alloying component with the product metal [22].

It can be deduced from the Figure 2.5. that when just aluminum or just silicon is added to system alone, the standard state thermochemistry is not favorable to reduce the rare earth oxides since the formation energies of rare earth oxides are lower than those of Al_2O_3 and SiO_2. Anyhow when silicon and aluminum are used together, ferrosilicon decreases the activity of rare earth metals produced by alloying with them [22]. The alloying action of ferrosilicon was explained in the patent file by

Mitchell et al. It was indicated in their study that the silicon added simultaneously with the aluminum acts as a “sink” or “sponge” for the reduced rare earth metals by forming an alloy with them immediately when the metals are in the liquid state. It is believed that foregoing effect of the silicon is due to the interactions between silicon and rare earth metals under certain conditions with the formation of RE-Si compounds or alloys [23].

Also amounts of the aluminum and ferrosilicon to be charged are important and they should be higher than the stoichiometric amounts calculated. At elevated temperatures of the reduction reaction a significant amount of aluminum is oxidized. Therefore, excessive amounts of aluminum up to 700% of stoichiometric amount should be used to compensate for the aluminum losses due to oxidation [21,22]. The need for excess ferrosilicon differs from the situation of aluminum. In Figure 2.6., a binary phase diagram which was taken from Bulanova’s study is given [27]. From this diagram it can be seen that there is a certain necessity of excessive ferrosilicon usage for Reaction 2. For example, if the final product of Reaction 2 is $(La,Ce)Si_{2-\alpha 2}$ which consists of 70 at. % (32 wt. %) Si, it can be calculated by using lever rule at room temperature that about 10 % of the product occurs as silicon rather than $(La,Ce)Si_{2-\alpha 2}$ and this unreacted silicon phase must be compensated by utilizing excessive amount of ferrosilicon in the charge. This fact is also shown in Table 2.6. The addition of excess aluminum and ferrosilicon is experimentally studied by Marchant et al. [25] and the results of this study are given in Table 2.7. and these results are in accordance with the theoretical expectations.

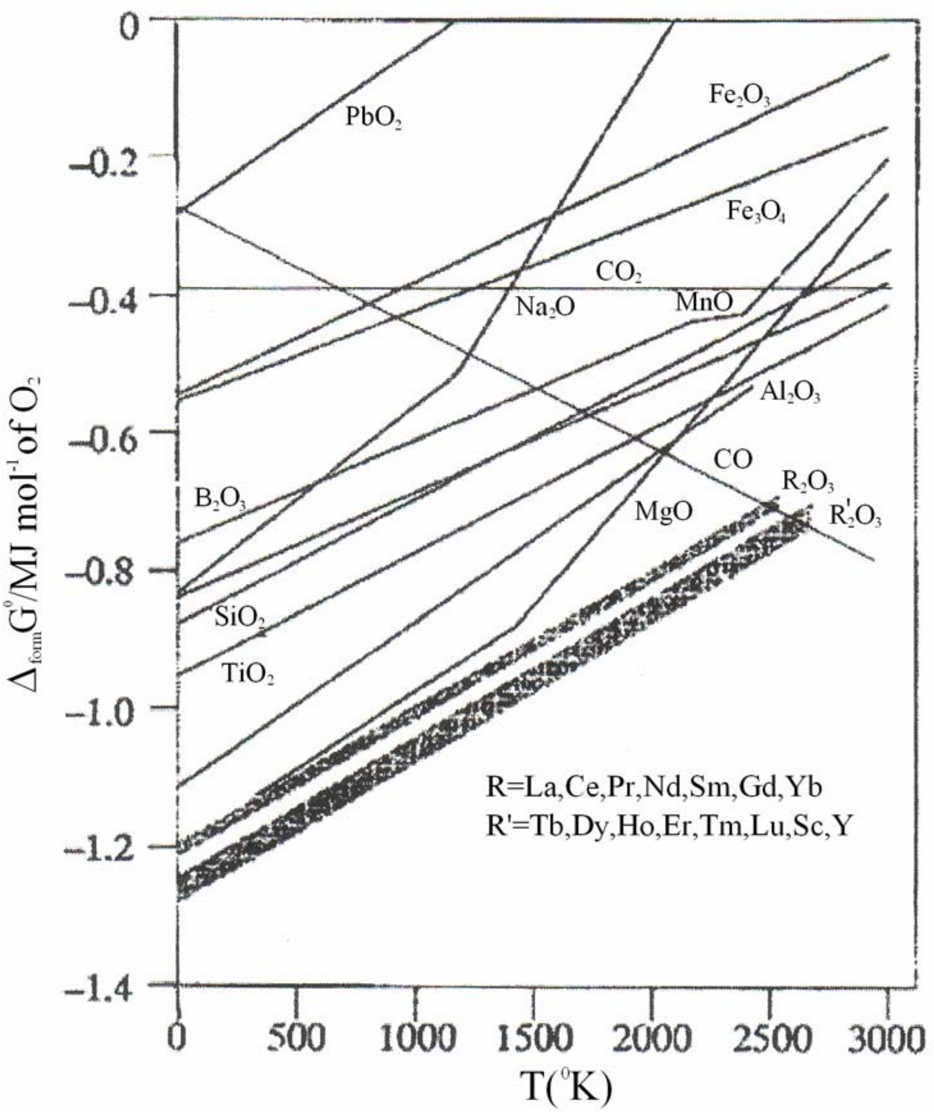


Figure 2.5. Formation energies of rare earth oxides and some other oxides vs. Temperature [26]

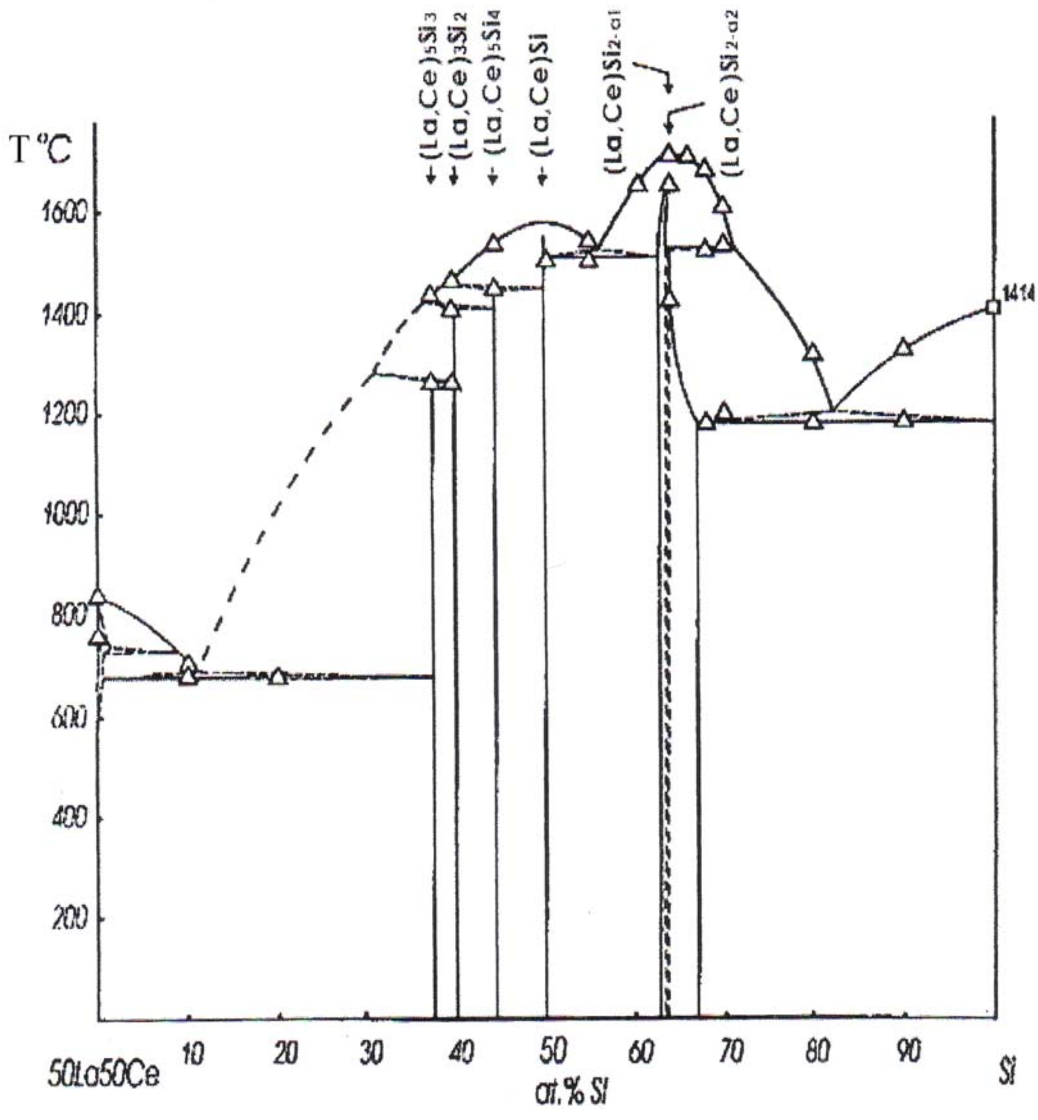


Figure 2.6. Binary phase diagram of (50%La-50%Ce)-Si [27]

Table 2.6. Phase compositions with respect to silicon content [27]

Silicon content in the alloy, at.%	*Phase composition according to microstructure and X-ray examinations*
0	{α-La,β-Ce}
10	{α-La,β-Ce}+ eutectic ((β-La,γ-Ce)+$(La,Ce)_5Si_3$)
20	$(La,Ce)_5Si_3$ + eutectic ((β-La,γ-Ce)+$(La,Ce)_5Si_3$)
30	$(La,Ce)_5Si_3$ + eutectic ((β-La,γ-Ce)+$(La,Ce)_5Si_3$)
37.5	$(La,Ce)_5Si_4$ + $(La,Ce)_3Si_2$ + $(La,Ce)_5Si_3$
39.9	(La,Ce)Si + $(La,Ce)_5Si_4$ + $(La,Ce)_5Si_3$
44.4	(La,Ce)Si + $(La,Ce)_5Si_4$
50.1	(La,Ce)Si
55	[(La,Ce)Si] + eutectic ((La,Ce)Si + $(La,Ce)Si_{2-\alpha1}$)
60.6	$(La,Ce)Si_{2-\alpha1}$ + eutectic ((La,Ce)Si + $(La,Ce)Si_{2-\alpha1}$)
62.5	$(La,Ce)Si_{2-\alpha1}$ + [eutectic ((La,Ce)Si + $(La,Ce)Si_{2-\alpha1}$]
64	$(La,Ce)Si_{2-\alpha2}$
66	$(La,Ce)Si_{2-\alpha2}$
68	$(La,Ce)Si_{2-\alpha2}$ + eutectic (($(La,Ce)Si_{2-\alpha2}$ + {Si})
70	$(La,Ce)Si_{2-\alpha2}$ + eutectic (($(La,Ce)Si_{2-\alpha2}$ + {Si})
80	$(La,Ce)Si_{2-\alpha2}$ + eutectic (($(La,Ce)Si_{2-\alpha2}$ + {Si})
90	{Si} + eutectic (($(La,Ce)Si_{2-\alpha2}$ + {Si})

Table 2.7. Effects of excessive amounts of aluminum and ferrosilicon addition in the charge [25]

Reductant	*Al in charge; percent of the stoichiometric amount*	*Fe-Si in charge; percent of the stoichiometric amount*	*Rare earth recovery (%)*
Al & Fe-Si	0	100	40
Al & Fe-Si	0	110	38
Al & Fe-Si	0	120	44
Al & Fe-Si	130	100	36
Al & Fe-Si	260	100	44
Al & Fe-Si	525	100	61

2.3.3.2.4.4 The Effect of Flux Additions

Flux addition provides important effects on recovery of the rare earth metals and percentage of the rare earth metals in the produced alloy. The slag should have some properties such as low viscosity, low melting point and high basicity in order to achieve thermochemical advantages with the addition of flux.

Mitchell et al. [23] indicated that activity of Al_2O_3 should be suppressed to prevent its reaction with the rare earth oxides and thus the rare earth metal loss in the slag phase. It is also found by Mitchell et al. that chemical activity of Al_2O_3 can be diminished gradually by a basic flux without decreasing the activity of rare earth metals and other alloying metals. It is an important fact for the success of Mitchell's method that the activity of Al_2O_3 with the metal oxides present be suppressed so that the reduction reaction of the rare earth oxides with Al and FeSi goes to completion.

The study shows that an excess of CaO as the flux material is important to achieve a basic slag in order to decrease the Al_2O_3 activity since Al_2O_3 acts as an acid. In that manner it can be said that regulating the CaO content means adjusting the basicity of the system. According to tests that Mitchell et al. has done the Al_2O_3 content in the liquid flux mixture should be between about 10 and 42 percent with a preferred percentage of about 20% [23].

Entrapment of rare earth metals in the slag phase is appreciable if the viscosity of the slag is high especially while working with large scales of charge. Marchant et al. studied in this case extensively and conducted experiments with different flux compositions to produce a more fluid slag and prevent the loss of values due to entrapment in the slag phase. They found that the amount of RE_2O_3 dissolved in the slag decreased with increasing CaO content and achieved the minimum loss with the flux consisting of 94 % CaO and 6 % MgO [23,25].

2.3.3.2.4.5. The Effect of Temperature and Holding Time

Holding time and temperature are important factors that have a significant influence on thermochemical properties of reaction and melting practice. There are some researchers who conducted experimental studies with these parameters.

In the study of Mitchell et al. [23], results show that temperature has an appreciable effect on the equilibrium of Reaction 3 which is given below;

$$RE_2O_3 + 2Al = 2RE + Al_2O_3 \quad (3)$$

A variation in temperature between 1127 °C and 1727 °C ends up with a decrease in the recovery of rare earth metals when getting close to the higher temperature. Thus, it is very advantageous from the recovery point of view to carry out the reduction process at the possible lowest temperature [23]. Morrice et al. [21] indicated that reaction temperature should be neither below 1450 °C nor above 1700 °C. A viscous slag is formed under 1400 °C and it makes alloy-slag separation and pouring difficult. Also above 1700 °C fuming occurs and furnace materials show poor performance [21]. Mehra et al. conducted experimental studies at 1500 °C and 1550 °C in another research. In this research it was found that increasing the temperature from 1500 °C to 1550 °C has not an appreciable effect on the recovery of rare earth metals, but from the aluminum loss point of view the lower temperatures are preferred since aluminum losses tend to increase at higher temperatures [22]. On the other hand Marchant et al. carried out their experiments at 1450 °C, 1500 °C and 1550 °C and found that the differences in the recovery values were very small. Beside this, the slag formed at 1450 °C was very viscous so that the entrapment of metal in the slag phase was relatively high [25].

To understand the effect of holding time Marchant et al. conducted several experiments with different holding times which were 10, 20 and 30 minutes. The results of these experiments showed that differences in rare earth recoveries and in rare earth contents of the alloy products were not appreciable [25].

2.3.3.2.5. Examples of Production Methods from Different Studies

The study of Mitchell et al. [23] was based on two important facts to gain higher metal recoveries; using a highly basic flux to lower the activity of Al_2O_3 in the flux and maintaining this flux at the possible lowest temperature at which the flux is in liquid state.

The process invented by Mitchell et al. [23] was performed in an induction furnace and it consisted of melting down a flux mixture of 90% CaF_2 and 10% CaO in a graphite crucible, adding to this mixture rare earth oxide and CaO in 1:1 ratio at a temperature of about 1371 ˚C and as a final step adding to this mixture aluminum and silicon in excessive amounts of the theoretically required for the reduction.

In a test carried out by Mitchell et al. [23] 8.2 kg CaF_2 and 0.9 kg CaO were melted as the first step of the process. In the second step 5 kg rare earth oxide and 5 kg CaO were charged into the melt and finally 1.8 kg Si and 2 kg Al were added as the reducing agents. Results of this test are given in Table 2.8.

Table 2.8. Results of a test from the study of Mitchell et al. [23]

Composition of the alloy product (wt. %)				***Rare earth metal recovery (%)***
RE's	Si	Fe	Al	
54.14	23.83	1.98	15.20	85.0

Morrice et al. [21] indicated that the reactor for their process might be any suitable one capable of generating and maintaining the reaction temperature, but utilizing an induction furnace was advantageous. Also, they found that any crucibles made of silicon carbide, boron nitride or graphite could be used as containers for the reactants while emphasizing that using graphite crucible could cause the formation of some calcium carbide.

It can be deduced from the study of Morrice et al. [21] that utilizing the rare earth source and calcium oxide in the form of powder, aluminum in the form of cuttings or turnings and ferrosilicon in the form of fragments is advantageous.

The process invented by Morrice et al. [21] consists of melting the charge materials in the reaction crucible, holding at a desired temperature for the time period required for completion of the reaction and pouring or tapping the melt into molds. Also separation of the products can be accomplished by allowing the melt to freeze and breaking the slag away from the alloy product.

In a test carried out by Morrice et al. [21] rare earth oxide ore, having 82.5% by weight of RE_2O_3, in an amount of 227 grams, ferrosilicon having 25% by weight iron, in an amount of 132 grams, aluminum metal in an amount of 68.5 grams, calcium oxide in an amount of 263 grams and magnesium oxide in an amount of 24 grams were placed into a silicon carbide crucible and melted at 1600 ˚C in an induction furnace. After a time period of 30 minutes, the melt was poured into a conical mold and allowed to freeze. Separation of the slag phase was done by breaking it away from the alloy product. The results of this test are given in Table 2.9.

Table 2.9. Results of a test from the study of Morrice et al. [21]

Composition of the alloy product (wt. %)				***Rare earth metal recovery (%)***
RE's	Si	Fe	Al	
46.0	46.0	8.9	3.2	91.5

Marchant et al. [25] conducted their tests in an induction furnace with graphite or densified silicon carbide crucibles. Rare earth oxides prepared from bastnasite flotation concentrates, aluminum turnings and fragments of ferrosilicon and some flux materials such as CaO and magnesia were utilized in their process as charge materials.

The charge composition of a test carried out by Marchant et al. [25] consisted of 681 grams mixed rare earth oxides, 309 grams ferrosilicon (78% Si), 182 grams aluminum, 681 grams CaO and 45 grams magnesia where CaO and MgO served as the flux and added on top of the other charge materials. The charge materials were melted and held at 1500 ˚C for 30 minutes and then the melt was poured into an iron mold. Separation of alloy product and slag was done by allowing the melt to freeze and breaking the slag away from the alloy product. The results of this mentioned test are given in Table 2.10.

Table 2.10. Results of a test from the study of Marchant et al. [25]

Composition of the alloy product (wt. %)				***Rare earth metal recovery (%)***
RE's	Si	Fe	Al	
52.6	27.6	10.7	3.8	80.0

The rare earth oxide mixture containing 95% REO as the rare earth source, commercially available 80% grade FeSi and aluminum rod scrap (>99%) as reducing agents were used in the study of Mehra et al. [24].

Two different flux mixtures; first one containing 100% CaO and 6.5% MgO and the second one containing 120% CaO and 165% CaF_2 were utilized by Mehra et al. [24] to increase the rare earth recovery (values are given by weight of REO). The optimum values of temperature and holding time were found as 1500 ˚C-1550 ˚C and 30 minutes, respectively.

In a test in the presence of CaO-MgO flux the charge containing 3.4 kg REO, 25 mm pieces of FeSi in an amount of 1.8 kg and 0.91 kg Al was loaded in a 250 mm diameter graphite crucible and covered with 3.4 kg CaO and 0.225 kg MgO. The charge was melted at 1550 ˚C and allowed to react for 30 minutes in an induction furnace. After completion of reaction the crucible was tilted and the product alloy was poured into an iron mold [24].

In another test taken from this study in the presence of CaO-CaF_2, 4.55 kg CaF_2 was melted first in a graphite crucible by utilizing an induction furnace. After this step 2.75 kg REO and 3.3 kg CaO were added into melt to form a molten bath of REO-CaO-CaF_2. As the final step 2.8 kg FeSi and 0.7 kg aluminum in lump form were added to the bath at 1500 ˚C and allowed to react for 30 minutes. The alloy product was cast into an iron mold to separate it from the slag phase [24]. The results of these two tests are given in the Table 2.11.

Table 2.11. Results of the tests from the study of Mehra et al. [24]

In the presence of CaO-MgO flux					In the presence of CaO-CaF_2 flux				
Composition of the alloy product (wt.%)				***RE metal recovery (%)***	***Composition of the alloy product (wt.%)***				***RE metal recovery (%)***
RE's	Si	Fe	Al		RE's	Si	Fe	Al	
55.12	33.0	5.0	4.0	75.8	40.0	40.4	10.0	5.1	82.8

Turgay [4] conducted his tests in an induction furnace using graphite crucibles. Three kinds of rare earth source were utilized in his study; one of them was a bastnasite type preconcentrate with 23.5% REO grade, the other two sources were rich rare earth oxide concentrates with 81.6% and 94.9% REO grades. The experiments done with the preconcentrate gave very low rare earth recoveries. Aluminum particles (99.9%) and ferrosilicon alloy (88% Si) as reducing agents, lime which was obtained by calcinations of $Ca(OH)_2$ or $CaCO_3$, quartz of 99% purity and fluorspar as the fluxing agents were the other charge materials of the tests carried out by Turgay.

Turgay [4] indicated that using excessive amounts of reducing agents was a must for obtaining a high rare earth recovery and that reaction temperature should be kept as low as possible at which a molten and fluid slag could be obtained.

In a test carried out by Turgay [4], 44 grams of rich rare earth oxide concentrate (81.6% REO), 750% of the stoichiometric amount of aluminum, 112% of the stoichiometric amount of ferrosilicon and 43.1 grams of lime were utilized as the charge materials. As the first step of the test the rare earth concentrate was melted in a graphite crucible at 1550 °C, then other charge materials were added together into the crucible and the charge was allowed to react for 30 minutes. After the holding time, crucible was taken out of the furnace and left to cool down. Separation of the metal and slag phases was done by breaking them by a hammer. The results of this test are given in Table 2.12.

Table 2.12. Results of the test from the study of Turgay [4]

Composition of the alloy product (wt. %)				***Rare earth metal recovery (%)***
RE’s	Si	Fe	Al	
50.1	28.1	7.7	7.4	81.1

CHAPTER 3

EXPERIMENTAL METHOD AND PROCEDURE

3.1. General

Optimization of the conditions of production of rare earth ferrosilicon alloy was the main aim of this study. For this purpose, a preconcentrate was prepared from an ore of bastnasite type which was taken from the Beylikahır-Eskişehir region of Turkey. The following part of this chapter will be about the choice of the production method, devices and materials which were utilized in the experiments.

3.2. Production Method

As it was mentioned in the literature survey part there are two reduction methods to produce a rare earth ferrosilicon alloy; carbothermic reduction and metallothermic reduction. Also it can be deduced that metallothermic reduction yields a better recovery and a better composition of the alloy product. Submerged arc furnace for the carbothermic reduction process was not available in the department although there were an induction furnace and a muffle furnace which could be utilized for the metallothermic reduction process. Also an electric arc furnace necessitated a high amount of rare earth metal source. Since the amount of the rare earth metal source was not enough to feed that kind of large furnace, metallothermic reduction process was selected for this study.

3.3. Reduction Furnace

After selection of the reduction method, the furnaces which could be utilized for the metallothermic reduction came under consideration. There were two kinds of furnace that could be selected; a programmable muffle furnace and an induction furnace. Programmable muffle furnace gave an opportunity that controlling of the temperature with it was easier than that with the induction furnace. But utilizing the muffle furnace made the additions to charge impossible at high temperatures. Especially, aluminum loss due to oxidation before reduction was very important. Because of the high heating rate and the opportunity for making the additions at high temperatures, it was thought that utilizing an induction furnace would be more advantageous.

3.4. Crucible

As it was mentioned in the literature survey part, materials which were not attacked by the slag formed during the process such as graphite or silicon carbide could be used to make crucibles.

Graphite crucibles could be machined easily and cheaply. So, it was decided to utilize graphite crucibles although formation of some calcium carbide was expected to take place by the reaction between the melt and graphite. It may be said that this choice was only dictated by the availability of the crucible materials. A schematic drawing of the crucible used is given in Figure 3.1.

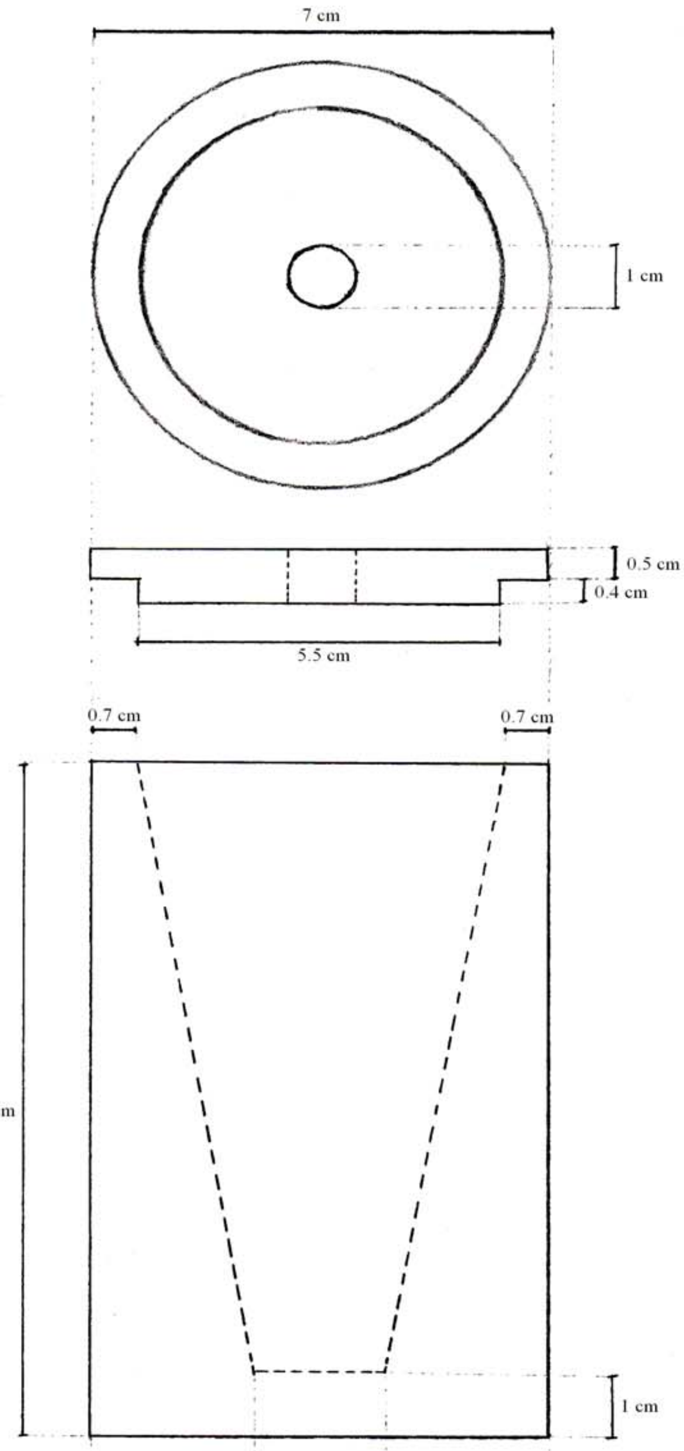


Figure 3.1. Technical drawing of the graphite crucible and its lid

3.5. Charge Materials

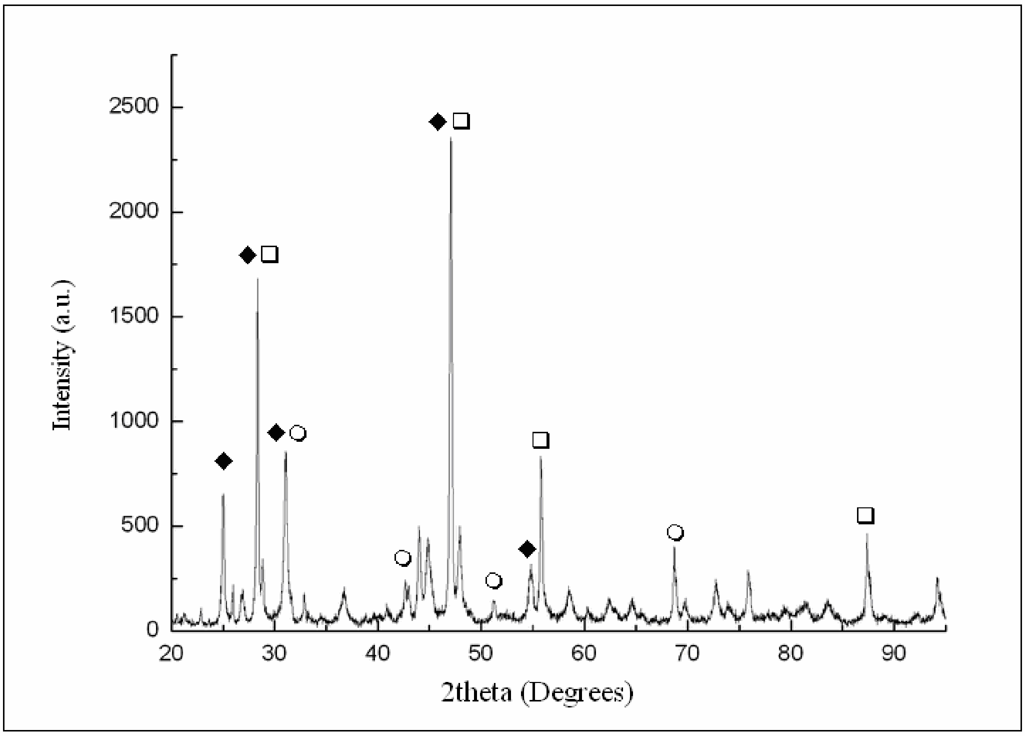
3.5.1. Rare Earth Metal Source

A bastnasite preconcentrate which was obtained by concentration of a sample taken from a rare earth ore body located in Beylikahır-Eskişehir region of Turkey was used in all the experiment as the rare earth metal source.

Concentration of this ore was done by attrition scrubbing followed by screening and desliming. For this purpose the ore sample was first ground to -10 Tyler mesh (-1.7 mm) and was subjected to attrition scrubbing with a 50% solid concentration for one hour. After screening from 400 mesh and dilution of -400 mesh (-38 microns), classification of the pulp by a series of hydrocyclones was done. A fine bastnasite preconcentrate with a 23.13 % REO grade was obtained as hydrocyclone overflow at the end of such concentration process. The composition of the obtained preconcentrate and its XRD analysis are given in Table 3.1. and Figure 3.2., respectively. Calculation of the composition of this preconcentrate from SEM analysis is given in Appendix A part.

Table 3.1. Composition of the preconcentrate

Compound	***Weight Conc. (%)***
La_2O_3	9.11
Ce_2O_3	14.02
CaF_2	35.44
$CaCO_3$	7.24
SiO_2	6.78
Fe_2O_3	7.97
$BaSO_4$	6.12
Al_2O_3	2.38
P_2O_5	2.16
MgO	0.95



◆: Bastnasite ❐: CaF_2 ❍: $BaSO_4$

Figure 3.2. XRD pattern of bastnasite preconcentrate

3.5.2. Reducing Agents

3.5.2.1. Choice of Reducing Agents

There were two possible candidates as the reducing agents for the metallothermic reduction process; calcium silicide and aluminum together with ferrosilicon. As it was mentioned in the literature survey part, both of these candidates were successfully used to obtain a high rare earth recovery in the previous studies. Since the aim of this study was to produce a rare earth ferrosilicon alloy, aluminum with ferrosilicon usage was found to be more advantageous. The high cost of calcium silicide was also an important reason for choosing aluminum with ferrosilicon as the reducing agent. So, in all the experiments of this study, aluminum together with ferrosilicon was utilized as the reducing agent.

3.5.2.2. Aluminum

Aluminum rod pieces about 0.5-1 cm. in length and 3 mm. in diameter with 99.9 % purity were used in all the experiments as aluminum source. The reason for using aluminum pieces rather than aluminum powder was its tendency for oxidation before reduction reaction.

3.5.2.3. Ferrosilicon

Ferrosilicon in the range of -18 +200 mesh size (-850 +75 microns) containing 73.23 % Si was used in all the experiments. Source of iron in the rare earth ferrosilicon alloys produced was ferrosilicon in all of the experiments.

3.5.3. Lime

Commercially available CaO in powder form with a 99.9% grade was the only fluxing agent utilized in all of the experiments.

3.6. Experiments

50 grams of rare earth preconcentrate was utilized for each experiment of this study and the calculation of the other charge materials which are CaO, Al and FeSi was done by taking this amount as the base.

At the beginning of all the experiments, 50 grams of preconcentrate was mixed under acetone in an agate mortar with the predetermined amount of CaO. Three spherical agglomerates were made from this mixture to prevent dusting problem that might be encountered during the melting process. The graphite crucible which was closed by a graphite lid was then placed into an induction furnace which had a power output of 41 kW and a melting capacity of 4 kg aluminum and heating process was started. At the center of the lid, there was a hole of about 1 cm in diameter for temperature measurement which was done by an optical pyrometer about every 1 minute.

After the predetermined reaction temperature was reached, the lid of the crucible was opened and agglomerates were charged into the crucible. Aluminum and ferrosilicon were added to crucible by a small shovel when agglomerates were melted completely and this was taken as the start of experiment. Holding the crucible at the reaction temperature for a predetermined time to complete the reaction was followed by taking it out and leaving at room temperature to cool down. The day after, crucible was broken down with a hammer for taking the produced metal and slag phases out. Then, the products were separated from each other by carefully breaking them with a hammer.

Metal and slag phases were weighed before preparing samples from them for EDS analyses at the scanning electron microscope (SEM). Rare earth recoveries of the experiments were calculated according to Equation 1 given below;

$$\frac{(\text{Metal wt.}).(\text{wt\%RE-metals})_{\text{in metal phase}}}{(\text{Metal wt.}).(\text{wt\%RE-metals})_{\text{in metal phase}} + (\text{Slag wt.}).(\text{wt\%RE-metals})_{\text{in slag phase}}} \text{ X } 100 \qquad (1)$$

Since both of the phases were not always homogeneous, samples taken for quantitative analysis might not always represent the whole composition of the products. So, while evaluating the results of this study it must be taken into account that there may be small deviations from the exact values. Flow chart of the experiments is given in Figure 3.3.

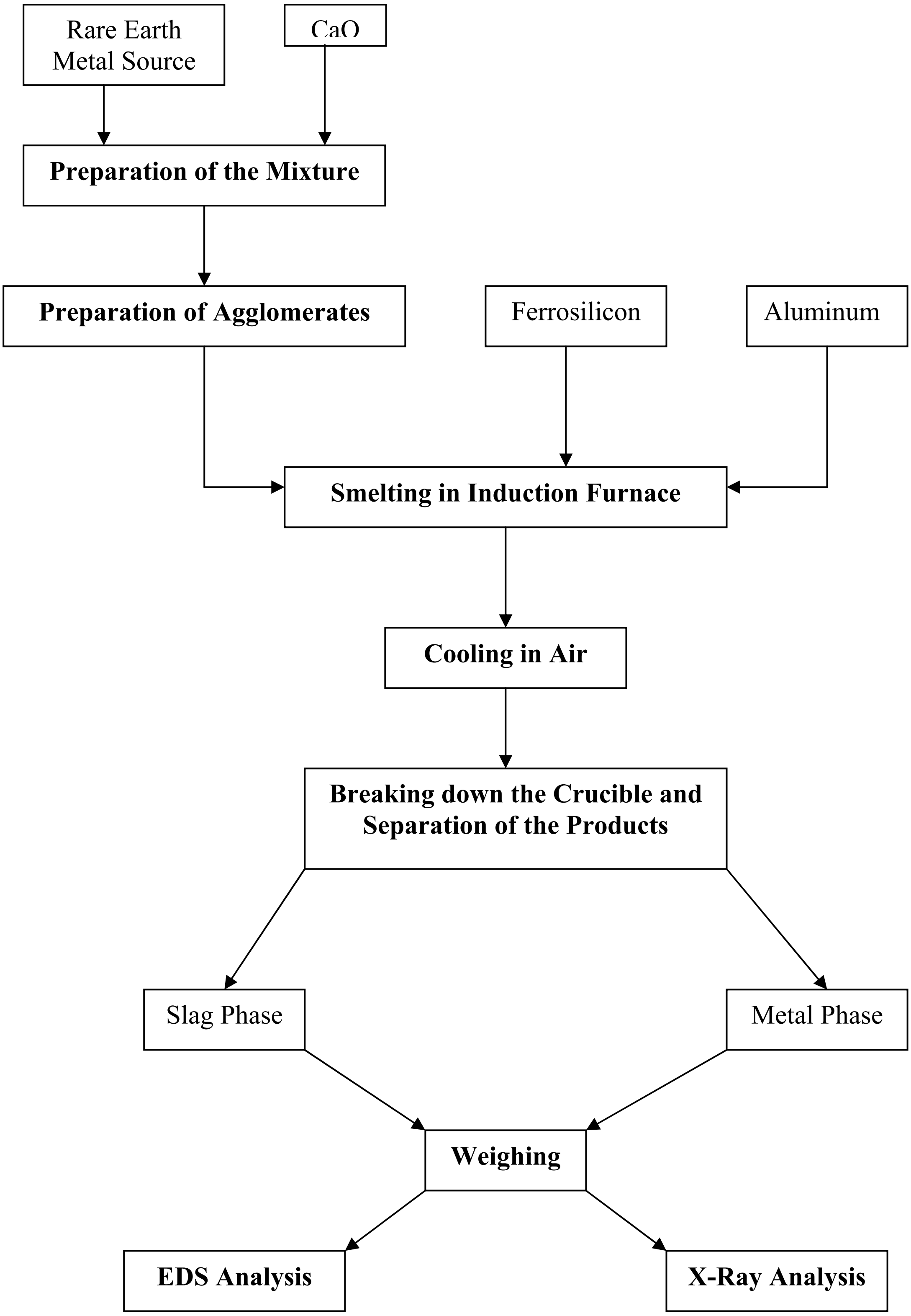


Figure 3.3. Flowchart of the experiments

3.7. Experimental Variables

The optimization of conditions of production of rare earth ferrosilicon alloy was studied using the variables given as ranges in Table 3.2.

Table 3.2. Experimental variables

Variables	***Range***
Basicity* of the slag phase	1.3 - 1.65 - 2
Holding time (min.)	15 - 30 - 45
Temperature (°C)	1450 - 1500 - 1550
Aluminum amount in excess of the stoichiometric amount (wt.%)	500 - 550 - 600 - 750
Ferrosilicon amount in excess of the stoichiometric amount (wt.%)	100 - 112 - 150

$$\text{* Basicity} = \frac{\text{CaO(wt.\%)} + \text{BaO(wt.\%)}}{\text{SiO}_2\text{(wt.\%)} + \text{Al}_2\text{O}_3\text{(wt.\%)}}$$

Experiments were done using the combinations of the parameters given above. The optimum reduction conditions were tried to be found.

CHAPTER 4

RESULTS AND DISCUSSION

4.1. General

In this chapter, results of the tests carried out with the chosen equipment and materials using the procedure which was mentioned in the previous chapter are given and discussed in order to understand the effects of the experimental variables on the production of rare earth ferrosilicon alloy by reduction with aluminum together with ferrosilicon.

4.2. Effects of the Experimental Variables

4.2.1. Effect of the Basicity of the Slag Phase

To understand the effect of the basicity of the slag phase on the rare earth recovery, three tests were made. Basicity of the slag phase was adjusted by changing the amount of CaO charged.

Basicity ratios of 1.3, 1.65 and 2 were obtained by utilizing 13.04 g, 17.84 g and 22.65 g of CaO, respectively, with 50 g of rare earth preconcentrate, 3.72 g of aluminum (600% of the stoichiometric amount) and 7.57 g of ferrosilicon (112% of the stoichiometric amount). Aluminum and ferrosilicon additions were made at 1500°C and the charge was allowed to react for 30 minutes for each of the experiments. Results of the experiments are given in Table 4.1. and Figure 4.1.

Table 4.1. The effect of the basicity of the slag phase on alloy composition and rare earth recovery

Basicity of the slag phase	***Composition of the alloy product (wt. %)***				***RE-metal recovery (%)***
	RE's	***Si***	***Fe***	***Al***	
1.3	36.2	36.3	22.2	5.3	56.0
1.65	39.1	33.6	24.4	2.9	53.5
2.0	41.7	32.0	23.9	2.3	40.0
2.0*	43.2	31.0	23.5	2.3	39.4

* This experiment was repeated in order to see whether it was reproducible or not

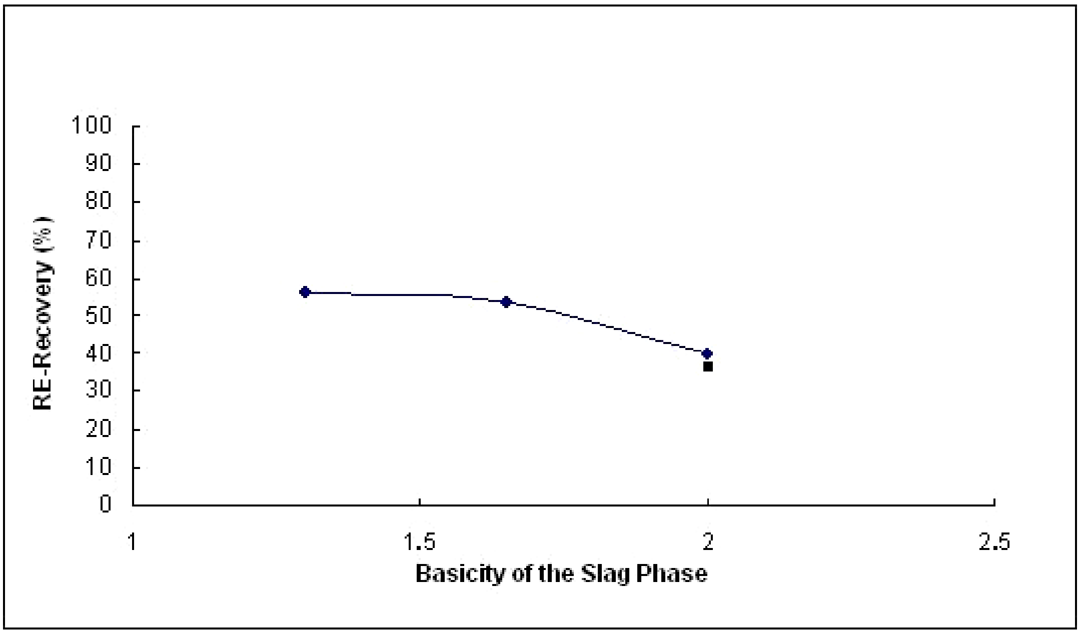
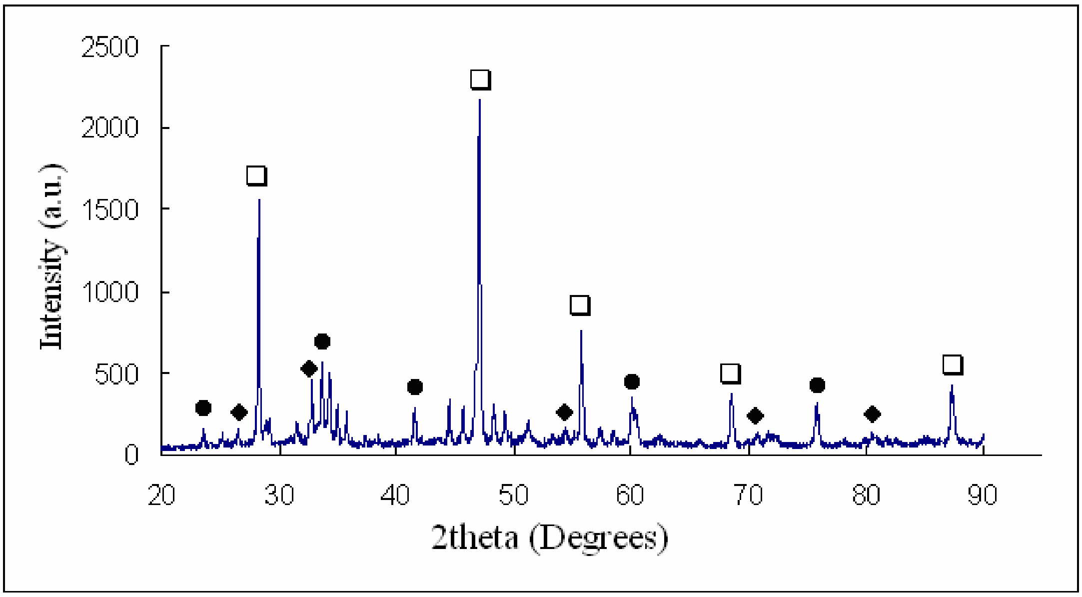


Figure 4.1. RE-metal recovery vs. Basicity of the slag phase

Recovery of the rare earth metal values slightly decreased from 56.0 % to 53.5% as the basicity of the slag phase increased from 1.3 to 1.65. Further increase of the basicity to 2 resulted in a high decrease of recovery to 40.0 %.

As mentioned in the literature survey part, a basic flux is necessary for suppressing the activity of Al_2O_3, so that the reduction reaction of the rare earth oxides with Al and FeSi goes to completion [23]. Also it was stated by Morrice et al. [21] that utilizing of the graphite crucible could cause the formation of some calcium carbide. XRD pattern which shows the formation of calcium carbide in slag phase is given in Figure 4.2. In the same figure, $CeAlO_3$ phase was also detected which may have formed due to Reaction 4 which is given below. The formation of $CeAlO_3$ resulted in low recovery of rare earths.

$$\frac{1}{2} Ce_2O_3 + \frac{1}{2} Al_2O_3 = CeAlO_3 \qquad (4)$$



◆: CaC_2 ❐: CaF_2 ●: $CeAlO_3$

Figure 4.2. XRD pattern of the slag phase with the basicity ratio of two

When the slag phase obtained from the experiment carried out with a slag basicity ratio of 1.3 was investigated under SEM, it was seen that the bright areas of SEM micrograph included high amounts of rare earths which meant that a part of the rare earth metals might be entrapped in the slag as can be seen in Figure 4.3. It could be said that slag phases with the basicity ratios of 1.65 and 2 were more viscous which could cause more entrapment problem than the slag with the basicity ratio of

1.3, since the basicity ratios of the slag phases were adjusted by CaO addition only.

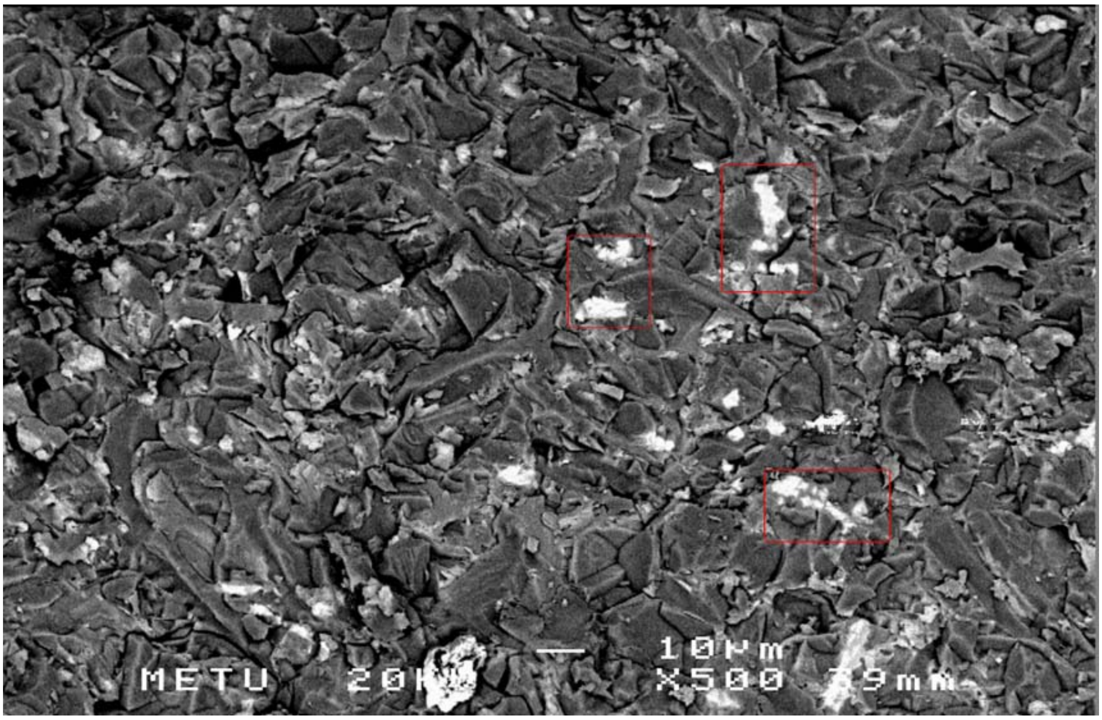


Figure 4.3. SEM micrograph of an experiment realized with a basicity ratio of 1.3.

In this manner, it can be concluded that as long as a basic and fluid slag was obtained, basicity of the slag should be kept at a value that prevents the formation of calcium carbide as much as possible.

4.2.2. Effect of Temperature

In order to understand the effect of temperature, at which the reduction reaction is carried out, on the recovery of rare earth metals as alloy product three tests were made at 1450°C, 1500°C and 1550°C.

50 grams of rare earth preconcentrate was reacted with 600 % of the stoichiometric amount of aluminum and 112 % of the stoichiometric amount of ferrosilicon required for reduction reaction in all of the experiments. 22.6 grams of CaO was used as the only fluxing agent which resulted in a slag basicity ratio of 2 in

all the runs. The charge mixture was allowed to react in furnace for 30 minutes. The results of these three tests are given in Table 4.2. and Figure 4.4.

Table 4.2. The effect of temperature on alloy composition and rare earth recovery

Temperature (°C)	*Composition of the alloy product (wt. %)*				*RE-metal recovery (%)*
	RE's	*Si*	*Fe*	*Al*	
1450	48.1	31.9	18.2	1.8	56.0
1500	41.7	32.0	23.9	2.3	40.0
1550	24.1	37.9	33.6	4.4	21.8

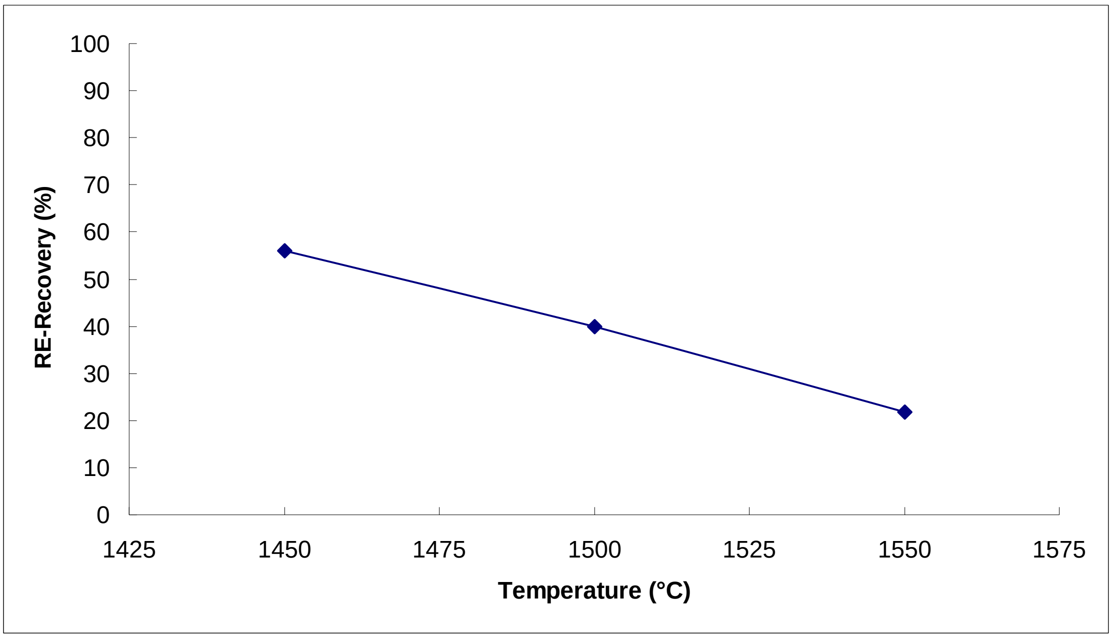


Figure 4.4. RE-metal recovery vs. Reaction temperature

While temperature increased from 1450 °C to 1550 °C, recovery of the rare earth metals as alloy product decreased continuously from 56.0 % to 21.8 %. These results showed that the temperature at which the reduction reaction was carried out was highly effective on the recovery of rare earth metals and the composition of alloy product as mentioned by the previous workers [21, 23].

Although it is expected that higher temperatures should give better recoveries since the viscosity of slag phase decreases with increasing temperature, the results are not in accordance with this expectation. This fact can be explained by the statement of Mehra et al. [22] which says that even a small decrease in reduction temperature reduces the aluminum losses. Rate of the oxidation of aluminum before reduction reaction increases while working at higher temperatures and results in a higher loss of the reducing agent and therefore a lower recovery of rare earths.

Mitchell et al. [23] indicated that temperature had a large influence on the equilibrium of Reaction 2 and carrying out the reduction at the lowest possible temperature had an advantage on recovery of the rare earth metals from the oxides.

Morrice et al. [21] mentioned in their study that temperatures below 1400 °C were not suitable for the reduction process because of the increasing slag viscosity. Having CaF_2 in the rare earth preconcentrate was an advantage for this study because existence of CaF_2 made it possible to decrease the temperature to 1450 °C while not vitally increasing the slag viscosity.

It can be said that, to obtain a higher rare earth recovery and better composition of alloy product, temperatures as low as possible which ensure a fluid and low viscosity slag should be utilized for the reduction process.

4.2.3. Effect of Aluminum Amount in the Charge

Since aluminum was the main reducing agent utilized throughout this study, its amount was a very important parameter for optimizing the conditions of rare earth ferrosilicon alloy production.

To understand the effect of aluminum amount in the charge, four tests were made with 500%, 550%, 600% and 750% of the stoichiometric amount of aluminum.

In all of the experiments, 50 grams of rare earth preconcentrate and 112 % of the stoichiometric amount of ferrosilicon were used with CaO as the fluxing agent, the amount of which was adjusted to set the basicity ratio to 1.3. Aluminum together with ferrosilicon were added to reaction mixture at 1500 °C and allowed to react for 30 minutes. Results of these four tests are given in Table 4.3. and Figure 4.5.

Recovery of the rare earth metal values increased from 23.3 % to 56.0 % with increasing amount of aluminum addition from 500 % to 600 % of the stoichiometric amount. Further increment in the amount of aluminum addition to 750 % of the stoichiometric amount resulted in a decrease of the rare earth metal recovery to 35.6%.

Table 4.3. The effect of aluminum addition on alloy composition and rare earth recovery

% Aluminum addition of the stoichiometric amount	***Composition of the alloy product (wt. %)***				***RE-metal recovery (%)***
	RE's	***Si***	***Fe***	***Al***	
500	23.9	37.6	36.5	2.0	23.3
550	30.3	33.7	33.2	2.8	32.3
600	36.2	36.3	22.2	5.3	56.0
750	32.1	35.7	26.5	5.7	35.6

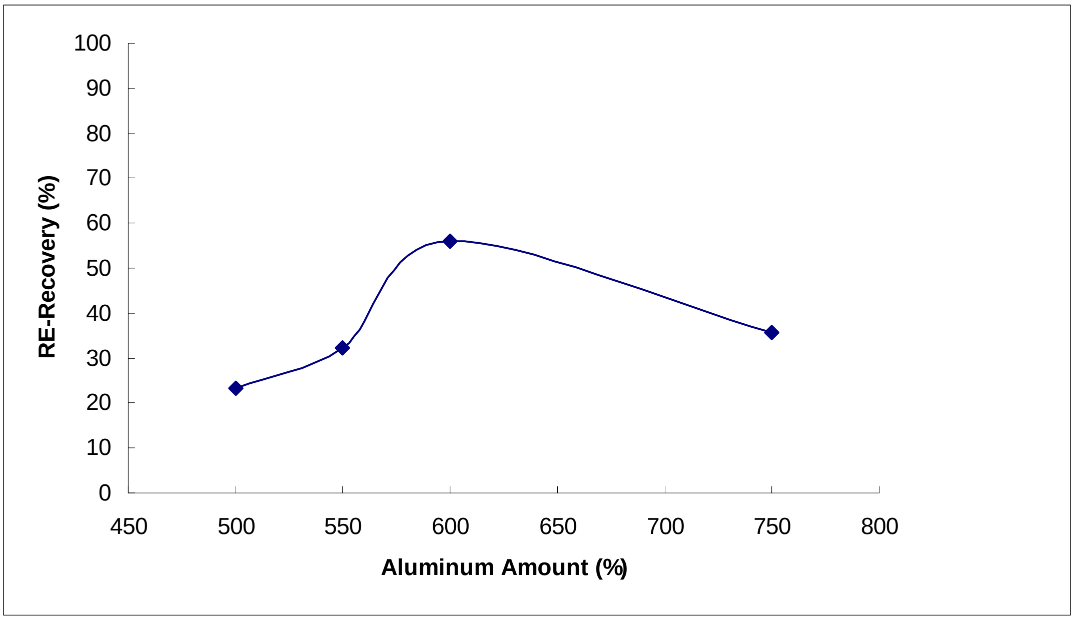


Figure 4.5. RE-Metal recovery vs. % Aluminum addition of the stoichiometric amount

At high temperatures, a significant amount of aluminum is oxidized before the reduction reaction. As it was mentioned by the previous workers [21, 23], the amount of aluminum to be charged should be in excess of the stoichiometric amount to compensate for the aluminum losses due to oxidation.

From the aforementioned aluminum oxidation point of view, it may be thought that rare earth metal recovery increases with increasing aluminum amount in the charge. But it is not an exact statement since an increment of aluminum addition amount results in a higher percentage of Al_2O_3 in the slag phase that leads to a higher activity of Al_2O_3. So, the driving force for Reaction 2 decreases with increasing activity of Al_2O_3. This fact may be shown by Equation 2.

$$3\ RE_2O_3 + 15\ Si + 2\ Al = 6\ RESi_2 + 3\ SiO_2 + Al_2O_3 \qquad (2)$$

$$\Delta G_2 = \Delta G^o_2 + RT\ \ln \frac{(a_{RESi_2})^6 \cdot (a_{SiO_2})^3 \cdot (a_{Al_2O_3})}{(a_{RE_2O_3})^3 \cdot (a_{Si})^{15} \cdot (a_{Al})^2} \qquad (2)$$

When the compositions of the alloy products were compared, it was observed that the percentage of aluminum in alloy product increased with increasing amount of aluminum charged. It can be deduced from the results that some of the aluminum added enters into the alloy product and amount of it increases when more aluminum is charged. As stated by Marchant et al. [25], some aluminum in the alloy product could be desirable since it makes the alloy more intact to prevent dusting problems while using as ladle additives. On the other hand, in the present study this beneficial effect of aluminum could not be observed because of the high iron content of the alloy, which served the same purpose.

In the study of Marchant et al. [25], the recovery of rare earth metal values increased sharply when the amount of aluminum charged increased from 260 % to 525 % of the stoichiometric amount required (Table 2.7). On the other hand, Mitchell et al. [23] indicated in their study that the alloying reactions became less efficient as the Al_2O_3 content (activity) increased and would stop at some point. Also, in the study of Morrice et al. [21], 700 % of the stoichiometric amount of aluminum was given as an upper limit to obtain a better recovery of rare earth metals. In the study of Turgay [4], 600 % of the stoichiometric amount of aluminum was found to be the optimum value to obtain the best recovery and alloy composition, since the recovery began to decrease over this amount of aluminum and the aluminum amount in the alloy product showed a considerable increase as the amount of aluminum addition reached to 700 % of the stoichiometric amount. The results of the present study are in accordance with the aforementioned ones.

It can be concluded from the above discussion that the aluminum addition should be in excess of the stoichiometric amount to compensate for the aluminum losses due to oxidation while keeping the Al_2O_3 activity as low as possible in slag phase. Six times of the stoichiometric amount of aluminum seems to be the best choice from the recovery and alloy composition points of view.

4.2.4. Effect of Ferrosilicon Amount in the Charge

Amount of ferrosilicon is a very important parameter for the production of rare earth ferrosilicon alloy since it is the source of both iron and silicon in the alloy product and the silicon content of it serves as reducing agent together with aluminum.

To understand the effect of ferrosilicon amount on the rare earth recovery and alloy composition three tests were made with 100 %, 112 % and 150 % of the stoichiometric amount of ferrosilicon. 50 grams of rare earth preconcentrate, 600 % of the stoichiometric amount of aluminum and CaO amount of which was adjusted to set the basicity ratio of slag phase to 1.3 were used with the predetermined amounts of ferrosilicon. Ferrosilicon was added at 1500 °C together with aluminum and duration was set to 30 minutes in each of the tests. Results of the tests are given in Table 4.4. and Figure 4.6.

Rare earth metal recovery increased from 33.5 % to 56.0 % while the amount of ferrosilicon addition increased from 100 % to 112 % of the stoichiometric amount. Further increment in the amount of ferrosilicon addition to 150 % of the stoichiometric amount resulted in a decrease of the rare earth metal recovery to 39.7 %.

Table 4.4. The effect of ferrosilicon addition on alloy composition and rare earth recovery

% Ferrosilicon addition of the stoichiometric amount	*Composition of the alloy product (wt. %)*				*RE-metal recovery (%)*
	RE's	*Si*	*Fe*	*Al*	
100	30.7	35.8	30.5	3.0	33.5
112	36.2	36.3	22.2	5.3	56.0
150	25.1	40.1	31.4	3.3	39.7

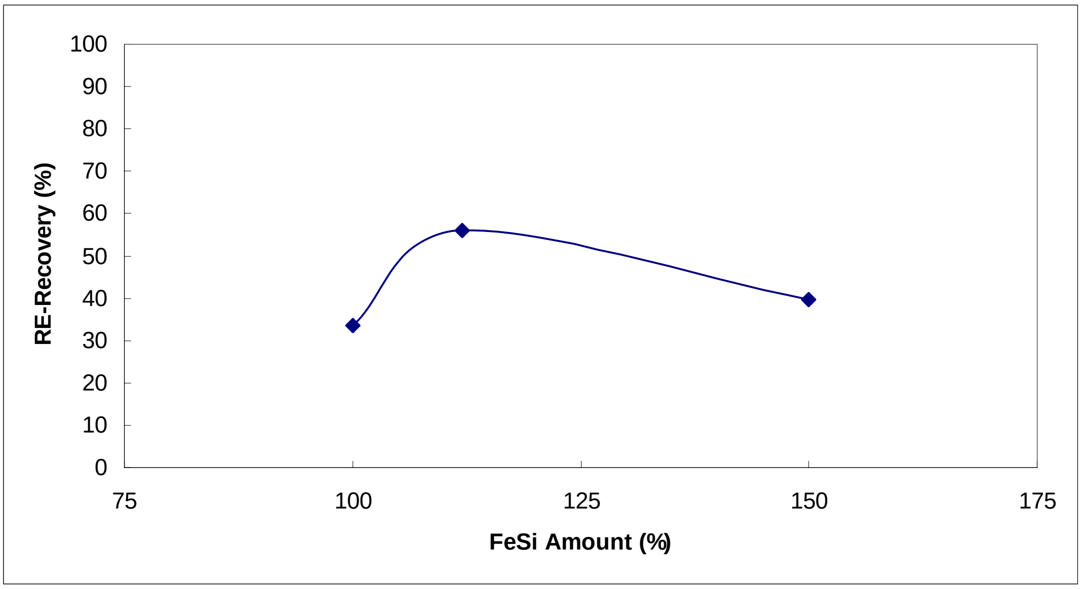


Figure 4.6. RE-Metal recovery vs. % FeSi addition of the stoichiometric amount

As mentioned in the literature survey part, ferrosilicon amount charged should be in excess of the stoichiometric amount required for Reaction 2. This certain necessity for excessive ferrosilicon was shown in Figure 2.6. and Table 2.6. [27]. From the SiO_2 activity point of view, ferrosilicon usage over 112% of the stoichiometric amount resulted in an increase of the SiO_2 activity in slag phase while preventing the completion of Reaction 2 and decreasing the rare earth metal recovery as alloy product.

It can be said that utilizing excess amount of ferrosilicon increases the rare earth recovery up to a point at which increasing SiO_2 activity began to decrease rare earth recovery. The optimum ferrosilicon addition was found as 112% of the stoichiometric amount.

4.2.5. Effect of Duration

Duration, the time period in which the reduction reaction was allowed to occur at the reaction temperature, was one of the parameters affecting the success of rare earth ferrosilicon alloy production.

To understand the effect of duration on rare earth metal recovery and alloy composition, three tests were realized with 15, 30 and 45 minutes of duration. In all of the runs 50 grams of rare earth preconcentrate was utilized as the rare earth metal source. CaO amounts were adjusted to set the basicity ratio of the slag phases to two. 600 % aluminum and 112 % ferrosilicon of the stoichiometric amounts were added into the charge which consisted of the rare earth preconcentrate and CaO at 1500°C. Results of the tests are given in Table 4.5. and Figure 4.7.

Table 4.5. Effect of duration on alloy composition and rare earth recovery

Duration (min.)	***Composition of the alloy product (wt. %)***				***RE-metal recovery (%)***
	RE's	***Si***	***Fe***	***Al***	
15	40.3	35.9	20.1	3.7	47.6
30	41.7	32.0	23.9	2.3	40.0
45	25.0	33.7	38.6	2.7	20.6

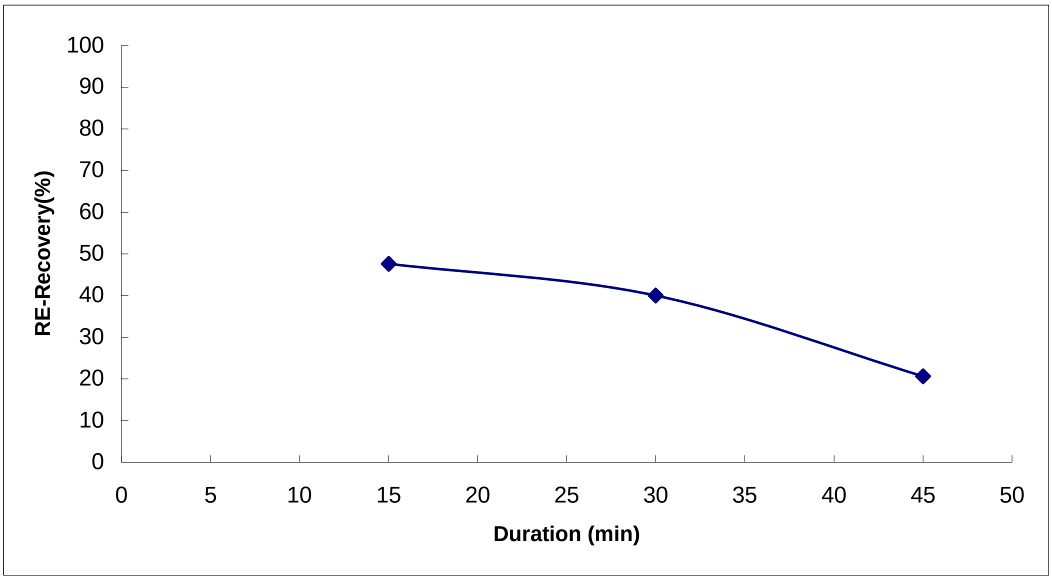


Figure 4.7. RE-Metal recovery vs. Duration

From Figure 4.7., it is seen that rare earth metal recovery was the highest (47.6%) with 15 minutes of duration period. Then, it showed 7.6 % decrease to 40.0% as the interval extended to 30 minutes, and on extending the duration period further to 45 minutes, the recovery dropped sharply to 20.6 %. There was not an appreciable difference between the alloy compositions of the tests with 15 and 30 minutes. Further extension of duration to 45 minutes resulted in a substantial decrease of rare earth grade of alloy.

As mentioned in the experimental method and procedure part, some of the calcium in lime reacted with the graphite crucible and formed calcium carbide. Formation of calcium carbide decreased the basicity of the slag which resulted in higher activity of Al_2O_3 and SiO_2, therefore affected the reaction thermochemistry adversely. The effect of calcium carbide formation became more pronounced at longer time intervals, namely 30 and 45 minutes of duration period. Results of the tests are in accordance with the studies of Morrice et al. [21] and Turgay [4] who also mentioned about the formation of calcium carbide while using graphite crucibles.

Apart from the results of these tests, extending the duration period over 15 minutes results in consumption of more energy and decrease in productivity, which are economically unfavorable. 15 minutes of duration period was found to be the optimum for completion of the reduction reaction while keeping the formation of calcium carbide as low as possible.

4.3. Experiment Performed Under the Optimum Conditions Determined

After realizing several experiments, it was found that utilizing 600 % aluminum of the stoichiometric amount and 112 % ferrosilicon of the stoichiometric amount with a basicity ratio of 1.3 and a holding time of 15 minutes at 1450 °C were advantageous for the production of rare earth ferrosilicon alloy from rare earth preconcentrate.

A final experiment was conducted using the findings in order to obtain the highest rare earth recovery. 50 grams of rare earth preconcentrate was utilized with the optimum values of the parameters which are summarized above. Results of the experiment are given in Table 4.6.

Table 4.6. Results of the experiment performed under the optimum conditions

Composition of the alloy product (wt. %)				***RE-metal recovery (%)***
RE's	***Si***	***Fe***	***Al***	
39.3	37.5	19.3	3.9	57.7

A rare earth ferrosilicon alloy with 39.3 % rare earth metal grade and 57.7 % rare earth metal recovery was obtained at the end of this test.

4.4. Experiment Performed Using the Preconcentrate with Higher REO Grade

After realizing the experiments with the rare earth preconcentrate containing 23.13 % REO, a preconcentrate containing 31.11 % REO was obtained by classifying the preconcentrate by a hydrocyclone once again. The composition of the obtained preconcentrate is given in Table 4.7. Calculation of the composition of this preconcentrate is given in Appendix B part.

An experiment was conducted utilizing 50 grams of rare earth preconcentrate containing 31.11 % REO with the optimum values of the parameters. Results of this experiment are given in Table 4.8.

Table 4.7. Composition of the preconcentrate containing 31.11 % REO

Compound	*Weight Conc. (%)*
La_2O_3	14.76
Ce_2O_3	16.35
CaF_2	25.58
$CaCO_3$	5.25
SiO_2	7.91
Fe_2O_3	9.56
$BaSO_4$	5.11
Al_2O_3	2.35
P_2O_5	1.61
MgO	1.05

Table 4.8. Results of the experiment made with the preconcentrate containing 31.11% REO

Composition of the alloy product (wt. %)				*RE-metal recovery (%)*
RE's	*Si*	*Fe*	*Al*	
40.4	31.2	25.0	3.4	58.1

As it can be seen from Table 4.6. and Table 4.8., the results obtained with two different preconcentrates having 23.13% REO and 31.11% REO, respectively, were about the same with respect to alloy composition and rare earth recovery.

CHAPTER 5

CONCLUSIONS

In this research work the optimization of conditions of metallothermic reduction of rare earth preconcentrate was studied. The following conclusions were drawn considering the experimental results:

1. As long as a basic and fluid slag was obtained, basicity of the slag should be kept at a value that prevents the formation of calcium carbide as much as possible since utilizing graphite crucibles cause the formation of calcium carbide.

2. To obtain a higher rare earth recovery and better composition of alloy product, temperatures as low as possible which ensure a fluid and low viscosity slag should be used for the reduction process. In this study, the optimum temperature of smelting was found to be 1450 °C.

3. Aluminum amount should be in excess of the stoichiometric amount to compensate for the aluminum losses due to oxidation while keeping the Al_2O_3 activity as low as possible in slag phase. 6 times of the stoichiometric amount of aluminum seems to be the best choice from the recovery and alloy composition points of view.

4. Utilizing the ferrosilicon in excess of the stoichiometric amount was found to be advantageous to obtain a better rare earth metal recovery up to a point where the increasing SiO_2 activity started to reduce the rare earth metal recovery. In this study, 112 % of the stoichiometric amount of ferrosilicon gave the highest recovery.

5. In order to achieve satisfactory rare earth metal recoveries, allowing the reduction reaction of rare earth oxides to occur for 15 minutes was found to be advantageous.

6. In order to increase rare earth metal recoveries in metallothermic reduction of rare earth preconcentrate, reducing agents such as CaSi should be tried as future work.

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APPENDIX A

CALCULATION OF THE COMPOSITION OF PRECONCENTRATE CONTAINING 23.13% REO FROM SEM ANALYSIS

Since SEM analyses give the elemental composition of the samples, percentages of compounds should be calculated from the results of SEM analyses.

SEM analysis and calculation of the compound composition of the rare earth preconcentrate containing 23.13 % REO are given below:

Element	***Weight Conc. (%)****
Mg	1.01
Al	2.22
Si	5.57
Fe	9.83
Ba	6.34
Ca	37.13
P	1.66
La	13.68
Ce	21.09

* Excluding; C, O, S and F

Mg = 24 g/mole, MgO = 40 g/mole

Weight percentage of MgO in the preconcentrate = 1.01 * (40/24) = 1.683 %

Si = 28 g/mole, SiO_2 = 60 g/mole

Weight percentage of SiO_2 in the preconcentrate = 5.57 * (60/28) = 11.935 %

Al = 27 g/mole, Al_2O_3 = 102 g/mole

Weight percentage of Al_2O_3 in the preconcentrate = 2.22 * (102/54) = 4.193 %

Fe = 56 g/mole, Fe_2O_3 = 160 g/mole

Weight percentage of Fe_2O_3 in the preconcentrate = 9.83 * (160/112) = 14.042 %

Ba = 137 g/mole, $BaSO_4$ = 233 g/mole

Weight percentage of $BaSO_4$ in the preconcentrate = 6.34 * (233/137) = 10.782 %

P = 31 g/mole, P_2O_5 = 142 g/mole

Weight percentage of P_2O_5 in the preconcentrate = 1.66 * (142/62) = 3.802 %

It was assumed that 13.8 % of the amount of Ca occurred as $CaCO_3$ and the rest which is 86.2 % of the amount of Ca occurred as CaF_2;

Ca = 40 g/mole, $CaCO_3$ = 100 g/mole, CaF_2 = 78 g/mole

Weight percentage of $CaCO_3$ in the preconcentrate = 37.13 * (13.8/100) * (100/40) = 12.81 %

Weight percentage of CaF_2 in the preconcentrate = 37.13 * (86.2/100) * (78/40) = 62.411 %

La = 139 g/mole, $LaFCO_3$ = 218 g/mole

Weight percentage of $LaFCO_3$ in the preconcentrate = 13.68 * (218/139) = 21.455 %

Ce = 140 g/mole, $CeFCO_3$ = 219 g/mole

Weight percentage of $CeFCO_3$ in the preconcentrate = 21.09 * (219/140) = 32.99 %

The sum of these percentage values = 176.103

Since the summation of percentage values does not equal to 100, they must be multiplied with a correction factor which is 100/176.103.

Corrected weight percentages of compounds are given in following table:

Compound	***Weight Conc. (%)***
$LaFCO_3$	12.18
$CeFCO_3$	18.73
CaF_2	35.44
$CaCO_3$	7.24
SiO_2	6.78
Fe_2O_3	7.97
$BaSO_4$	6.12
Al_2O_3	2.38
P_2O_5	2.16
MgO	0.95

Calculation of REO grade of the preconcentrate;

La = 139 g/mole, $LaFCO_3$ = 218 g/mole, La_2O_3 = 326 g/mole

Weight percentage of La_2O_3 in the preconcentrate = 12.18 * (139/218) * (326/278) = 9.11 %

Ce = 140 g/mole, $CeFCO_3$ = 219 g/mole, Ce_2O_3 = 328 g/mole

Weight percentage of Ce_2O_3 in the preconcentrate = 18.73 * (140/219) * (328/280) = 14.02 %

Total REO grade of the preconcentrate = 9.11 + 14.02 = 23.13 %

APPENDIX B

CALCULATION OF THE COMPOSITION OF PRECONCENTRATE CONTAINING 31.11% REO FROM SEM ANALYSIS

SEM analysis and calculation of the compound composition of the rare earth preconcentrate containing 31.11 % REO are given below:

Element	***Weight Conc. (%)****
Mg	1.08
Al	2.16
Si	6.40
Fe	11.59
Ba	5.20
Ca	26.36
P	1.22
La	21.81
Ce	24.18

* Excluding; C, O, S and F

Mg = 24 g/mole, MgO = 40 g/mole
Weight percentage of MgO in the preconcentrate = 1.08 * (40/24) = 1.8 %

Si = 28 g/mole, SiO_2 = 60 g/mole
Weight percentage of SiO_2 in the preconcentrate = 6.4 * (60/28) = 13.714 %

Al = 27 g/mole, Al_2O_3 = 102 g/mole

Weight percentage of Al_2O_3 in the preconcentrate = 2.16 * (102/54) = 4.08 %

Fe = 56 g/mole, Fe_2O_3 = 160 g/mole

Weight percentage of Fe_2O_3 in the preconcentrate = 11.59 * (160/112) = 16.557 %

Ba = 137 g/mole, $BaSO_4$ = 233 g/mole

Weight percentage of $BaSO_4$ in the preconcentrate = 5.2 * (233/137) = 8.843 %

P = 31 g/mole, P_2O_5 = 142 g/mole

Weight percentage of P_2O_5 in the preconcentrate = 1.22 * (142/62) = 2.794 %

It was assumed that 13.8 % of the amount of Ca occurred as $CaCO_3$ and the rest which is 86.2 % of the amount of Ca occurred as CaF_2;

Ca = 40 g/mole, $CaCO_3$ = 100 g/mole, CaF_2 = 78 g/mole

Weight percentage of $CaCO_3$ in the preconcentrate = 26.36 * (13.8/100) * (100/40) = 9.094 %

Weight percentage of CaF_2 in the preconcentrate = 26.36 * (86.2/100) * (78/40) = 44.308 %

La = 139 g/mole, $LaFCO_3$ = 218 g/mole

Weight percentage of $LaFCO_3$ in the preconcentrate = 21.81 * (218/139) = 34.205 %

Ce = 140 g/mole, $CeFCO_3$ = 219 g/mole

Weight percentage of $CeFCO_3$ in the preconcentrate = 24.18 * (219/140) = 37.824 %

The sum of these percentage values = 173.219

Since the summation of percentage values does not equal to 100, they must be multiplied with a correction factor which is 100/173.219.

Corrected weight percentages of compounds are given in following table:

Compound	***Weight Conc. (%)***
$LaFCO_3$	19.75
$CeFCO_3$	21.84
CaF_2	25.58
$CaCO_3$	5.25
SiO_2	7.91
Fe_2O_3	9.56
$BaSO_4$	5.11
Al_2O_3	2.35
P_2O_5	1.61
MgO	1.05

Calculation of REO grade of the preconcentrate;

La = 139 g/mole, $LaFCO_3$ = 218 g/mole, La_2O_3 = 326 g/mole

Weight percentage of La_2O_3 in the preconcentrate = 19.75 * (139/218) * (326/278) = 14.76 %

Ce = 140 g/mole, $CeFCO_3$ = 219 g/mole, Ce_2O_3 = 328 g/mole

Weight percentage of Ce_2O_3 in the preconcentrate = 21.84 * (140/219) * (328/280) = 16.35 %

Total REO grade of the preconcentrate = 14.76 + 16.35 = 31.11 %