SOLVENT EXTRACTION OF SCANDIUM FROM PREGNANT LEACH SOLUTION OF NICKEL LATERITES

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ABSTRACT

SOLVENT EXTRACTION OF SCANDIUM FROM PREGNANT LEACH SOLUTION OF NICKEL LATERITES

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The aim of this thesis study is the extraction and recovery of scandium from lateritic nickel-cobalt ores by using the solvent extraction method. In this study, different organic and scrubbing reagents were investigated in order to find the most suitable organic extractant for the extraction of scandium with low impurity co-extraction and scrubbing reagent to remove the extracted impurities from the loaded organic phase.

In the first part, different organic reagents that are DEHPA, Cyanex 272, Cyanex 923, Ionquest 801 and Primene JMT, were investigated. After the determination of the most suitable organic extractant, synergetic systems were examined and for this reason, TBP and isodecanol, which are defined as modifiers in solvent extraction systems, were used with the previously determined organic extractant. In addition to these, the effects of kerosene type, the pH of the aqueous solution and the volume ratio of organic to aqueous phase on extraction were investigated. Therefore, it was determined that 5% DEHPA + 1% TBP + 94% D80 with A/O: 10/1 phase ratio at pH=0.8 for 10 minutes mixing duration were suitable conditions for scandium extraction.

After the extraction, the suitable scrubbing reagents were investigated for the loaded organic. In this part, iron and aluminum are the most critical impurities as well as nickel and cobalt and the main aim is to remove particularly these impurities from the loaded organic phase. In consideration of this, oxalic acid, HCl and H_2SO_4 were used in the experiments with different molarities. As a result of the series of experiments, 0.75M oxalic acid at O/A: 3/1 phase ratio was determined as a suitable condition for scrubbing.

Keywords: Hydrometallurgy, Solvent Extraction, Scandium, Nickel, Laterite

ÖZET

NİKEL LATERİTLERİNİN METALLE YÜKLÜ ÇÖZELTİSİNDEN SKANDİYUM SOLVENT EKSTRAKSİYONU

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Bu tez çalışmasının amacı, lateritik nikel-kobalt cevherlerinden skandiyumun solvent ekstraksiyon yöntemi kullanılarak ekstrakte edilmesi ve geri kazanılmasıdır. Bu çalışmada, skandiyumu en yüksek verimlilik ve en az kirlilik ile ekstrakte eden organik reaktif ile elde edilen yüklü organiği temizlemek için en uygun temizleme reaktifi araştırıldı, bunları belirlemek amacıyla çeşitli organik ekstraktantlar ve temizleme reaktifleri denendi.

İlk bölümde, DEHPA, Cyanex 272, Cyanex 923, Ionquest 801, Primene JMT olmak üzere farklı organik reaktifler kullanıldı. Skandiyum için en uygun organik ekstraktant belirledikten sonra, sinerjetik sistemler incelendi ve bu amaçla, solvent ekstraksiyon sistemlerinde modifiye edici olarak tanımlanan TBP ve izodekanol, önceden belirlenmiş organik özütleyici ile kullanıldı. Bunlara ilaveten, gazyağının tipinin, sulu solüsyonun pH'ının ve organik fazın sıvı çözelti ile hacimsal oranının ekstraksiyon üzerine etkisi araştırıldı. Sonuç olarak, %5 DEHPA + %1 TBP + % 94 D80 komposizyonuna sahip organik fazın A/O: 10/1 faz oranında, pH=0.8 de, 10 dakika karıştırma süresi ile skandiyum ekstraksiyonu için en uygun koşul olduğu tespit edildi.

Ekstraksiyon işleminden sonra yüklü organik için en uygun temizleme reaktifi araştırıldı. Bu bölümde, demir ve alüminyum, nikel ve kobaltın yanı sıra en kritik kirlilik yaratan elementler olarak belirlendi ve araştırmalar bu elementler üzerinden yapıldı. Bu bölümün asıl amacı olan yüklenmiş organik fazdan özellikle bu kirlilikleri gidermek için deneylerde oksalik asit, HCl ve H_2SO_4 farklı molaritelerde kullanıldı ve yapılan seri deneyler sonucunda 0.75M oksalik asidin O/A: 3/1 faz oranında temizleme için en uygun koşul olduğu tespit edildi.

Anahtar Kelimeler: Hidrometalurji, Solvent Ekstraksiyonu, Skandiyum, Nikel, Laterit

To my esteemed colleague dear father

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NOMENCLATURE

SYMBOL OR ABBREVIATION	**MEANING**
DEHPA	Di-2-EthylHexyl Phosphoric Acid
TBP	Tributylphosphate
CYANEX 272	Bis(2,4,4-trimethylpentyl) phosphinic acid
CYANEX 923	Trialkyl phosphine oxide
IONQUEST 801	Bis(2-ethylhexyl) phosphate
HDEHPA	Bis(2-ethylhexyl) phosphate
LIX 63	Aliphatic α-hydroxy oxime
LIX 65	Alkyl β-hydroxy benzophenone oxime
TOPO	Trioctylphosphine oxide
PRIMENE JMT	C16-22-tert-alkyl; 16,16dimethylheptadecan-1-amine
EDTA	Ethylenediaminetetra acetic acid
ALAMINE 336	Tri-octyl/decyl amine
ALIQUAT 336	Trioctylmethylammonium chloride
SX	Solvent Extraction
PLS	Pregnant Leach Solution
S/L	Solid-Liquid Separation
MHP	Mixed Hydroxide Product

SNU	Secondary Neutralization Underflow
SOFC	Solid Oxide Fuel Cells
D	Distribution Coefficient
E	Extraction Coefficient
$\boldsymbol{S_B^A}$	Selectivity Index
O/A	Organic to Aqueous Volume Ratio

CHAPTER 1

INTRODUCTION

Scandium is classified as the lightest member of rare earth elements. Scandium, which is the first transition metal, has a unique position in the periodic table. Because of this, it has different properties in comparison to other rare earth elements. Moreover, scandium also has three outer valance electrons and it substitutes for major elements in the minerals; such as, iron and aluminum, which have three valance electrons similar to scandium. [1]

While scandium is widely distributed in the Earth's crust, it is generally present at low concentration levels. Hence, at present, only few minerals whose major constituent is scandium are known. Because of this, the main resources of scandium are generally effluents, wastes and slags that are obtained during the production of uranium, tungsten, aluminum, nickel, molybdenum, titanium and other rare earth elements. Since scandium is produced as a by-product of these production sheets, it cannot be produced at high levels. Nevertheless, today scandium is generally used as mainly three different areas. The first and widespread usage area of scandium is in Al-Sc, Mg-Sc and Al-Mg-Sc alloys. These alloys are generally used in fighter jets, aerospace industry and high technical sporting equipment. Another usage area of scandium is in solid oxide fuel cells as solid electrolytes. Finally, scandium compounds can be used in lighting applications such as high intensity vapor lamps that are used in stadium lights and in studios for the film and television industry. [2, 3]

Furthermore, the recovery of scandium is done by using mainly two different enrichment processes. The first is the solvent extraction method that is liquid–liquid ion exchange and it is one of the important separation processes in hydrometallurgy. It provides extraction, concentration, separation and purification of dissolved non-ferrous metals in the solution and nowadays it is being used commonly in uranium, copper, nickel, cobalt, zinc, tungsten, molybdenum and rare earth industries. Moreover, it involves three different stages, which are extraction, scrubbing and stripping parts. In the extraction part, the solution that contains the non-ferrous metal ions is contacted with the organic phase. In this process, the desired element such as scandium is extracted to the organic phase from the solution. After this stage, scrubbing reagent is contacted with the loaded organic phase in order to remove impurities, which are co-extracted with scandium like iron and aluminum. Following the scrubbing part, the stripping stage in which scandium is stripped from purified loaded organic phase with suitable reagent is carried out. In other words, the organic phase acts as exchange media and thus, the scandium enriched aqueous solution is obtained. At the end of this process, the precipitation and purification processes can be carried out in order to produce highly purified scandium compounds such as oxide, fluoride, hydroxide, acetate, oxalate, chloride and iodide. [4,5,6]

The other method is the ion exchange process, which involves reactions between ions in aqueous solution and insoluble solid resin. It is generally used in the uranium and other rare earth metal industries. Furthermore, it is able to recover the metals that are present in extremely low concentrations that cannot be recovered by the using solvent extraction method in the mine wastes. [6]

In this study, the main aim is to find the suitable organic and scrubbing reagents for scandium extraction from the pregnant leach solution (PLS), which was obtained during processing of nickel laterites from (Manisa) Gördes region of Turkey and the removal of the co-extracted impurities from the loaded organic phase after extraction.

CHAPTER 2

LITERATURE REVIEW

2.1. Scandium and Rare Earth Elements

Rare earth metals are found seldom in specific minerals and they are originally isolated. Because of this, the recovery, purification and refining processes of rare earth metals are still a challenging issue in the world. Rare earth metals include lanthanides, scandium and yttrium and are given in Table 2.1 with some of their properties. Although yttrium and scandium are not classified as lanthanides, due to their similarities, both of them can be considered as rare earth metals. [7]

Generally, igneous, sedimentary and metamorphic rocks include rare earth deposits. The concentration and distribution of rare earth elements in these deposits can vary with respect to rock forming and hydrothermal processes, which consist of enrichment in magmatic hydrothermal fluid separation into mineral phases and precipitation, subsequent redistribution and concentration via weathering and some other surface mechanism. In addition to these, according to the environment in deposits, rare earth deposits can be divided into two parts. While the first part is primary deposits related to igneous and hydrothermal processes, the other part is secondary deposits associated with sedimentary processes and weathering. [7]

Scandium prevalently occurs in granitic pegmatites and placer deposits that are classified as secondary deposits of rare earth elements. [8] Pegmatites are heavily igneous rocks that form during the terminal part of magma crystallization.

They mainly include abundant amount quartz, feldspar and mica and due to similarities between the composition of granite and pegmatites, they can be called granite pegmatites in order to show their mineralogical composition. [9] While placer deposits are concentrated with heavy minerals and as a result of coastal processes and rivers, they are also deposited with sand and gravel. [7]

Table 2.1 Some properties of rare earth elements including scandium. [7]

Element	**Symbol**	**Atomic Number**	**Atomic Weight**	**Density (g/cm^3)**	**Melting Point**℃	**Vickers Hardness** (10 kg load, kg/mm^2)
Scandium	Sc	21	44.95	2.989	1541	85
Yttrium	Y	39	88.90	4.469	1522	38
Lanthanum	La	57	138.90	6.146	918	37
Cerium	Ce	58	140.11	8.160	798	24
Praseodymium	Pr	59	140.90	6.773	931	37
Neodymium	Nd	60	144.24	7.008	1021	35
Promethium	Pm	61	145.00	7.264	1042	-
Samarium	Sm	62	150.36	7.520	1074	45
Europium	Eu	63	151.96	5.244	822	17
Gadolinium	Gd	64	157.25	7.901	1313	57
Terbium	Tb	65	158.92	8.230	1356	46
Dysprosium	Dy	66	162.50	8.551	1412	42
Holmium	Ho	67	164.93	8.795	1474	42
Erbium	Er	68	167.26	9.066	1529	44
Thulium	Tm	69	168.93	9.321	1545	48
Ytterbium	Yb	70	173.04	6.966	819	21
Lutetium	Lu	71	174.97	9.841	1663	77

2.2. The Properties of Scandium and Its Geology

Scandium is generally classified as a rare earth metal with 17 elements comprising of yttrium, and 15 lanthanides. [7] In the year 1879, scandium was discovered in euxenite mineral [$(Y,Ca,Ce,U,Th)(Nb,Ta,Ti)_2O_6$] which contains mainly uranium, thorium and rare earth metals including scandium. [8] Through the years following this discovery, it was clarified that there were only few minerals in the Earth classified as the mineral of scandium, although scandium is widely distributed in the Earth's crust.

Moreover, these minerals are generally granitic pegmatites and placer deposits and due to wide distribution of scandium in the Earth's crust, it is generally found in the minerals in trace amounts. Although eleven major scandium minerals are found in the whole world i.e., three of which are phosphates and the others are silicates as given in Table 2.2. The main and unique mineral of scandium is thortveitite in which scandium is present as scandium silicate ($Sc_2Si_2O_7$). [9] Thortveitite is found scarcely in the world, and known deposits of this mineral in the Earth are found in Norway, Madagascar and Italy. The average content of scandium in the Earth's crust is 22 ppm. [10]

Table 2.2 Scandium bearing minerals.

Bazzite	$Be_3(Sc,Al)_2Si_6O_{18}$
Cascandite	$Ca(Sc,Fe^{++})Si_3O_8(OH)$
Jervisite	$(Na,Ca,Fe^{++})(Sc,Mg,Fe^{++})Si_2O_6$
Juonniite	$CaMgSc(PO_4)_2(OH).4(H_2O)$
Kolbeckite	$ScPO_4.2(H_2O)$
Magbasite	$KBa(Al,Sc)(Mg,Fe^{++})_6Si_6O_2OF_2$
Pretulite	$ScPO_4$
Scandiobabingtonite	$Ca_2(Fe^{++},Mn)ScSi_5O_{14}(OH)$
Thortveitite	$(Sc,Y)_2Si_2O_7$
Titanowodginite	$Mn^{++}(Ti,Ta,Sc)_2O_8$
Heftetjernite	$ScTaO_4$

However, if the world production of scandium is considered, the production of scandium from thortveitite mineral is not a common way of scandium recovery. It can be stated that the considerable amount of scandium is generally produced as the by-product of various metals such as; uranium, nickel, aluminum, vanadium, tungsten, titanium and some rare earth elements. [5] In other words, scandium is naturally found in other metal bearing minerals such as aluminum phosphate minerals, some silicate minerals and oxide minerals in the world as well as scandium bearing mineral such as thortveitite as seen in Table 2.3. Furthermore, in the ores, scandium generally substitutes for the major elements such as; iron, and aluminum, which have similar chemical and physical properties with scandium. Because of this, the ores contain low amount of scandium in the range of 0.002-0.005%.

[5]***Table 2.3*** *Minerals of some elements containing scandium.*

Form	Mineral Name	Content of Sc_2O_3 (%)
Silicates	Thortveitite	25.0 - 48.3
	Zircon	0.005 - 0.3
	Beryl	0.0005 - 1.2
	Garnet	0.02 - 0.4
	Olivine	0.0003 - 0.02
	Pyroxene	~ 0.04
Phosphates	Xenotime	0.0015 - 1.5
	Monazite	0.002 – 0.5
	Apatite	0.0003 – 0.08
Oxides	Davidite	~ 0.02
	Columbite	0.01 – 0.8
	Uraninite	0.15 - 0.2
	Wolframite	0.005 – 1.3
	Magnetite	0.001 – 0.04
	Hematite	~ 0.15
	Titanomagnetite	0.0002 – 0.02
	Ilmenite	0.0015 – 0.15
	Rutile	0.005 – 0.16
	Laterite	0.003 – 0.03

Iron, aluminum and scandium have similar properties and they can act in similar ways to each other in reactions and minerals. First, each of them has three valance electrons and because of this, scandium can easily substitute iron or aluminum in the minerals due to the approximately similar size of the cations of these elements. Additionally, in hydrometallurgical respect, they have nearly same chemical properties in the reactions.

To illustrate, based on the solubility of ions; iron, scandium and aluminum cations precipitate at about the same pH in the solution. Therefore, the similar behavior of these ions can cause some problems in the extraction and recovery processes of scandium both in ore preparation and in hydrometallurgical processes

2.3. The Applications of Scandium,

Until 1970s, the scandium production was at low levels. According to the literature, scandium is known to be used only for experimental purposes in 1960s, unlike today. Due to its scarcity and high cost of production, different elements or materials, which were more available and had similar properties as scandium, were used in the commercial applications of scandium in those years. However, today scandium is being used for different purposes, such as, aerospace and electronic components, as filaments in halogen lighting, application in welding wire, laser research, as solid electrolyte in solid oxide fuel cell, as alloying element mainly in Al-Sc and Al-Mg alloys, as well as, metallurgical research. [11] Nowadays, the main and the most important areas of usage, on the other hand, are Al-Sc alloys and solid oxide fuel cells. [8,12]

Industrially, Al-Sc alloys are the main applications of scandium. These alloys are mainly used in military applications, aerospace industry and sporting equipment. Scandium has high solubility in aluminum and it enables a combination of strength, toughness, hardness and applicable microstructure in alloy. [10,11] This alloy was initially used in Soviet Union for military demands. Due to lower density and higher strength of this alloy in comparison with Al-Mg and Al-Li (8xxx) alloys. [9] Al-Sc alloys were used in MIG 21 and MIG 29 fighter jets in the era of Cold War. [13,14] With small additions of scandium into aluminum in molten state, a desirable phase of dispersoid Al_3Sc intermetallics form in the matrix as seen in Figure 2.2. It provides equilibrium between aluminum and scandium, thermodynamically and it changes microstructure and provides superior behavior to resultant alloy that are grain refinement, superplasticity, outstanding precipitation hardening behavior, corrosion resistance and weldability.

Because of scandium addition, equiaxed grains form in microstructure, and these stabilize grain boundaries with the help of dispersoid in microstructure and improve the weldability and ability of alloy to bend under stresses (superplasticity). Due to this superior behavior and lightweight properties, these alloys are generally used in special areas such as aerospace industry. [2]

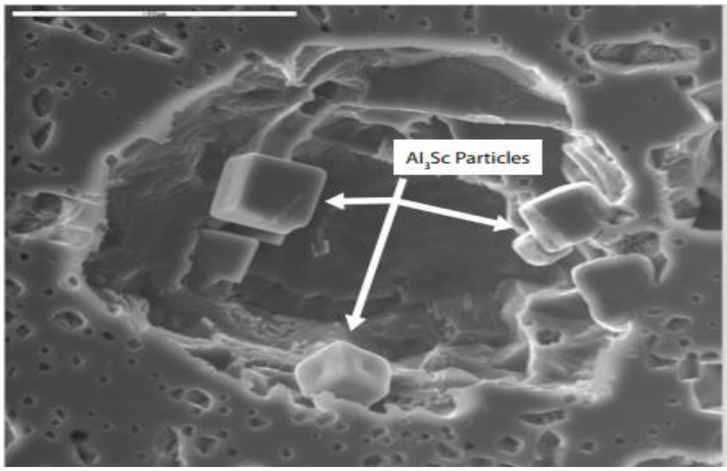

Figure 2.1 SEM micrograph of Al_3Sc particles. [2]

According to the phase diagram in Figure 2.3, the maximum equilibrium solubility of scandium is achieved with approximately 0.38 wt.% scandium in the aluminum alloy under high temperature condition. Hence, the increasing scandium content causes deterioration in the properties of the alloy due to the formation of secondary Al_3Sc particles in the matrix. In consideration of these factors, it can be stated that the desirable amount of scandium is between 0.1 to 0.5 wt.% in aluminum. [15]

Therefore, it can be said that a small addition of scandium improves the mechanical and physical characteristics of the alloys such as, high strength, low density, unique precipitation hardening characteristics and high thermal stability. Thus, these alloys can be used for various areas where lightweight material with special properties is the requirement. [2]

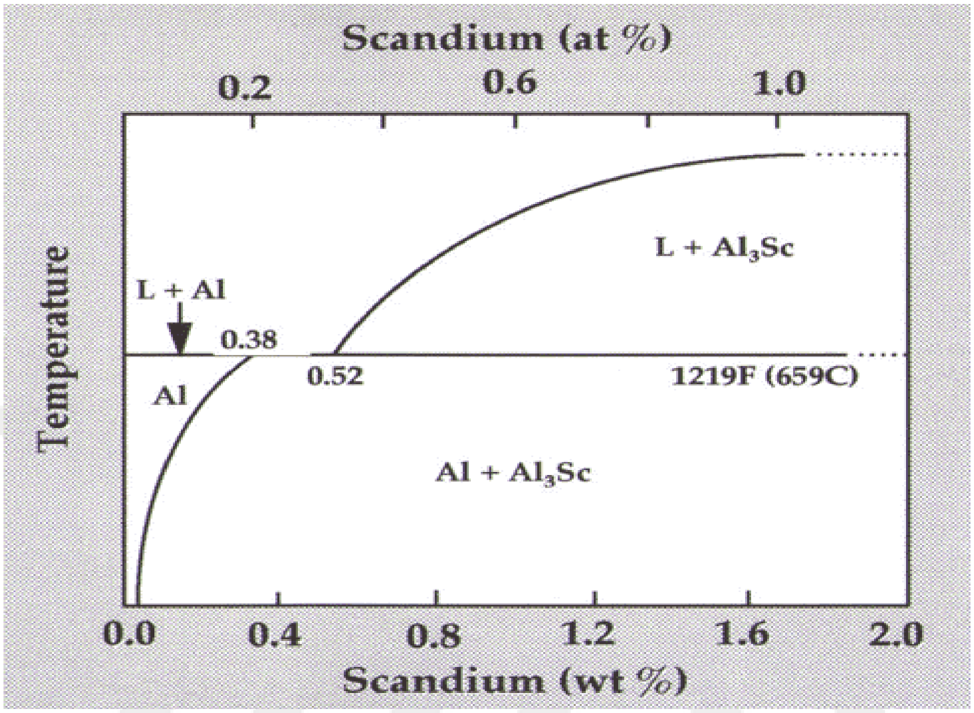

Figure 2.2 A binary phase diagram of Al-Sc. [15]

Moreover, scandium can be also added into Al-Mg alloys as well as the aluminum alloys in order to improve the mechanical properties of these. According to the literature, one of the advantages of scandium addition to the alloys is to provide increment in yield strength and other properties. [14]

Furthermore, Mg-Sc alloys are also used in various applications such as aircraft engines. The use of lightweight material in aircraft engines provides to save electricity and reduce energy consumption. Moreover, the additives of rare-earth metals, particularly scandium up to 0.5 wt% have positive effects on the mechanical and heat resistance properties of the magnesium alloys, and it provides to the alloy appropriate feature for the engines. [2]

Another consumption area of scandium is in solid oxide fuel cells (SOFC) as solid electrolyte. Solid oxide fuel cell is an electrochemical cell that produces electrical current with heat and CO_2 from fuel and oxygen source at very high temperature (~1000°C) as seen in Figure 2.5.

It provides energy conservation and it is mainly described as environmental friendly process. In spite of the advantages of solid oxide fuel cell, some problems, such as, thermal fatigue in system, expensive alloy requirement and rapid oxidizing of metal components, can take place as a result of high processing temperature. In addition to these problems, generally zirconia, which requires some stabilizer in processing since it, cannot be stabilized at high temperature used as solid electrolyte. Therefore, yttrium oxide is commonly used in solid oxide fuel cells in order to stabilize zirconium oxide and increase conductivity of solid electrolyte (YSZ). However, when zirconium oxide is stabilized with scandium oxide, Sc_2O_3, it provides higher oxygen-ion conductivity, higher efficiency, and reduction of the cost of using thermal shielding in the process, the long-term stability of the electrolyte and higher operating life of the electrolyte by allowing low operating temperatures. Because of these reasons, even if scandium oxide has absolutely 100 times higher price than yttrium oxide, Bloom Energy in California, USA has started to use scandium oxide as solid electrolyte in order to provide significant improvements in operation. [8,18,19]

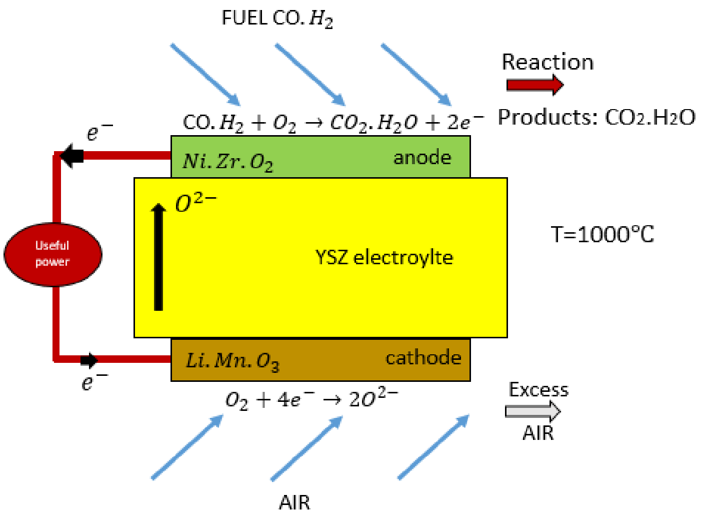

Figure 2.3 The chemistry of solid oxide fuel cell. [8]

Moreover, scandium also replicates sunlight effectively and so, scandium compounds can be used in lightening applications, such as, halogen lighting as filament, laser technology and research, and high intensity mercury vapor lamps which are used in stadium light and in studios for the film industry.

Furthermore, scandium compounds such as, Sc_2O_3 and $ScVO_4$, can be used in TV or computer monitors. In these applications, scandium ions in the compounds act as the activator ions or the host for phosphorus. Consequently, they create appropriate phosphorus compounds, which can be used in display of televisions.

Nevertheless, due to high production cost of scandium, today, the other elements or their compounds are still used in discussed applications. In addition to the cost, the availability of scandium is another critical issue. For example, scandium oxide has superior properties and it can replace yttrium oxide in the applications, especially solid oxide fuel cells. However, yttrium has extremely higher world supply today, which is approximately 11000 tones contrary to scandium. Therefore, if the availability of scandium oxide can be increased in the world, the commercial acceptance of scandium can increase considerably. Therefore, in the future, it can easily replace the commercially used some metals. [8]

2.4. The Economic Aspect of Scandium and Its Products

In the whole world, the main suppliers of scandium are China (from titanium and rare earths), Kazakhstan (from uranium) and Russia (from apatite). Nowadays, the global supply of scandium oxide is limited and its prices range from \$3500 to \$5000 per kilogram based on purity, and quality features as given in Table 2.4. [20]

Even if the collected data for the rare earth elements and special metal markets generally cannot achieve to provide a good view to understand supply chain of these critical metals due to lack of information, according to Minerals Commodity Summary on scandium published by USGS, the price of scandium oxide is currently estimated to be US \$4600/kg for 99.99% grade (in 2016). [21]

Table 2.4 USGS Prices for different scandium products. [21]

Salient Statistics-United States	**2012**	**2013**	**2014**	**2015**	**2016**
Price, yearend, dollars:					
✓ **Compounds, per gram:**					
a) Acetate,99.9% purity, 5 gram sample size	50.1	51.9	43.0	43.0	44.0
b) Chloride,99.9% purity, 5 gram sample size	143.0	148.0	123.0	123.0	126.0
c) Fluoride,99.9% purity, 1- 5 gram sample size	244.0	253.0	263.0	263.0	270.0
d) Iodide,99.9% purity, 5 gram sample size	220.0	228.0	187.0	187.0	149.0
e) Oxide,99.9% purity, 5 kilogram lot size	4.7	5.0	5.0	5.1	4.6
✓ **Metal:**					
Scandium, distilled dendritic, per gram, 2 gram sample size	206.0	213.0	221.0	221.0	228.0
Scandium, ingot, per gram, 5 gram sample size	169.0	175.0	134.0	134.0	107.0
Scandium-aluminum alloy, per kilogram, metric-ton lot size	220.0	155.0	386.0	220.0	340.0
Net import reliance as a percentage of apparent consumption	100	100	100	100	100

Moreover, according to the International Trade Commission (ITC), the volume of global market of scandium oxide was 2-10 tons per year in 2013. On the other hand, in 2014, some other institutions have estimated the volume of global supply of scandium oxide at least 10 tons per year, but these estimations do not include scandium containing master alloys, which are currently sold from stockpiles of Russia and other unknown sources of scandium in global market. [8]

In addition to these, scandium oxide prices can vary with respect to quality, availability, volumes of sold product, source and demand. For example, in solid oxide fuel cell and the other special applications, the radioactive elements and other impurities may cause some problems. Hence, the composition of used compounds is the most critical parameter for the customers in these industries.

On the other hand, while the high quality oxide product (above 99%) is necessary in solid oxide fuel cell industry and the other electrical applications, the quality is not the main parameter in master alloy production. In consideration of these factors, while the quality of scandium compounds is essential for some areas, it is not the main parameter to define the cost of its compounds due to difficulties in recovery and production and its scarcity. Moreover, the quantities of the sold products should not be exceeding 10-kilogram amount due to the same reasons. [8]

Moreover, the price of aluminum scandium alloy containing 2 wt.% Sc was $340 per kilogram in 2016 with respect to USGS publication and scandium metal in the pure state is also available but it is very expensive due to its scarcity. [21]

2.5. The Sources of Scandium

In spite of the wide distribution of scandium in the lithosphere and solid solution formation in more than 100 minerals, scandium is found in only trace amount in the ores. For this reason, these ores cannot be considered as a reserve for scandium. Consequently, scandium is mainly obtained as a by-product during processing of various ores or from processed tailing and residues. Wolframite, nickel laterites, tungsten residue, waste fluid in the production of titanium white, rare earth minerals and red mud originating from bauxite are the important sources of scandium.

In the world; China, Russia, Ukraine, Kazakhstan and USA are known as main scandium producers. While in Russia and Kazakhstan, scandium is recovered from uranium bearing deposits and from appetites in Kola Peninsula, in Ukraine, scandium was also produced as a by-product during the processing of iron ore at Zheltye Voda. Moreover, in China scandium is being recovered from tin, tungsten and iron bearing deposits in Jiangxi, Guangxi, Guangdong, Fujian, Zhejiang, Provinces.

In addition, the most important and still operative resource of China is the rare earth element deposit in Inner Mongolia at Bayan Obo. Furthermore, in Australia nickel and cobalt resources contain scandium and in Madagascar and Norway, pegmatites include thortveitite which is scandium enriched mineral**.** In addition to these, USA has significant scandium resources. The main resources are the fluorite tailings from the Crystal Mountain deposit near Darby, MT which includes thortveitite and some of the other scandium-enriched minerals. The other deposits from which scandium can be recovered are tungsten, aluminum, cobalt, iron, molybdenum, nickel, phosphate, tantalum, tin, titanium, zinc, and zirconium ores. [1,5,8,22] In addition to these, red mud tailings that form during processing of bauxite by the Bayer process are the most important scandium resources in the world. Generally, depending on the type of the ore and sensitivity of the processing routes, the tailings of Bayer process contain approximately 50-100 ppm scandium. Due to high scandium concentration and environmental hazards of the red muds, today, scandium recovery as well as getting rid of these tailings is being investigated. [8]

2.5.1. Recovery of Scandium as a By-product from Nickel Laterites

Nickel is generally used in production of stainless steel (65% total production in 2016), in electroplating and in manufacturing of various alloys. Nickel ores can be divided into two parts with respect to the type of the ores, which are sulfides and oxides. In the world, the majority of nickel is refined from sulfide ores. However, due to the nearly extinction of sulfide ores, the new trend is extraction and refining nickel from lateritic type ores. In Figure 2.6, the lateritic nickel ore distribution in the world is given. [23]

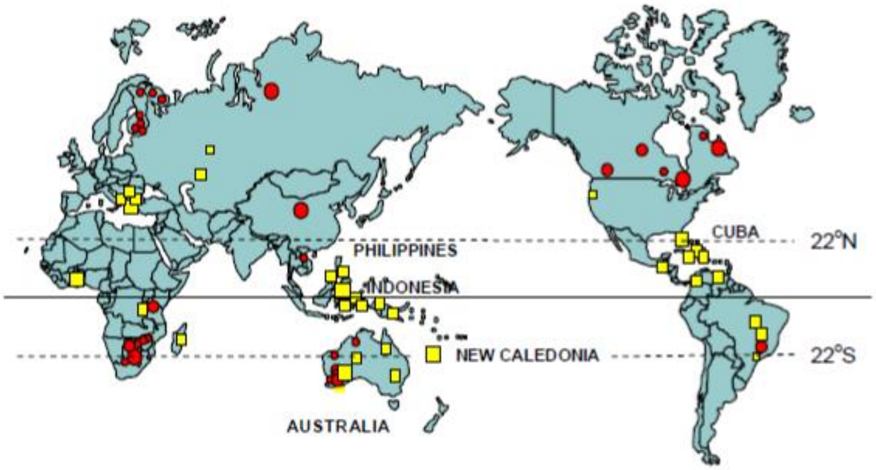

Figure 2.4 Laterite ores distribution in the world. [23]

According to the literature, about 40% nickel production of world is provided from laterites. Commercially, different types of processes are carried out with the different part of laterite profiles for nickel recovery. For example, while the hydrometallurgical techniques, which include sulfuric acid leaching and reduction roast-ammonia leaching, are commonly applied towards upper part of laterites (low magnesium part), the pyrometallurgical processes such as smelting are used in processing of lower part of laterites (high magnesium silicates parts). [23,24,25]

Due to high cost of processing facilities and high-energy consumption, the pyrometallurgical processes for recovery of nickel from the laterite ores are not preferable. Therefore, the main processing routes for limonitic nickel laterites are hydrometallurgical techniques. On the other hand, the laterites include different profiles and not all of the layers of laterites are suitable for processing with hydrometallurgical techniques. In such cases, the pyrometallurgical techniques may be preferred if it is economical for processing. Different laterite profiles with their compositions are given in Table 2.5.

Even if the collected data for the rare earth elements and special metal markets generally cannot achieve to provide a good view to understand supply chain of these critical metals due to lack of information, according to Minerals Commodity Summary on scandium published by USGS, the price of scandium oxide is currently estimated to be US $4600/kg for 99.99% grade (in 2016). [21]

In addition, the thickness of the layer, the chemical and mineralogical composition and the progress of each layer formation can vary from place to place. Particularly, the climate and the other factors that are topography, drainage, tectonic, parent rock type and structure influence the nature of laterite profiles. [25] These varieties are shown in Figure 2.7.

Table 2.5 The name and composition of the laterite layers and the suitable processes for the each layer to recover Ni.

The name of the layer of laterites	Composition of the layer	Proper processes for recovery of Ni
Limonite, asbolane	1%-1.7% Ni, 0.1% - 0.2% Co	Pressure acid leaching(PAL) or Caron process
Nontronite	1%-5% Ni, ≥0.05% Co	Pressure acid leaching(PAL) or smelting
Serpentine	1.5%-10% Ni, 0.1%Co	Pyrometallurgical processing (ferronickel and matte smelting)
Garnierite	10%-20% Ni, 0.05%, 0.1%Co	Pyrometallurgical processing (especially ferronickel and matte smelting)

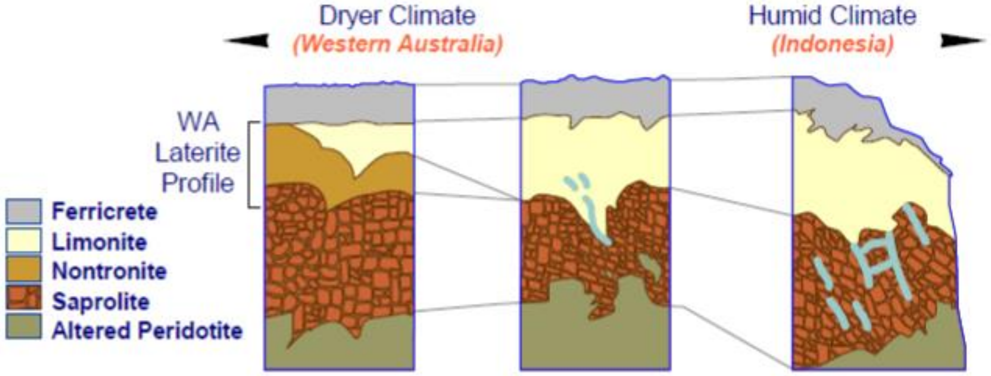

Figure 2.5 The nature of laterite profiles. [25]

According to Figure 2.8, the price of nickel has been decreasing dramatically with the passing years. Moreover, according to the literature many projects have been closed down in the past or experiencing some economic difficulties now. Because of this, the investment in nickel is very risky for investors due to low price of nickel and high cost of the building of the production plants. [11]

Figure 2.6 The price of Nickel varies with passing years. [26]

Therefore, the nickel producers should find a solution in order to generate profits and it can be said that producing by-products would be a solution for helping its high production costs. Scandium is one of the important by-products, which can be obtained during the processing of the nickel laterites, and the production of this by-product can provide high profits due to its high price and scarcity. Nickel laterites commonly contain considerable amount of scandium, which is enough for extraction, recovery and purification processes. For example, the nickel laterites in Australia contain high amount scandium, the average grade being 76 ppm. Moreover, scandium mainly enriches in high iron content layers such as limonite in laterite ores and a great majority of scandium in limonite layers are generally found in iron oxides (goethite) or manganese oxides (asbolane). [11,13]

According to Figure 2.9, in processing of the nickel laterites, after high-pressure acid leaching, neutralization treatment is carried out which includes precipitation processes at variable pH values with respect to the solubility of the different metal ions. Neutralization treatment is conducted in order to purify the solution, which passes through further precipitation processes to obtain MHP product. On the other hand, in this part of the process, scandium precipitate is obtained after two precipitation steps which are conducted at about pH=3 and pH=4.75. Scandium can be recovered from the second precipitate by using various hydrometallurgical techniques.

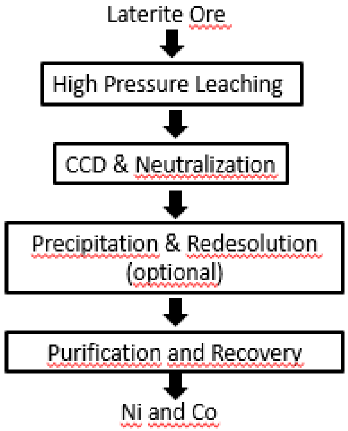

Figure 2.7 The processing route of nickel laterites by hydrometallurgical techniques. (HPAL) [25]

The residue is re-leached in order to take scandium from the precipitate to the leach liquor. Then, this solution should be neutralized for purification of the solution and in order to obtain suitable aqueous phase for solvent extraction method. Therefore, at the end of the process, scandium enriched and purified solution is obtained for extraction and recovery of scandium. [17]

In solvent extraction method, different organic reagents can be preferred such as; DEHPA, DEHPA+TBP, Cyanex 272, Ionquest 801, which depends on the chemistry of the solution and the organic extractant and the selectivity of the extractant with respect to scandium.

After the extraction, for scrubbing and stripping purposes, NaOH, H_2SO_4, etc., can be used with different molarities and these reagents should be chosen with respect to the chosen organic extractant in the extraction part. After the stripping part, either purified and scandium enriched solution or scandium hydroxide or the other types of scandium compound precipitates may be obtained. [5,27]

Although ion exchange is not sufficient to remove all impurities from the solution, it is an effective method to remove mainly Al, Ca and Mg impurities out of the system. Hence, this method can be carried out before or after solvent extraction method in order to obtain highly purified and scandium enriched solution at the end of the process. [5,29]

2.5.2. Recovery of Scandium as a By-product from Wastes of Alumina Production

Scandium can be recovered from tailings, waste liquors and residues that form during processing of other metals. Red mud is one of the scandium sources, which form during the Bayer processing of the bauxite ores. These ores are the most common aluminum ores and the Bayer process is a common process in the world, which is used for treating of bauxite ores.

In recent years, aluminum production is expected annually to be 50 million tons and because of this production, 200 million tons of red mud waste is simultaneously produced every year. [27] Red mud also includes radioactive elements and excess amount of alkali. Because of this, if it is stockpiled in huge amount, red mud can affect environment negatively.

On the other hand, scandium is enriched in red mud wastes in significant amount, which depends on the type of ore and processing routes. Therefore, the recovery of scandium and other valuable metals can help to overcome ecological problems, which occur due to these wastes. Red mud wastes mainly include iron, aluminum, calcium, silicon, titanium, zirconium, sodium as well as scandium, uranium and other rare metals such as yttrium and thorium. [28]

Due to the presence of radioactive elements, some difficulties are present for recovery and separation of scandium from these elements, particularly; iron, aluminum and titanium that are also present in huge amounts in red mud wastes. Moreover, iron is the most problematic element for all of the recovery processes of scandium due to the similar behavior of their ions in the processing. Therefore, there is a lot of investigation in order to overcome these problems. As stated in the literature, after the combination of hydrometallurgical and pyrometallurgical techniques, some extra purification methods need to be conducted such as; solvent extraction, ion exchange and selective precipitation as seen in Figure 2.10.

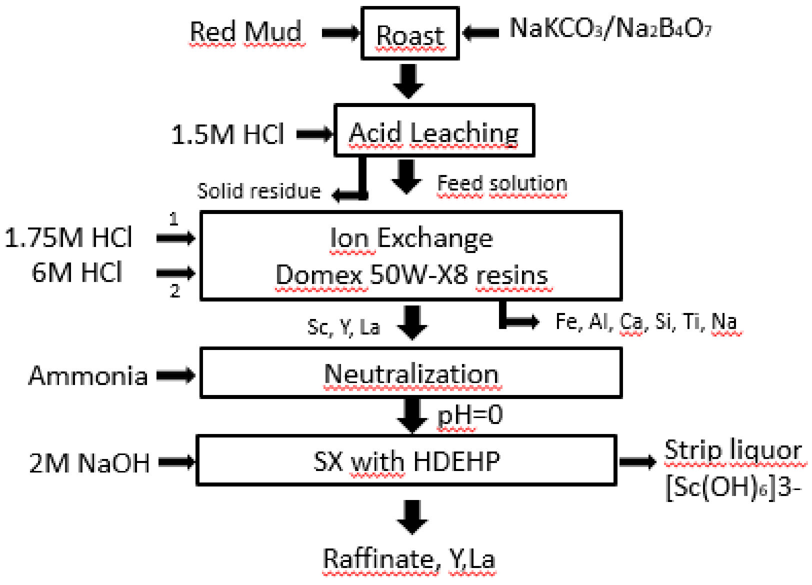

Figure 2.8 An example flowsheet of scandium recovery from red mud wastes. [5]

According to the literature, red mud is totally dissolved in the strong mineral acids with or without roasting treatment. After acid leaching with H_2SO_4 or HCl or HNO_3, ion exchange method can be carried out with using various resins which is appropriate for scandium extraction from leach liquor. [28] Moreover, after ion exchange method in order to obtain high purity scandium oxide, solvent extraction method should be applied. [5]

Various investigations were done in order to find the suitable organic extractant and scrubbing and stripping reagents for obtaining scandium enriched solution or the precipitate.

According to these investigations, DEHPA, EHEHPA, Cyanex 272, Cyanex 301 can be used with different percentages and if it is necessary, these extractants can be used in synergetic systems with neutral organophosphorus extractants such as, TBP and TOPO. After the extraction, the loaded organic can be stripped by using NaOH in order to obtain high purity scandium enriched solution. [29]

Moreover, according to the literature, after the extraction with DEHPA+TBP, HCl can be used as the scrubbing reagent in order to remove the impurities remaining in the loaded organic phase, particularly iron. Finally, strong NaOH can be used for stripping of scandium from the loaded organic phase and obtaining $Sc(OH)_3$ precipitates with high purity. [27]

2.5.3. Recovery of Scandium as a By-product from Uranium ore

Scandium is found in trace amounts in the different uranium minerals such as uranite, autunite and coffinite. These minerals are processed in different locations in the whole world, such as, Utah, Colorado, Nevada, Wyoming, Idaho, New Mexico, Arizona in USA and in Canada, Russia, South Africa. [30]

In order to recover scandium from uranium ores, various techniques are applied in all over the world. Such processes generally involve solvent extraction as well as multiple precipitation methods to separate uranium and the other valuable metals from each other.

For uranium extraction, Di-2-ethylhexyl phosphoric acid, heptadecyl phosphoric acid or dodecyl phosphoric acid in kerosene or Primene JMT can be used according to the literature. [31] In the extraction processes, thorium and scandium are also co-extracted and even if organic phase is stripped with strong HCl, they still remain on the loaded organic. Therefore, HCl stripping is done for separating uranium. [14,32]

After separating uranium from the loaded organic phase, the remaining thorium and scandium values are obtained by using ammonium bifluoride solution or HF in order to separate these values from titanium and the other impurities remaining in the solution. Obtained precipitate is converted to hydroxide form with metathesis process in which KOH or NaOH is used.

Moreover, after the converting process, the obtained precipitate is either leached with strong mineral acids such as HNO_3 to take scandium and thorium values into the solution or leached with excess amount of NaOH to obtain scandium hydroxide precipitate.

If scandium and thorium values are taken into the solution, respectively iodate precipitation with potassium iodate and oxalate precipitation with oxalic acid are applied in order to separate these values from each other. The former process provides the separation of thorium values from the solution and the latter provides scandium oxalate precipitation prior to calcination to obtain high purity scandium oxide compound. If excess amount NaOH is used for leaching, scandium hydroxide precipitate is obtained and it is leached with strong mineral acid such as, HCl. Therefore, the oxalate precipitation and calcination processes are carried out in order to obtain the end product which is highly purified scandium oxide

In addition to these, sometimes iron reduction can be applied in the extraction part in order to decrease iron co-extraction and increase the quality of the product. [1,10]

2.5.4. Recovery of Scandium as a By-product from Tungsten Ores

Tungsten minerals such as wolframite (iron-manganese tungstate, $FeWO_4$/$MnWO_4$) and scheelite (calcium tungstate, $CaWO_4$) include scandium in trace amounts. Tungsten ores are normally processed by using alkali digestion method to produce tungsten.

Furthermore, the residue of this process contains considerable amount of scandium. The residue can be leached with using H_2SO_4 or HCl to decompose of this and after leaching and filtration processes, solvent extraction method is applied to obtain high purity scandium compound.

According to the literature, after HCl leaching to decompose wolframite residue, DEHPA is preferred as the organic extractant to take scandium from the leach liquor to the organic phase and it is mentioned that conditioning is sometimes applied with ammonium thiocyanate in order to increase scandium extraction. [33] After the extraction with DEHPA, HCl is preferred as the scrubbing reagent and NaOH is used as the stripping reagent in order to obtained $Sc(OH)_3$ precipitate prior to calcination as seen in Figure 2.11. In addition to these, according to some other sources, Primene JMT can be used in the extraction part instead of DEHPA and then HCl acid stripping is carried out. [1,34]

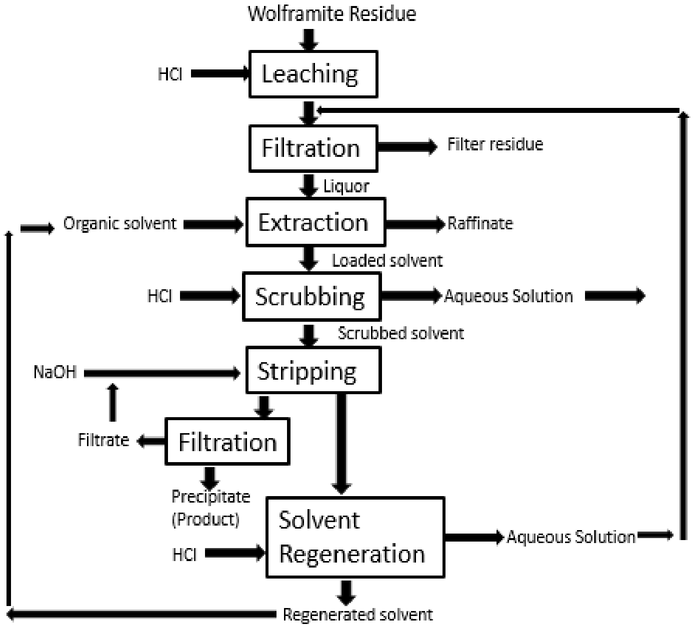

Figure 2.9 Flowsheet of recovery of scandium from the residue of wolframite processing. [33]

2.5.5. Recovery of Scandium as a By-product from Titanium Ore

In ilmenite ore, which is titanium-bearing ore, scandium is originally present in a trace amount such as 0.0104% Sc. During chlorination process to produce TiO_2 pigments from these ores, scandium considerably increases in the slag or waste solution of this process.

According to the literature, the ilmenite slag includes considerable amount of scandium, which is nearly 128 ppm with high concentration of the impurities such as, MgO, CaO, SiO_2, TiO_2 and Al_2O_3. This slag is roasted with Na_2CO_3 and then leached with hydrochloric acid (solid to liquid ratio: 2/1). Then, the obtained leach solution is contacted with the organophosphorus compounds such as HDEHPA and TBP to extract scandium from the solution to organic phase and HCl is used as the scrubbing reagent, while NaOH is preferred as the stripping reagent. After the stripping, $Sc(OH)_3$ precipitate is obtained which is consequently dissolved and precipitated with using different reagents in order to produce high purity scandium oxide at the end of the processes. In addition to these, sometimes HCl or the other strong mineral acids can be used as the stripping reagent in the processes. Furthermore, if the strong mineral acids are used in the stripping of scandium, selective precipitation method should be carried out to obtain the end product which is highly purified scandium compound. [5]

On the other hand, two production methods are present for producing TiO_2 pigments which are sulphate and chloride processes. For example, in the chloride process, scandium sometimes enriches in the waste solution instead of slag. In order to recover scandium from this solution, solvent extraction method should be used and DEHPA or TBP can be used for extraction of scandium from the chloride media. The pH of the solution is also an important parameter in the extraction. Hence, the pH should be adjusted to lower values in order to decrease impurity co-extraction, particularly iron. After extraction, NaOH is used as the stripping reagent at higher pH values to obtain scandium hydroxide precipitate. If there are radioactive elements such as, uranium or thorium, additional steps would be necessary, i.e., iodinate precipitation to produce high purity scandium compound at the end of the process.

In the first stage of TiO_2 production, if waste solution contains sulphate ions, TBP can be preferred as the extraction reagent due to high scandium extraction efficiency in the sulfate media.

In addition to these routes, titanium-bearing wastes can be also obtained during these processes and these wastes can be leached with H_2SO_4 to provide decomposition. After the leaching process, Cyanex 923 can be used as the organic extractant for scandium extraction. Furthermore, H_2O_2 is used as the scrubbing and dilute H_2SO_4 is used as the stripping reagents in this processing route. [1,5,17,28]

2.6. The Methods of Recovery of Scandium

During the recovery process of the desired metal ions from the ore, dissolution processes are carried out and as a result, the other metals can be also dissolved into the solution with the desired metal ions. These metal ions should be separated from each other and the main aim of the separation process is to obtain high quality product at the end of the all processes. These metal ions can be separated by using solvent extraction, ion exchange, electrowining, carbon adsorption, cementation and chemical precipitation methods in general. However, the rare earth metals can be separated by using mainly solvent extraction and ion exchange methods as stated in the literature. [6,34,35,36]

2.6.1. Solvent Extraction

Solvent extraction, i.e., liquid-liquid extraction method, is performed with using organic extractant of which ions are dissolved by using kerosene. Kerosene is immiscible with the aqueous phase, which contains the dissolved metal ions. The organic ions should have the chemical affinity with the desired metal ions in this method in order to take the desired ions from the impure aqueous phase to organic phase. Therefore, it can be stated that in solvent extraction method two immiscible solutions should be used and due to this, it is called liquid-liquid ion exchange method as well solvent extraction.

Industrially, solvent extraction method is generally conducted in the mixer-settler equipment, which is illustrated in Figure 2.12 and this equipment contains two parts, which are mixer and settler part.

While in the mixer part, the mixer provides the dispersion of the organic phase in the aqueous phase to the small droplets that increase ion exchange kinetics. The settler part is for the phase disengagement. In the extraction part, metal ions are selectively absorbed by the organic phase and after this part, the obtained loaded organic phase goes through the scrubbing part in order to remove the co-extracted impurities in the loaded organic phase. Finally, the purified loaded organic phase is stripped generally by using highly acidic solution in order to obtain pure and concentrated solution that includes the desired metal ions.

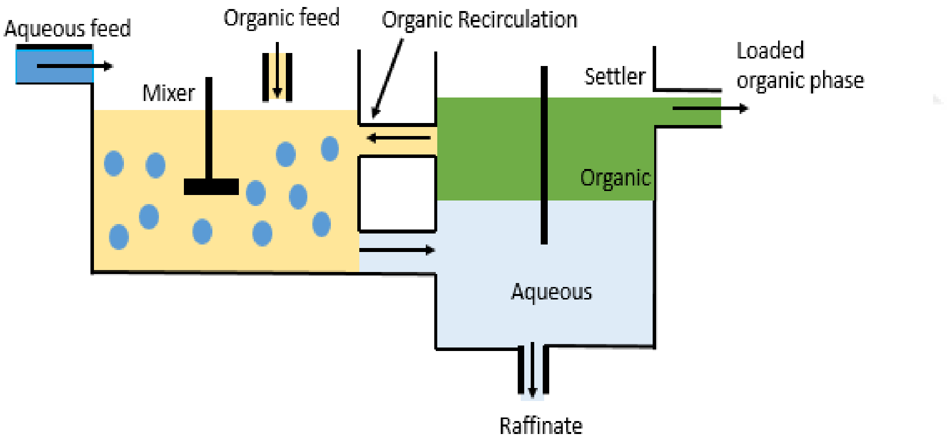

Figure 2.10 A laboratory mixer settler equipment which represents the loading stage of solvent extraction method. [37]

Furthermore, at the end of the process, conditioning is sometimes necessary for aqueous phase in order to recover the residual solvent, which escapes into the aqueous phase during the processing. Conditioning step provides the use of the organic extractant efficiently by preventing solvent loss.

Moreover, crud that may form during both the scrubbing, stripping parts and particularly, the extraction part is the most significant problem in the solvent extraction method. Crud is the mixture, which involves the aqueous, organic and the solid matter, and it has to be removed from the system in order to achieve the extraction with high efficiency. Removing of the crud can be achieved with the modifiers used in the extraction part and/or with applying conditioning process.

Therefore, it can be said that the solvent extraction method includes, the extraction, scrubbing and stripping parts as seen in Figure 2.13 in order to obtain purified and concentrated solution from the impure and dilute leach liquor.

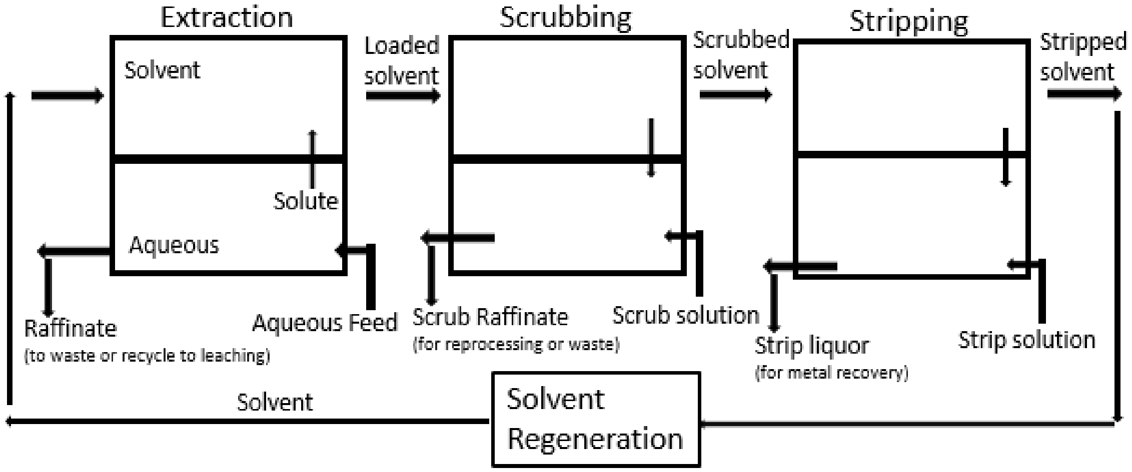

Figure 2.11 Flowsheet of the solvent extraction method. [38]

2.6.1.1. Extraction part

The organic phase mainly involves the diluent, organic extractant and the modifiers if it is necessary for the process. The nature of this phase is very important for successful separation and providing specific chemical selectivity to the organic phase. The diluent such as, alkyl aromatics, naphthenes, paraffin, kerosene (aliphatic), which are mainly water-immiscible oils, helps to distribute the organic extractant droplets in the organic phase.

Therefore, in the process, while the diluent provides successful phase disengagement, the extractant determines the chemical selectivity of the extractant through the metal ions due to presence of its specific functional group in their chemical structures and modifiers is used to for preventing crud and third phase formation. Schematic demonstration of extraction part of solvent extraction is given in Figure 2.14.

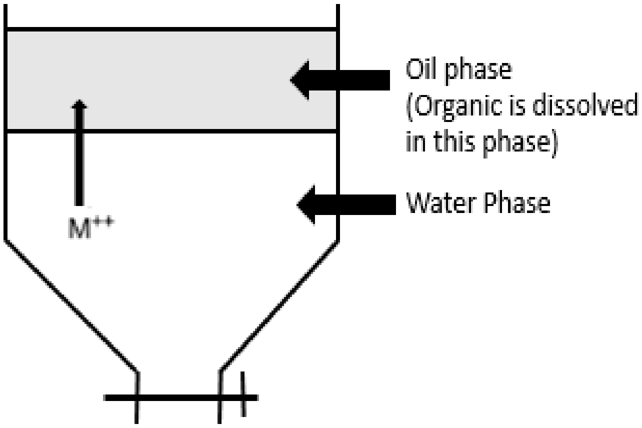

Figure 2.12 Schematic demonstration of extraction part of solvent extraction. [39]

A) Selection of suitable organic extractant

Selection of the suitable organic extractant is the key to the successful extraction with high efficiency. There are some essential parameters for the selection, which are solvent selectivity, distribution coefficient, capacity of the extractant, the solvent solubility, the density of the extractant, recoverability, tendency of the extractant to corrosion, viscosity, flammability and toxicity of the extractant and the cost of the reactant.

- *Solvent selectivity:* Used solvent in the process should have high affinity to extract the desired metal ions selectively from the solution.
- *Distribution coefficient:* The ratio of the concentration of the desired ions in the organic phase to the concentration in the aqueous phase is called distribution coefficient and higher distribution coefficient means easier and more efficient extraction.

- *Capacity of the organic phase:* The used organic extractant in the process should have high extraction capacity. In other words, unless it has high ability to absorb desired ions from the aqueous phase, a large amount of extractant should be used in the extraction processes. The schematic diagram of extraction that shows the capacity of the organic extractant is given in Figure 2.15.

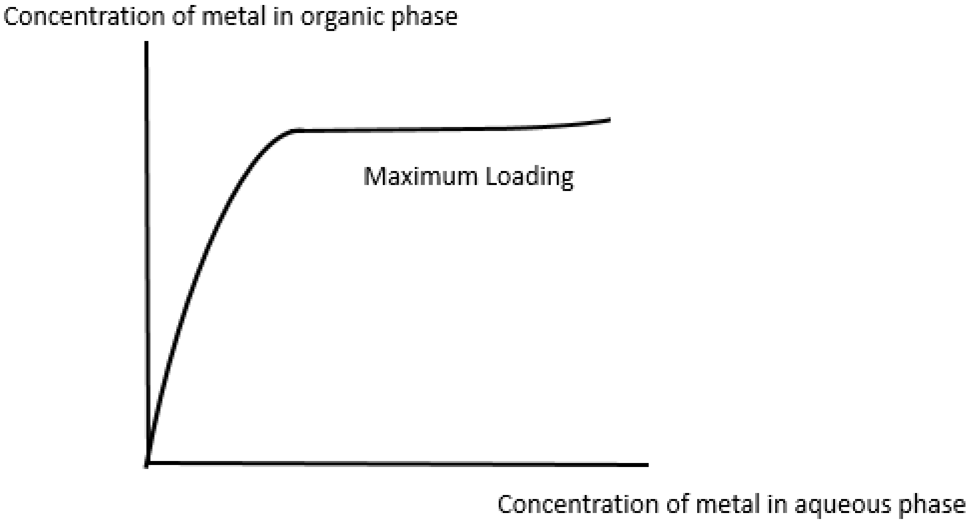

Figure 2.13 The schematic diagram of extraction which shows the capacity of the organic extractant. [6]

- *Solvent solubility:* The used extractant should be insoluble in the aqueous phase. Since in the liquid-liquid extraction processes, two immiscible liquids should be preferred in order to extract and concentrate the desired ion.
- *Density of the extractant:* In order to achieve rapid and easy phase separation, the difference between the density of the organic phase and that of aqueous phase should be as high as possible.
- *Recoverability:* Recycle of the solvent is an essential issue in the solvent extraction method in order to decrease the cost of the total process. Hence, the solvent should be recoverable to achieve this purpose.

- *Tendency of the extractant to corrosion:* In the solvent extraction method, generally special equipment is used, which is called mixer-settler. In order to prevent this equipment from corrosion as used in either laboratory or industry, the chosen organic extractant for the process should not have corrosive properties.
- *Viscosity, flammability and toxicity of the extractant:* In order to provide safe handling, viscosity, flammability and toxicity of the chosen extractant should be as low as possible.
- *Cost of the extractant:* The chosen extractant in the process should be commercially available and inexpensive. [6]

B) Type of the Extractants

The type of the organic extractant is also the other issue in the solvent extraction process in order to determine chemical reactions between the metal ions and the organic extractant and to provide selectivity to the organic phase. There are mainly three different types of extractants with respect to the chemistry of the extraction reactions, which are ion exchange, solvating and coordination extractants. Moreover, each extraction reaction is based on hydration and neutralization regardless of the type of the extractant.

Ion Exchange Extractants

These types of extractants involve cationic and anionic extractants both of which rely on ion exchange mechanism.

- *Cationic Extractants:* These types of extractants are generally acidic compounds and in the extraction reaction, their hydrogen ions and the desired metal ions in the aqueous phase replace with the each other. In the extraction, the strength of acid group is also an important parameter. Since if electronegativity increases between acidic group and the desired metal ion, it means that the extractant becomes more effective in the processes.

For example, carboxyl acids (Versatic acids and Naphthenic acids), alkyl phosphoric acid extractants (DEHPA, EHPA and Cyanex 272). [37]

$\overline{2RH_{org}} + 2M^{+2} \rightarrow \overline{R_2M_{org}} + 2H^{+}_{aq}$ [6] **[Rx 1]**

- *Anionic Extractant:* These types of the extractants are mainly classified as basic extractants and they have excess hydrogen ions in their structures, which react with the hydroxyl or the other anions in the solution. Nevertheless, the industrial usages of these types of the extractants are limited. Moreover, the known anionic extractants, which are used industrially, are amine compounds. These types of the extractants are able to extract complex metallic ions from the aqueous solutions. Some of the examples of these are Primene JMT, Alamine 336 and Aliquat 336. [37]

$B^{n-} + \overline{nR_4N^+A^-} \rightarrow \overline{(R_4N^+)_n}B^{n-} + nA^-$ [6] **[Rx 2]**

Solvating Extractants

Solvating type of the extractants are neutral compounds of which extraction mechanism is based on the transfer of neutral metal complex or salt from the aqueous solution to organic phase. In the first step of the extraction reaction, the metal ions and the water molecules replace with the each other and then ion association occurs which provides neutrality to the organic phase. The solvating extractants generally contain polar oxygen atoms in order to accept the hydrogen ions and the accepted ions come together with the negatively charged metal complexes. The best-known solvating extractants are ketones, ethers, esters, alcohols, phosphates (TBP, tri-n-butyl phosphate) and phosphines (TOPO, trioctyl phosphine oxide). [37] The extraction reaction can be shown as:

$(MA)(H_2O)_m + n\overline{S_{org}} \rightarrow \overline{MA(H_2O)_{m-n}(S)_n} + nH_2O$ [6] **[Rx 3]**

Coordination Extractants

The extraction reaction with using coordination extractants relies on ion dissociation and association in order to form the coordinated complex. The most common coordination extractants are chelating reagents such as; LIX and EDTA that are mainly used in the copper industry. [37]

2.6.1.1.1. General Principles of Extraction Part

The performance of the solvent extraction method is determined with respect to shake out test measurements which tests are carried out by using a separatory funnel. By these measurements, the parameters of the solvent extraction are determined in order to characterize the extraction reactions.

These parameters are distribution coefficient (D), selectivity index (S), percent extracted (E) and extraction isotherm:

- Distribution coefficient,

$$D = \frac{Concentration\ of\ extracted\ element\ in\ the\ organic\ phase\ after\ the\ extraction}{Concentration\ of\ extracted\ element\ in\ the\ aqueous\ phase\ after\ the\ extraction}$$

- Percent Extraction,

$$E\,(\%) = 100 * m_o / (m_o + m_a)$$

  The percentage extraction E (%) states the percentage of extracted species in relation to its total quantity $m_o + m_a$. The variable m_o and m_a represent the quantities of the species under consideration in the organic and aqueous phases, respectively, after reaching equilibrium. m_o is only equal to the amount of extracted substance if fresh unloaded reagent has been used in extraction. So, percent extraction indicates the fraction of the extraction of the specific elements from the feed solution.

- Selectivity index, $S_B^A = \frac{Distribution\ coefficient\ of\ the\ metal\ A\ ions}{Distribution\ coefficient\ of\ the\ metal\ B\ ions}$

  Selectivity index is used to determine the tendency of the extractant through which two elements such as A and B are separated during the extraction.

- Extraction isotherm is a graph that plots the concentration of the specific element in the organic phase to aqueous phase with respect to variable A/O ratios as shown Figure 2.16. Also, these isotherms can be used in order to determine the number of extraction stages for achieving efficient extraction with using McCabe-Thiele Method. [6]

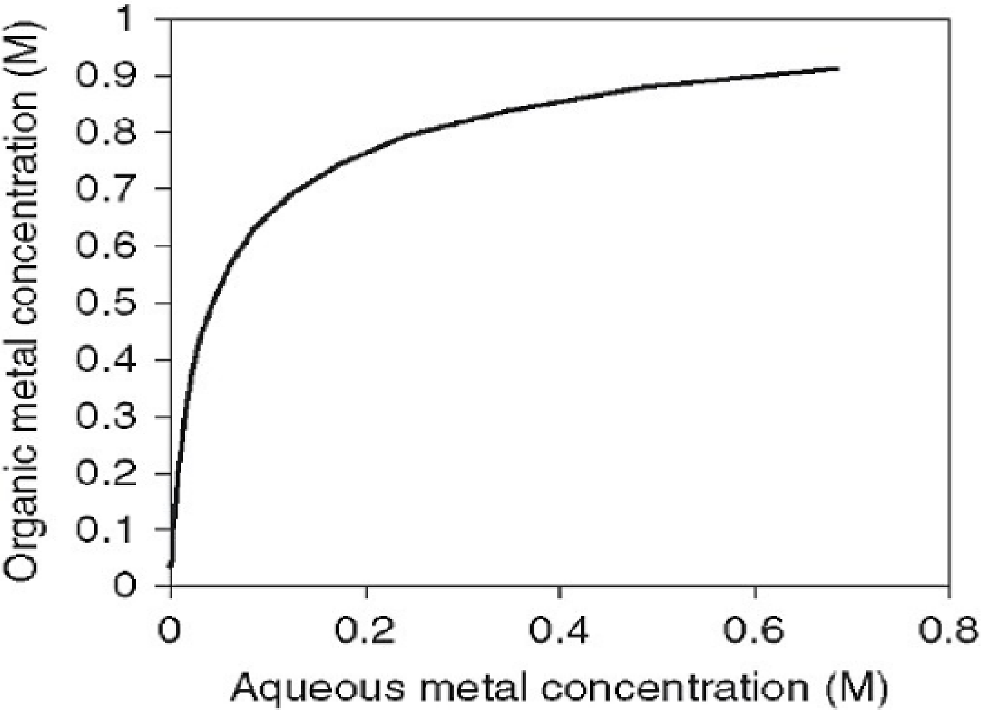

Figure 2.14 Solvent extraction isotherm. [39]

Therefore, the extraction efficiency relies on, the concentration, the pH of the aqueous phase (due to the replacement between H^+ ions in the organic phase and the metal ions in the aqueous phase) and the organic to aqueous phase volume ratio.

2.6.1.1.2. Additives in the Extraction Part

The organic extractant contains not only the organic extractant, but also includes some additives that are the diluent and modifiers**.**

- *Diluent* is the necessary reagent in the extraction part in order to adjust the proper viscosity and the density of the organic phase for better mixing. So, it can be stated that the diluents are used for dissolving or diluting of the extractant which are generally selected from hydrocarbons. The selected diluent can be either aliphatic, aromatic or the mixture of them and this depends on the mechanism of the extraction. However, the diluent has not any capacity to extract the desired ions from the aqueous phase; it only helps to enhance the extraction quality. The used diluents for the industrial purposes should be chosen with odorless property due to the working safety. In Table 2.5, the commonly used diluents are given.

Table 2.6 Industrially used diluents. [38]

Diluent	**Sp. Gravity (20 ℃)**	**Boling Point (℃)**	**Flash Point**
Aromatic			
Benzene	0.833	80	
Tolune	0.873	110	6.6
Xylene	0.870	138	
Solvesso 100	0.876	157	
Solvesso 150	0.931	188	
Shellsol D60	0.78-0.81	179 - 213.9	
EXXSOL D80 Fluid	0798	200 - 250	>77
Medium Aromatic			
Escald 100	0.797	193	
Low Aromatic			
Escaid 100	0.816	199	
Naptha 140 Flash	0.785	60.5	
Aliphatic			
Mineral Spirits	0.785	157	
Odorless 360	0.761	177	
Aliphatic with Napthenes			
Isoparo L	0.767	189	
Shell 140	0.79		
Kermac 470 B	0.81		

- *Modifiers* are sometimes used in order to reduce the potential of the crud formation, to prevent third phase formation and to increase the quality of phase disengagement, as well as to provide high solubility of the metal complexes. The modifiers are selected from either long chain alkyl alcohol such as isodecanol or neutral extractants like TBP. The usage of the modifiers improves the extraction, scrubbing and stripping parts and the known modifiers in the industry are given in Table 2.7.

Table 2.7 List of commonly used modifiers. [38]

Modifier	**Sp. gravity**	**Flash point (℃)**
2- Ethylhexanol	0.833	85
Isodecanol	0.841	104
Nonylphenol	0.95	140
Tri-n-butyl phosphate	0.973	193

2.6.1.1.3. Synergetic Systems

In order to increase the extraction efficiency and the kinetics of the extraction, two different extractants can be used together in the organic phase, whether they are the same type reagents or not. This is known as synergetic systems in the solvent extraction, in which the one component has lower or no extraction ability to the desired metal ions. However, when this component comes together with another component that has high capacity to extract the metal ions, it can be seen that the extraction efficiency and the kinetics of the extraction increase, considerably.

For example, DEHPA has high affinity to extract uranium from the sulfate solutions, while TBP has no capacity to extract uranium. However, when TBP is added into the organic phase together with DEHPA, the extraction efficiency of uranium from the solution significantly increases. Moreover, LIX 63 and LIX 65 are commonly used together in the copper industry and it is known that LIX 63 increases the kinetics of the copper extraction.

Therefore, DEHPA+TBP and DEHPA+TOPO in uranium and rare earth metals extraction, LIX 63+LIX65 in the copper industry are the important examples of the synergetic systems. [6]

2.6.1.2 Scrubbing and Striping Part

- *Scrubbing part:* The main aim of this part is to remove the impurities, which are co-extracted to the organic phase with the main metal ions that are still present in the solution. For the scrubbing purposes, acidic or alkali solutions are used by adjusting the pH of these solutions to the proper values, which should be chosen with respect to not only the behaviors of impurities, but also the behaviors of the desired metal ions at that pH. [39,40,41,42]

- *Stripping part:* After the scrubbing part, highly purified loaded organic phase is obtained which is concentrated with the desired metal ions. The aim of the stripping part is to re-take these metal ions from the purified loaded organic phase to aqueous phase, called as strip solution. In other words, stripping process is the reverse of the extraction process. Mainly highly acidic solutions or sometimes alkali solutions can be used as the strip solution again at the proper pH for stripping of the desired metal ions, selectively.

2.6.2. Ion Exchange Method

The mechanism of the ion exchange is similar to the solvent extraction. However, in the ion exchange method, the extraction reactions take place between the impure aqueous solution and the insoluble solid resin that is substituted for the liquid organic extractant in the solvent extraction method.

The ion exchange is more precise than the solvent extraction, since it can achieve extraction of extremely low quantities of the ions and increases their concentration. Therefore, although the solvent extraction is more prevalent process, the ion exchange method is more preferable and economic process for the extraction of low concentration of the metals.

The ion exchange method mainly includes adsorption and elution parts, which have similar mechanisms with the extraction, and stripping parts, respectively:

- *Adsorption part:* In this part, the aqueous solution passes through the resin beds. As a result of this, cationic or anionic resins can achieve to take the metal ions from the aqueous solution.
- *Elution part:* The suitable solution passes through the loaded resin beds in order to take the metal ions into the solution, selectively. At the end of this part, the purified and concentrated solution is obtained.

Ion exchange resins can be divided into two parts, which are cationic and anionic resins, as shown Table 2.8. Flowsheet of the ion exchange method is given in Figure 2.17.

Table 2.8 Some examples of cationic and anionic resins.

Cationic Resins		**Anionic Resins**	
Analite	$(Na[Si_2ALO_6].H_2O)$	Kaolinite	$(Al_4[Si_4O_{10}][OH]_8)$
Chabazite	$([Ca,Na][Si_2ALO_6]_2.6H_2O)$	Hydroxapatite	$(Ca_2(PO_4)_2Ca_2]OH)$
Montmorillonite	$(Al_2[Si_4O_{14}(OH)_2].nH_2O)$		

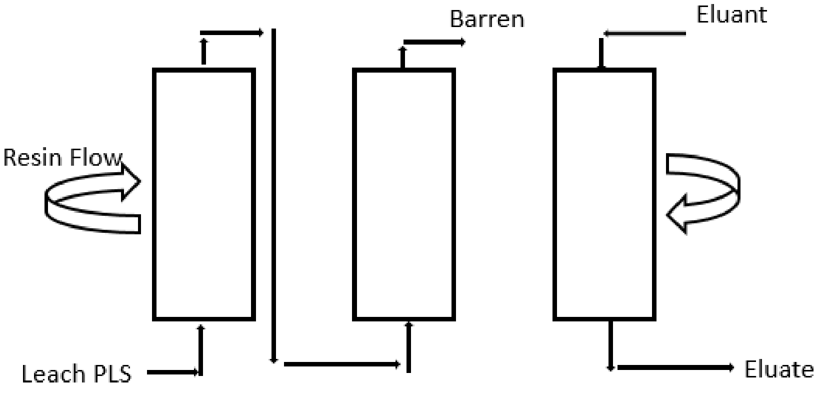

Figure 2.15 Flowsheet of the ion exchange method. [6]

The steps of the ion exchange method:

- The leach liquor passes through the resin columns until almost all of the desired metal ions are taken from the PLS to the solid and insoluble resin. This is the adsorption part and at the end of this part, the obtained effluent solution is called as barren solution.
- After the adsorption part, the columns should be rinsed and backwashed with water in order to clean the impurities remaining after adsorption for the later processes.
- Then, the loaded resin goes through elution by using the proper eluent in order to separate the metal values from each other.
- The purified and concentrated solution (eluate) containing the desired metal is obtained which may pass thorough the precipitation processes in order to obtain the suitable metal compound precipitate for the recovery.

Therefore, ion exchange method is used for the purposes:

- To concentrate and purify the metal ions in the leach liquors.
- To recover the metal ions from the mine waters or tailing streams.
- To separate the metal ions which has similar chemical properties with each other from the leach solutions e.g., rare earth metals. [6]

CHAPTER 3

EXPERIMENTAL MATERIALS AND METHODS

3.1. Introduction to the Preparation of PLS

In Nikel Kobalt Madencilik A.Ş. (META) company titanium lined autoclave is used for the processing of laterite nickel-cobalt ores after up-grading by physical concentration methods to produce mixed nickel-cobalt hydroxide precipitate. At the end of the process, the intermediate product obtained is called mixed hydroxide precipitate (MHP). The flowsheet of MHP production at Gördes is given in Figure 3.1.

According to the production circuit of MHP as given in Figure 3.1, after the ore preparation and high pressure acid leaching process (HPAL), the obtained leach solution includes non-ferrous dissolved metal ions, particularly nickel, cobalt and the other elements, such as, magnesium, iron, aluminum, chromium, manganese, scandium and trace amount of the other metal ions. In this method, the control of the pH and the temperature of the solution are important parameters. Therefore, the solution passes through two neutralization stages prior to the precipitation of MHP product in order to remove impurities from the solution.

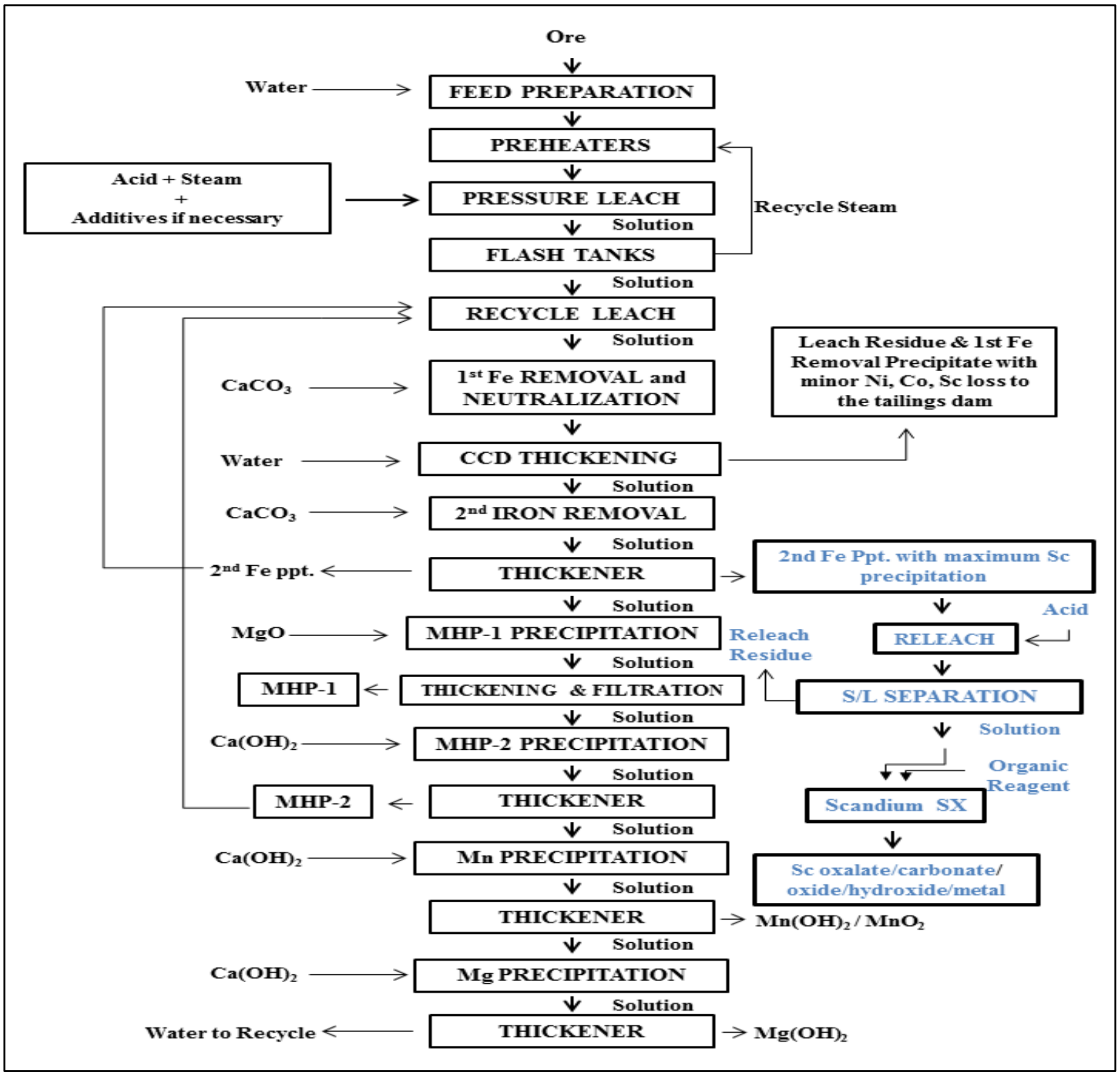

Figure 3.1 Mixed hydroxide precipitation (MHP) circuit. [43]

According to the solubility data of ions at the room temperature, the dissolved ions in the aqueous solution precipitate in the order of Fe(III) > Al(III) > Sc(III) > Cr(III) > Cu(II) > Fe(II) > Zn(II) > Ni(II) > Co(II) > Mn(II) > Mg(II) > Ca(II) with increasing pH as seen in Figure 3.2. [44,45]

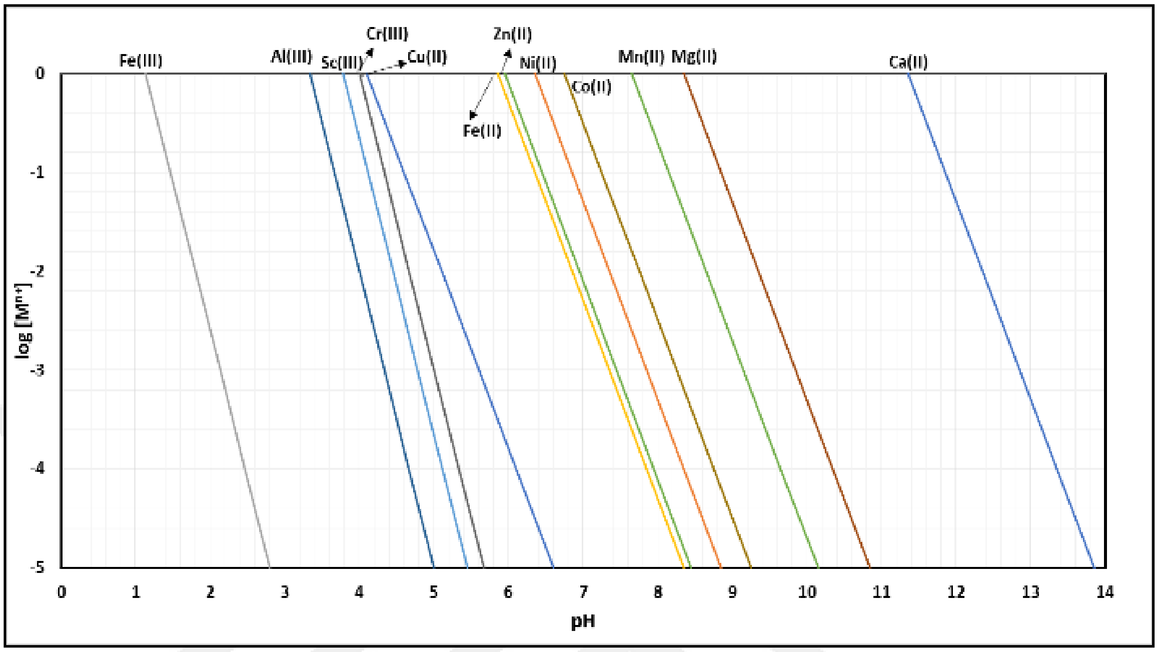

Figure 3.2 The solubility product data of ions at 25°C according to molar concentration of ions. [44,45]

With respect to these data, it can be stated that the aim of the first neutralization part in MHP production circuit is to precipitate the maximum amount of iron and the limited amounts of aluminium and chromium from the solution with the minimum nickel, cobalt and scandium losses. For this reason, the pH of the solution is controlled at about 2.75 in the process. Then, the second neutralization is carried out in order to remove impurities still remaining in the solution particularly; iron, aluminium and other impurities which are predicted to precipitate at about pH=4.75. According to the solubility data, it can be said that the maximum scandium precipitation occurs at the second neutralization stage.

Therefore, the scandium recovery process starts after this point with the formed precipitate. On the other hand, in MHP production circuit, after these two neutralization stages, the purified solution passes through further precipitation processes, which are conducted to obtain MHP product and to clean the remaining solution after obtaining intermediate product of nickel and cobalt for being recycled back to the circuit. [23,46]

Therefore, it can be stated that in the mixed nickel-cobalt hydroxide precipitation (MHP) production circuit, the scandium enriched precipitate is obtained after the pH controlled secondary purification process and solid-liquid separation with a thickener. The obtained precipitate named as secondary neutralization underflow (SNU), is re-leached with 100 g/L H_2SO_4 for 1 hour at 60°C temperature in order to take considerable amount of scandium into solution. After the following solid-liquid separation (S/L) in a press filter, the solution passes through the neutralization part in which the solution is purified at about pH 2.5 by using $CaCO_3$ slurry at about 90°C. As a result, the scandium rich pregnant leach solution (PLS) is finally obtained. [46]

This study was started after obtaining the purified pregnant leach solution from the secondary neutralization precipitate and solvent extraction method was carried out for the extraction and recovery of scandium from this solution. In the literature, similar recovery process of scandium has been carried out from MSP (mixed sulphide precipitate) production circuit in the CORAL BAY. However, sulphur content is the major problem in this process. Due to this reason, additional processes are necessary for recovery of scandium from MSP production circuit. The leach residue which contains high amount scandium should be neutralized and a sulphidation agent should be added in order to obtain nickel sulphate as the main product of the process and separate scandium from the residue to the sulfuration liquid. Due to lower Sc content, this liquid passes through ion exchange process instead of solvent extraction method for recovery of scandium. [54]

In the first part of this thesis study, the different organic extractants and the suitable conditions for extraction such as, the effect of modifiers and diluent in the organic phase, the effect of the volume ratio of the aqueous to organic phases and the effect of the pH of the pregnant leach solution on extraction efficiency, were investigated in order to extract the highest amount of scandium with less impurity co-extraction from the solution. The organic extractants are classified as acidic, neutral and basic reagents. Therefore, since the aim of the first part of the study is to find a suitable extractant for scandium extraction, the extraction efficiencies of the different types of organic reagents were compared with each other.

For this reason, the acidic organophosphorus compounds which are Ionquest 801 (Bis(2-ethylhexyl) phosphate), DEHPA (Di(2-ethylhexyl) phosphoric acid), Cyanex 272 (Bis(2,4,4-trimethylpentyl) phosphinic acid), a neutral organophosphorus compound; such as, Cyanex 923 (Trialkyl phosphine oxide) and a basic extractant, Primene JMT were tested. After determining the appropriate extractant, the effect of the modifiers, which were TBP (tri-butyl phosphate) and isodecanol, the long chain alkyl alcohol, on scandium extraction were examined. Modifiers are generally used with the main extractant in order to decrease the possibility of third phase formation and improve the quality of phase separation, particularly. Therefore, these modifiers were tried with different volume percentages at the same A/O ratio, which was 1/1. Then, the effect of diluent in the organic phase was examined and for this purpose, different types of kerosene that were D60 and D80 were investigated. The flash point of D60 is nearly 60°C and the other one's is 80°C. After determining the proper composition of organic phase and appropriate extractant modifier and kerosene type in the organic phase, the parameters that were related to aqueous phase was started to be examined. For this purpose, the effect of the pH of the pregnant leach solution on extraction and the suitable organic to aqueous phase ratio (O/A) were investigated. In the second part, the appropriate scrubbing reagent was tried to be determined for cleaning impurities from the loaded organic phase that were co-extracted with scandium in the extraction part. For this purpose, different scrubbing reagents such as; sulphuric acid, hydrochloric acid and oxalic acid, were examined in the second part of study with the proper A/O ratio. In addition to these, the necessary number of stages was tried to be determined for both the extraction and scrubbing parts by using McCabe-Thiele Method. [51,52]

3.2. Pregnant Leach Solution Characterization

The pregnant leach solution (PLS) which was used in the extraction experiments, the loaded organic prepared with respect to the results of the extraction experiments and used in the scrubbing part were analyzed with inductively coupled plasma optical emission spectrophotometer (ICP-OES) in META chemical analysis laboratory in Gördes and the composition of PLS is given in Table 3.1.

Table 3.1 Composition of PLS and loaded organic (ppm).

Elements	**Al**	**As**	**Ca**	**Co**	**Cr**	**Cu**	**Fe**	**Mg**	**Mn**	**Na**	**Ni**	**Sc**	**Zn**
PLS	15549	33	640	294	405	92	2356	328	203	6	5598	46	137
Loaded Organic	5	<1	<1	<1	<1	<1	1252	<1	<1	<1	<1	463	<1

3.3. Experimental Procedures

After the re-leaching and purification parts, the pH of the obtained pregnant leach solution was reduced from 2.5 to 0.8 with the addition of sulfuric acid. Since according to the literature, the pH of the solution should be as low as possible in order to provide superior scandium extraction efficiency and selectivity. [14] Both extraction and scrubbing experiments were conducted in a 250 ml beaker with magnetic stirring and the following phase separations were done by using a separatory funnel. After having determined the suitable conditions for extraction, the loaded organic phase stock was prepared for scrubbing part by the experiment that was carried out under the previously determined conditions in a 2000 ml beaker.

The experiments were performed with O/A: 1/1 phase ratio in order to determine the proper extractant, diluent, modifier and scrubbing reagent, and the appropriate conditions for both the extraction and scrubbing parts. On the other hand, the experiments which were carried out in order to determine the proper O/A ratio for both parts of the process were performed with different volume ratios such as O/A: 1/1, 1/3, 1/5, 1/7, 1/10, 1/15 in extraction and A/O: 1/1, 3/1, 5/1, 7/1, 10/1, 15/1 in scrubbing.

Furthermore, all of the experiments were conducted at room temperature (25°C ± 1) and for 10 minutes mixing duration in aqueous continuous mode. The chemical analyses of aqueous phase after each experiment were done by using ICP-OES.

CHAPTER 4

RESULTS AND DISCUSSION

Solvent extraction is the method for recovery, extraction and purification of the desired elements from the impure pregnant leach solution. This method has three different stages, which are extraction, scrubbing and stripping parts. In this study, extraction and scrubbing parts were taken into consideration and the investigation was divided into two parts. In the first part, the main aim was to provide the highest scandium extraction with low impurity co-extraction and hence, the suitable conditions, such as appropriate regents and the composition of these in the organic phase, the pH of the aqueous solution and the volume ratio of the aqueous to organic phases (A/O) for the extraction were investigated. Then, the loaded organic phase stock was prepared in the determined extraction conditions for scrubbing experiments.

In the second part of the study, the impurities co-extracted were taken into consideration and the suitable scrubbing reagents were started to be investigated. In this part, iron was accepted as the main impurity due to its concentration in the loaded organic phase, and the chemical and physical similarities between scandium and iron ions. In consideration of this, the different scrubbing reagents were tried in order to determine the appropriate reagent and the conditions, such as the volume ratio of the aqueous to organic phases (A/O) and the number of stages for removing the highest amount impurities from the loaded organic phase.

4.1. Extraction of Scandium from Pregnant Leach Solution

In the extraction part, scandium was extracted from the leach liquor by means of the suitable organic phase that included the organic extractant, modifier and the diluent in the proper composition. However, the extraction efficiency was affected by different parameters, some of which were related to the organic phase and some of the others depended on the aqueous phase. Therefore, this part was divided into two based on the parameters with respect to the relationship between the organic phase and the aqueous phase.

Moreover, in this part, as well as iron; aluminum, nickel and cobalt were taken into consideration as the main impurities. Aluminum ions, like iron, have similar properties with scandium ions in the reactions and in the extraction processes since they all have three valance electrons. Moreover, nickel and cobalt were also important impurities in PLS, because scandium was being extracted and recovered during HPAL processing of lateritic nickel-cobalt ores and for this reason, the extraction behavior of nickel and cobalt were also investigated in the process.

4.1.1. Organic Part

The organic phase consisted of the extractant, modifier and diluent in the proper composition. Therefore, the selection of the suitable reagents for the stated aims and the determination of the proper composition for the extractant were very essential to obtain high extraction efficiency of scandium with low impurity concentration in the loaded organic phase. Therefore, initially the selection of the extractant, diluent and modifier with appropriate amounts were the main purposes of this part of the study.

4.1.1.1. Determination of the Proper Organic Extractant for Scandium

In order to determine the proper reagent for scandium, different organic reagents were investigated in this study. Ionquest 801 (Bis(2-ethylhexyl) phosphate), DEHPA (Di(2-ethylhexyl) phosphoric acid), Cyanex 272 (Bis(2,4,4-trimethylpentyl) phosphinic acid), Cyanex 923 (Trialkylphosphine oxide) and Primene JMT were used with different volume percentages in kerosene D60, as shown in Table 4.1. The used volume percentages were determined with respect to the capacity of the organic extractant. The analytical data obtained are given in the Appendix.

Table 4.1 Some of the extractants used in the experiments with chosen volume %

Type of the used extractant	**Used organic extractants for extraction**		**Volume percentages of the extractant in diluent (D60)**
Acidic Reagents	Ionquest 801	Bis(2,4,4-trimethylpenthyl) phosphonic acid	3 vol%
			4 vol%
			5 vol%
			6 vol%
			7 vol%
	DEHPA	Di(2-ethylhexyl) phosphoric acid	2 vol%
			3 vol%
			4 vol%
			5 vol%
			6 vol%
	Cyanex 272	Bis(2,4,4-trimethylpentyl) phosphinic acid	2 vol%
			3 vol%
			4 vol%
			5 vol%
			6 vol%

Neutral Reagent	Cyanex 923	Trialkylphosphine oxide	3 vol%
			4 vol%
			5 vol%
			6 vol%
			7 vol%
Basic Reagent	Primene JMT	C16-22-tert-alkyl; 16,16dimethylheptadecan-1-amine	5 vol%
			6 vol%
			7 vol%
			8 vol%
			9 vol%

A. Extraction of Scandium from Sulfate Media by DEHPA

Di(2-ethylhexyl) phosphoric acid (DEHPA or HDEHP) is an acidic organophosphorus compound whose formula is $(C_8H_{17}O)_2PO_2H$. It is commonly used in several hydrometallurgical processes; such as, the separation and purification of uranium, zinc, copper, cobalt, manganese, and rare earth metals.

The used volume percentages were determined with respect to:

- Basis of 100 ml organic phase that includes 1 ml DEHPA with 99 ml kerosene D60.

$$Sc^{+3}_{(aq)} + 3\{H^{+} - DEHPA\}_{(org)} = 3H^{+3}_{(aq)} + Sc(DEHPA)_{3_{(org)}} \qquad \textbf{[Rx 4]}$$

- 1 ml DEHPA is $\frac{the\ density\ of\ DEHPA:\ 0.965\frac{gram}{liter}}{the\ molecular\ weigth\ of\ DEHPA:\ 322\frac{gram}{mol}} = 2.997\ x10^{-3}mol$

- Therefore, $2.997\ x10^{-3}mol$ DEHPA can be loaded with maximum 44.92 mg Scandium according to the following calculation:

$$\frac{2.997\ x\ 10^{-3} mol}{3}\ x\ atomic\ weight\ of\ scandium\ 44.96\,\frac{gram}{mol}$$

$$= 44.92\ mg\ Sc$$

- Pregnant leach solution used in the experiments contained 46 mg scandium per liter and 100 ml organic phase that included 1% DEHPA can load 44.92 mg scandium theoretically. Considering the presence other metals in PLS, the volume percentage of DEHPA was started to be tried from 2 to 6 vol% in kerosene D60 in the experiments.

According to Figure 4.1, DEHPA extracted scandium with low impurity co-extraction. It was noticed that the scandium extraction was completely achieved and the amount of iron, cobalt, aluminum and nickel co-extractions were limited. Furthermore, more DEHPA concentration in the organic extractant means more hydrogen ions. Hence, more hydrogen ions can be replacing with scandium and the other metals. For this reason, the volume percentage of DEHPA in the organic phase should be adjusted, properly. If the volume percentage of DEHPA is increased too high values, the impurity co-extraction also increases dramatically. On the other hand, if the volume percentage of DEHPA is too low in the kerosene, the extraction efficiency of scandium decreases considerably. Since hydrogen ions in the organic phase is not enough to replace with scandium ions in pregnant leach solution, efficiently.

Thus, it can be stated that according to the experimental findings, the efficiency of scandium extraction with 5% DEHPA in kerosene D60 was approximately 96% with low impurity concentrations in the loaded organic phase. Moreover, it was found out that, the higher volume percentages of DEHPA addition meant higher impurity co-extractions, especially iron. As a result, 5 vol% DEHPA in kerosene D60 was chosen as the suitable condition for the scandium extraction. This choice was also related to the need of recycling of the organic in a continuous process.

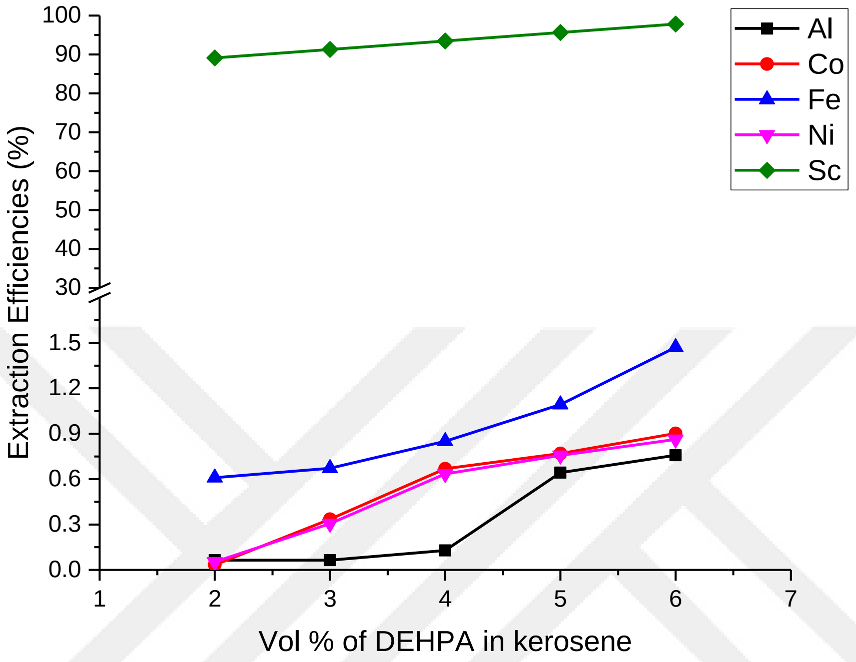

Figure 4.1 Extraction efficiencies of Sc, Fe, Co, Ni, Al with increasing volume percentage of DEHPA in kerosene D60.

B. Extraction of Scandium from Sulfate Media by Cyanex 272

CYANEX 272 extractant is a phosphinic acid which is acidic organophosphorus compound with $(C_8H_{17})_2P(O)OH$ formula. It is the proper reagent for separating cobalt from nickel and it is extensively used in the extraction and separation of rare metal earths and zinc.

The used volume percentages were determined with respect to:

- Basis of 100 ml organic phase that includes 1 ml Cyanex 272 with 99 ml kerosene D60.

$$Sc^{+3}_{(aq)} + 3\{H^{+} - Cyanex\ 272\} = \ 3H^{+3}_{(aq)} + Sc(Cyanex\ 272)_{3_{(org)}} \qquad \textbf{[Rx 5]}$$

- 1 ml Cyanex 272 is $\frac{the\ density\ of\ Cyanex\ 272:\ 0.92\frac{gram}{liter}}{the\ molecular\ weigth\ of\ Cyanex\ 272:\ 290\frac{gram}{mol}} = 3.172\ x10^{-3}mol$

- Therefore, $3.172\ x10^{-3}mol$ Cyanex 272 can be loaded with maximum 47.54 mg scandium according to the following calculation:

$$\frac{3.172\ x\ 10^{-3}mol}{3}\ x\ atomic\ weight\ of\ scandium\ 44.96\frac{gram}{mol}$$

$$= 47.54\ mg\ Sc$$

- Pregnant leach solution used in the experiments contained 46 mg scandium per liter and according to the theoretical calculations, 100 ml organic phase, which includes 1% Cyanex 272, is able to extract 47.54 mg scandium. Hence, in the experiments, the volume percentage of Cyanex 272 was chosen to vary between 2 to 6 vol% in kerosene D60.

According to Figure 4.2, although the maximum scandium extraction with low impurity concentration in the loaded organic phase was achieved by using 6 vol% Cyanex 272 in kerosene D60, as a result of the comparison of the scandium extraction efficiencies of DEHPA and Cyanex 272, it can be stated that the scandium extraction efficiency of Cyanex 272 was extremely lower than DEHPA, nearly 21%.

Thus, it can be said that Cyanex 272 is not the proper reagent for scandium extraction from the pregnant leach solution under investigation.

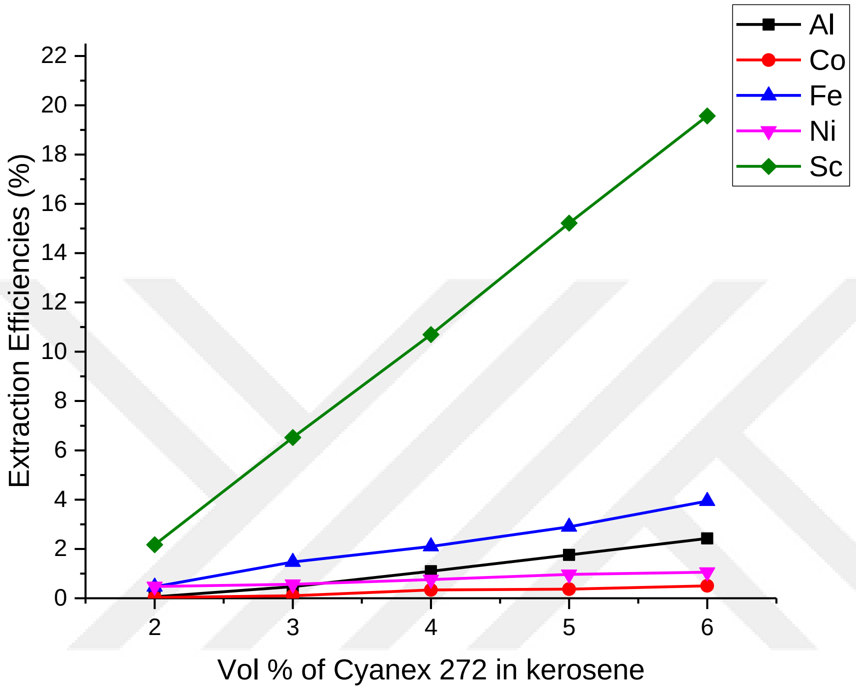

Figure 4.2 Extraction efficiencies of Sc, Fe, Co, Ni, Al with increasing volume percentage of Cyanex 272 in kerosene D60.

C. Extraction of Scandium from Sulfate Media by Ionquest 801

Ionquest 801 is Bis(2-ethylhexyl) phosphate which is also an acidic organophosphorus compound. It is mainly used in the extraction process of zinc from sulfate or chloride media. Moreover, it is used in the extraction and purification of the other cations; such as, copper, nickel and aluminum. [50]

The used volume percentages were determined with respect to:

- Basis of 100 ml organic phase that includes 1 ml Ionquest 801 with 99 ml kerosene D60.

$$Sc^{+3}_{(aq)} + 3\{H^{+} - \text{Ionquest 801}\} = 3H^{+3}_{(aq)} + Sc(\text{Ionquest 801})_{3_{(org)}} \qquad \textbf{[Rx 6]}$$

- 1 ml Ionquest 801 is $\frac{the\ density\ of\ Ioquest\ 801:\ 0.965\,\frac{gram}{liter}}{the\ molecular\ weigth\ of\ Ionquest\ 801:\ 322.42\,\frac{gram}{mol}} =$ $2.999\ x10^{-3}mol$

- Therefore, $2.999\ x10^{-3}mol$ Ionquest 801 can extract maximum 44.94 mg of scandium according to the following calculation:

$$\frac{2.999\ x\ 10^{-3}mol}{3}\ x\ atomic\ weight\ of\ scandium\ 44.96\,\frac{gram}{mol}$$
$$= 44.94\ mg\ Sc$$

- Pregnant leach solution included 46 mg scandium per liter and according to the theoretical calculations; the maximum loading capacity of the 100 ml organic phase that included 1% Ionquest 801 is 44.94 mg scandium. Therefore, the volume percentage of Ionquest 801 was used between 3 to 7 vol% in kerosene D60 in the experiments.

According to Figure 4.3, Ionquest 801 was not the appropriate extractant for scandium extraction from the sulfate solution under study. Since, not only the scandium extraction, but also the control of co-extraction of the other metals from pregnant leach solution (PLS) could not be achieved with using this extractant regardless of changing to the volume percentage of the extractant. According to the literature, in order to achieve high scandium extraction efficiency, multiple extraction processes can be carried out. By multiple processes, the impurities that cause some problems in the extraction of scandium can be partially eliminated. [31]

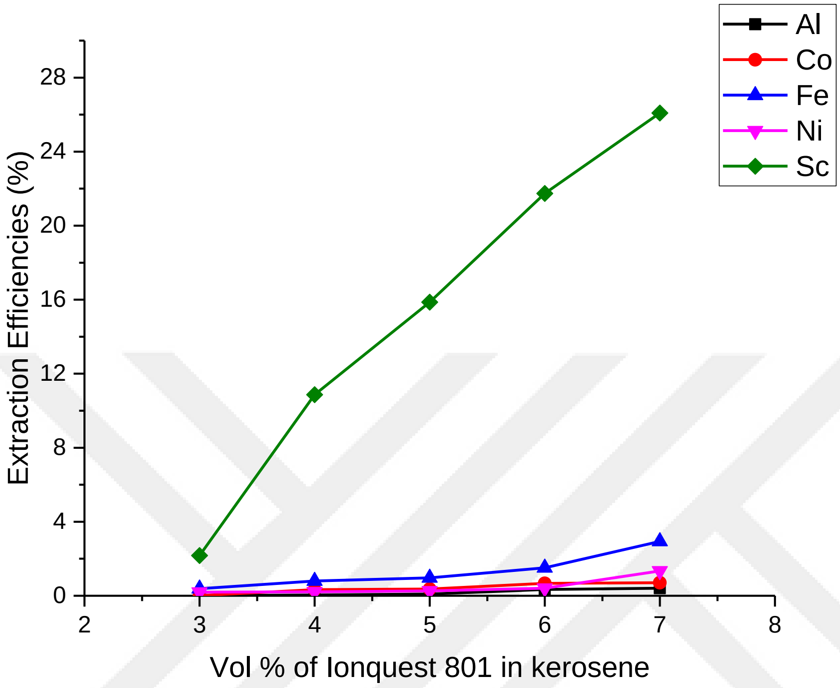

Figure 4.3 Extraction efficiencies of Sc, Fe, Co, Ni, Al with increasing volume percentage of Ionquest 801 in kerosene. D60.

D. Extraction of Scandium from Sulfate Media by Cyanex 923

Cyanex 923, similar to TOPO according to the literature, is liquid Trialkylphosphine oxide and it is a neutral organophosphorus reagent. The main applications of this extractant are in the solvent extraction processes and the recovery of solutes; for example, it can be used in the removal of arsenic impurities from copper electrolytes. Furthermore, this organic extractant sometimes is used as modifier in the solvent extraction systems. However, in this study, Cyanex 923 was used as the organic extractant based on the literature. D. Li and Wang have investigated the extraction process of scandium from sulfate media in their study and they have achieved high scandium extraction efficiency with low impurity co-extractions at the end of the process while using Cyanex 923 as the organic extractant. [47,50]

Also, the volume percentages used in the experiments were determined with respect to:

- Basis of 100 ml organic phase that includes 1 ml Cyanex 923 with 99 ml kerosene D60.

$$\frac{Sc_2(SO_4)_3.5(H_2O)_{aqu} + 3\{\text{Cyanex 923 }\}_{org}\ 3H_2O_{aqu} +}{Sc_2(SO_4)_3.2(H_2O).3\{Cyanex\ 923\}_{org}}$$ **[Rx 7]**

The reaction is different from cationic and anionic extractants, since the extraction mechanism of the neutral reagents is generally based on the transfer of the metal complexes from the aqueous solution to the organic phase.

- 1 ml Cyanex 923 is: $\frac{the\ density\ of\ Cyanex\ 923:\ 0.88\frac{gram}{liter}}{the\ molecular\ weigth\ of\ Cyanex\ 923:\ 348\frac{gram}{mol}} = 2.529\ x10^{-3}mol$

- Therefore, $2.529\ x10^{-3}mol$ Cyanex 923 can load 37.90 mg scandium according to the following calculation:

$$\frac{2.529\ x\ 10^{-3}mol}{3}\ x\ atomic\ weight\ of\ scandium\ 44.96\frac{gram}{mol}$$
$$= 37.90\ mg\ Sc$$

- Pregnant leach solution included 46 mg scandium per liter and according to the theoretical calculations, 100 ml organic phase with 1% Cyanex 923 is able to load approximately 37.90 mg scandium. Consequently, the volume percentage of Cyanex 923 was chosen between 3 to 7 vol% Cyanex 923 in kerosene D60, in the experiments.

According to the results in Figure 4.4, only low amount of scandium could be extracted by using Cyanex 923 as the organic extractant. In addition to this, if the amount of the impurity co-extractions of Cyanex 923 was compared with the other extractants, it could be stated that Cyanex 923 co-extracted higher amount of impurities than the acidic reagents such as DEHPA, Cyanex 272 and Ionquest 801.

Thus, according to the results, it was concluded that this organic reagent was not suitable for both the scandium extraction and the limited co-extraction of impurities from the solution.

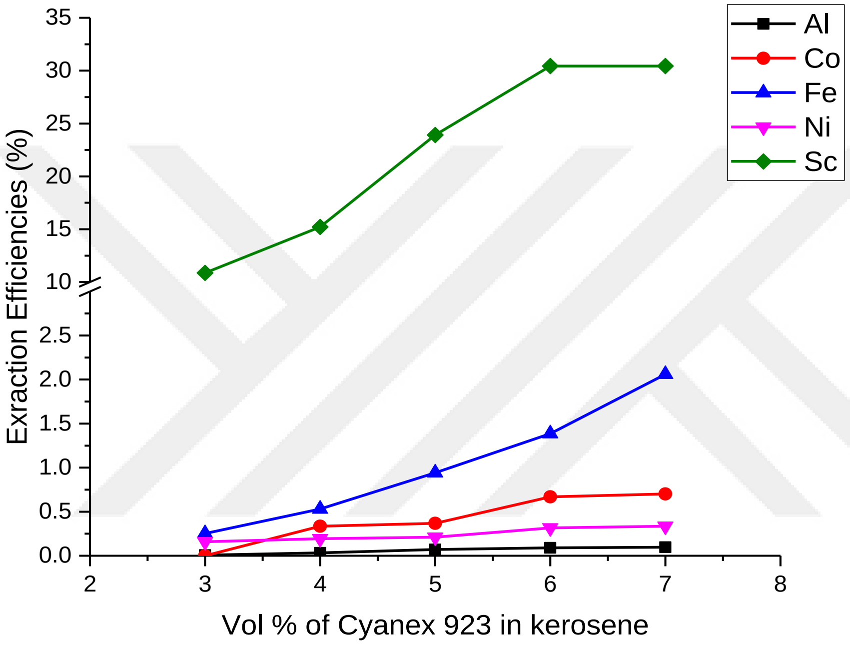

Figure 4.4 Extraction efficiencies of Sc, Fe, Co, Ni, Al with increasing volume percentage of Cyanex 923 in kerosene D60.

E. Extraction of Scandium from Sulfate Media by Primene JMT

Primene JMT, which is a basic organic extractant, is a unique member of the family of primary amines. Primene JMT has many special properties such as, resistance to oxidation, high fluidity, low viscosity and high solubility in hydrocarbons i.e., kerosene. Furthermore, this reagent can be used as the lubricant or fuel additive as well as an organic extractant for the solvent extraction processes. Industrially, Primene JMT is extensively used in the extraction, separation and purification of uranium and the other rare earth metals. [14,50] Moreover, the volume percentages used in the experiments were determined with respect to:

- Basis of 100 ml organic phase, which includes 1 ml Primene JMT with 99 ml kerosene D60.

$$2Sc(SO_4)_3{}^{3-}{}_{aqu} + 3\overline{(\mathrm{RN}H_3)_2SO_4}_{org} = 3SO_4{}^{2-}{}_{aqu} + 2\overline{(RNH_3)_3Sc(SO_4)_3}_{org}$$

[Rx 8]

Primene JMT is represented as $\overline{(\mathrm{RN}H_3)_2SO_4}$ in the equation.
The reaction is different from the all of the other reagents used in this investigation, since the extraction of the basic reagents takes place between the anions and the excess hydrogen ions which are present in the structure of the extractant. [6,53]

- 1 ml Primene JMT is: $\frac{the\ density\ of\ Primene\ JMT:\ 0.819\frac{gram}{cm^3}}{the\ molecular\ weigth\ of\ Primene\ JMT:\ 283.54\frac{gram}{mol}} = 2.888\ x10^{-3}mol$

- Therefore, $2.888\ x10^{-3}mol$ Cyanex 923 can load 43.28 mg scandium according to the following calculation:

$$\frac{2.888x\ 10^{-3}mol}{3}\ x\ atomic\ weight\ of\ scandium\ 44.96\frac{gram}{mol}$$
$$= 43.28\ mg\ Sc$$

- The Pregnant leach solution used in the investigation included 46 mg scandium per liter and according to the theoretical calculations, 1% Primene JMT in 100 ml organic phase can load 43.28 mg scandium. Consequently, the volume percentage of Primene JMT was adjusted between 3 to 9 vol% Primene JMT in kerosene D60, in the experiments.

According to the results given in Figure 4.5, Primene JMT could extract scandium with high efficiency that was approximately 94% from the sulfate medium. Moreover, this extractant provided low impurity co-extraction similar to DEHPA.

The increasing volume percentage of the extractant means increasing the amount of the functional group in the organic phase, which can react with scandium, and the other ions present in pregnant leach solution (PLS). Thus, in order to obtain high scandium extraction efficiency with limited impurity co-extractions, 8 vol% of Primene JMT was the proper amount for the extraction process.

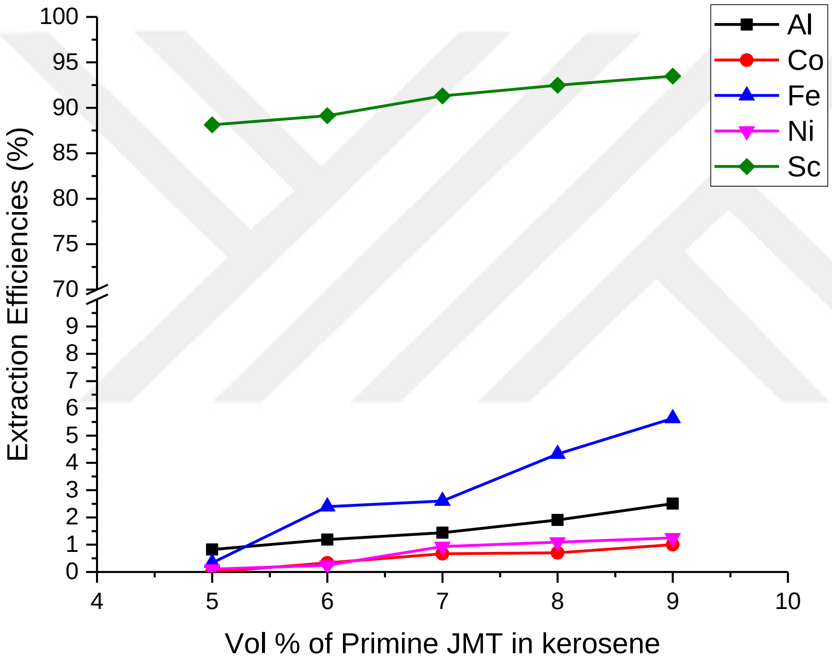

Figure 4.5 Extraction efficiencies of Sc, Fe, Co, Ni, Al with increasing volume percentage of Primene JMT in kerosene D60.

Comparison of Scandium Extraction Efficiencies of Different Organic Extractants

According to Figure 4.6, the highest extraction efficiency was achieved with 6 vol% of DEHPA in kerosene D60. However, when the impurity co-extractions were taken into consideration, the best condition for the extraction of scandium with the limited impurity co-extractions was determined as 5 vol% DEHPA in kerosene D60.

Moreover, according to the results, Primene JMT was also a good extractant for scandium. However, DEHPA had higher affinity to extract scandium when DEHPA and Primene JMT were compared with each other. As well as scandium extraction efficiency, Primene JMT is a more expensive reagent and it has high solubility in kerosene D60, which may cause extractant loss in the progress of the process. Therefore, it can be stated that Primene JMT was not preferable for this system. Thus, because of the availability, lower cost in comparison with the other reagents and high affinity to extract scandium, it was decided that the best extractant for scandium extraction was DEHPA in kerosene D60.

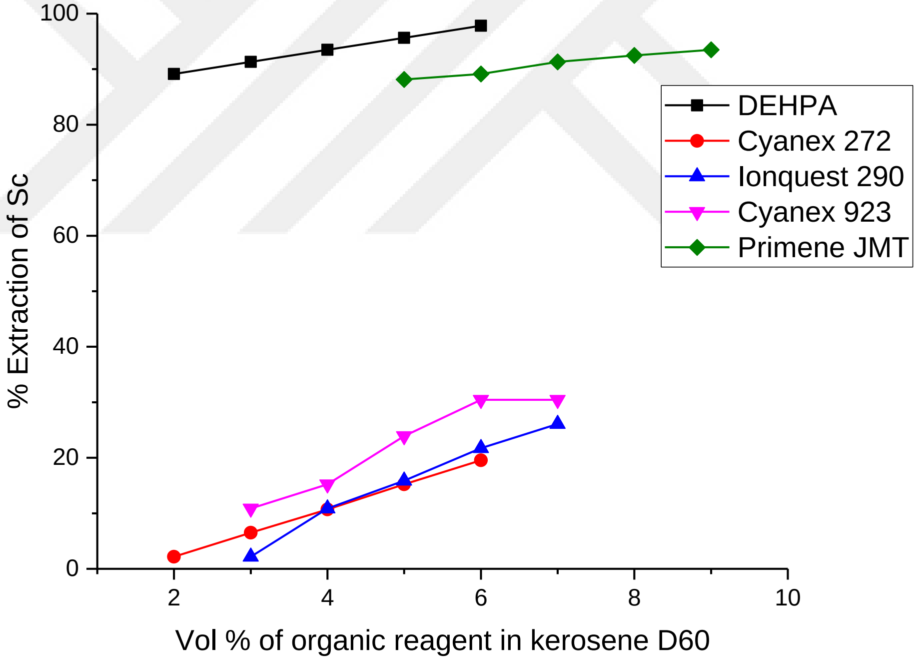

Figure 4.6 Percentages of the extraction of scandium for different extractants with different vol % of organics in kerosene D60.

According to the literature, distribution coefficient indicates the distribution of the specific element in the organic and aqueous phases after the extraction process. In other words, higher distribution coefficient means higher extraction efficiency. Moreover, the selectivity index of the organic reagents can be calculated in consideration of the distribution coefficients of the elements. Selectivity index shows the selectivity of the specific element from the other elements. The calculations of the distribution coefficients and selectivity indexes of DEHPA and Primene JMT organic reagents with high scandium extractions are given in Table 4.2. From the table, it can be seen that, the highest distribution coefficient of scandium could be achieved with using 5 or 6 vol% DEHPA in kerosene D60. The selectivity index of iron (S^{Sc}_{Fe}) for DEHPA and Primene JMT was the lowest as compared to the selectivity’s of other metals under the same conditions. However, DEHPA had higher distribution coefficients and selectivity indexes as compared to Primene JMT. In consideration of these calculations and to limit the extraction of iron around 1% as seen in Figure 4.1, 5 vol% DEHPA was chosen as the best condition for scandium extraction.

Table 4.2 Distribution coefficients and selectivity indexes of DEHPA and Primene JMT organic reagents used in the experiments.

Extractant	**%Vol**	D_{Al}	D_{Co}	D_{Fe}	D_{Ni}	D_{Sc}	S^{Sc}_{Al}	S^{Sc}_{Co}	S^{Sc}_{Fe}	S^{Sc}_{Ni}
DEHPA	2	0.0006	0.0003	0.0061	0.0005	8.20	13666	27333	1344	16400
	3	0.0008	0.0033	0.0067	0.0030	10.49	13112	3178	1565	3496
	4	0.0013	0.0067	0.0085	0.0063	14.33	11023	2139	1686	2275
	5	0.0064	0.0077	0.0110	0.0076	22.31	3486	2897	2028	2935
	6	0.0076	0.0091	0.0149	0.0087	30.54	4018	3356	2049	3510
Primene JMT	3	0.0082	0.0001	0.0034	0.0011	7.42	905	74200	2182	6745
	4	0.0119	0.0033	0.0223	0.0025	8.20	689	2733	368	3280
	5	0.0146	0.0067	0.0267	0.0094	10.49	718	1566	393	1116
	6	0.0195	0.0070	0.0452	0.0110	12.30	631	1757	272	1118
	7	0.0256	0.0101	0.0596	0.0126	14.58	569	1444	245	1157

4.1.1.2. Additives in Solvent Systems – Modifiers, Diluents (D80-D60)

A. Diluents

In this part, the effect of diluent in the solvent extraction systems was investigated and for this purpose, two different types of the kerosene were tested in the extraction processes. D80 and D60 kerosene diluents whose flash points are 80°C and 60°C, respectively were used in the experiments.

According to the results summarized in Table 4.3, while there was no significant effect of the type of the kerosene on the scandium extraction efficiency, the organic phase, which included kerosene D80, co-extracted lower amount of impurities when it was compared with the organic phase that contained kerosene D60. Moreover, the higher flash point of D80 is also essential parameter for providing more safe working conditions. Therefore, it was concluded that with respect to impurity co-extraction and the flash point of the kerosene, D80 was chosen as the suitable diluent for the extraction processes.

Table 4.3 ICP analysis results of the experiments which were carried out with the different types of kerosene.

Elements	Al, ppm	Co, ppm	Fe, ppm	Ni, ppm	Sc, ppm
PLS	15549	294	2356	5598	46
Extraction with 5% DEHPA + 95% D80 (A/O: 1/1) – Aqueous phase	15315	215	2169	5450	<1
Extraction with 5% DEHPA + 95% D60 (A/O: 1/1) - Aqueous phase	15177	170	1856	5114	<1

B. Modifiers

The modifiers are very important for increasing the extraction efficiency of scandium and decreasing the co-extracted impurity concentrations in the loaded organic phase as well as preventing the third phase and crud formations in the solvent extraction systems. When the extractants and the modifiers are used together in the organic phase for the extraction, according to the literature, these systems are generally called synergetic systems. [37,38,39]

Therefore, after being determined the suitable organic extractant and diluent for the scandium extraction, the effect of the modifiers was investigated. For this purpose, TBP and isodecanol reagents in kerosene D80 were used to determine whether modifiers are necessary for the extraction processes or not and to find the proper extractant to be used as the modifier in this process, if it is necessary.

The volume percentages of the modifiers given in Table 4.4 were chosen according to the findings reported in the literature. [32,40,41,42]

Table 4.4 Modifiers used in the experiments with different volume percentages.

Used modifiers with 5 vol% DEHPA		**Properties of the modifier**	**Volume percentages of the used modifiers**
TBP	**Tributyl phosphate**	Neutral organophosphorus compound	5% DEHPA + 95% D80
			5% DEHPA + 1% TBP + 94% D80
			5% DEHPA + 2% TBP + 93% D80
Isodecanol	**8-methylnonan-1-ol; 8-methyl-1-nonanol**	Long chain alkyl alcohol	5% DEHPA + 95% D80
			5% DEHPA + 1% Isodecanol + 94% D80
			5% DEHPA + 2% Isodecanol + 93% D80

a) DEHPA and TBP

TBP is a neutral organophosphorus compound, which is extensively used in the synergetic systems in order to increase the selectivity of the extractant, enhance the extraction efficiency and prevent third phase formation.

In the previous part of the thesis, although the organic phase with 6 vol% of DEHPA gave the maximum scandium extraction, the organic which included 5 vol% of DEHPA in D80 was determined as the best condition for the extraction due to the incremental value of the impurities in the loaded organic phase with the increasing volume percentage of the extractant in kerosene. When TBP was used together with 5 vol% of DEHPA in kerosene D80, the scandium extraction efficiency increased with low impurity co-extractions. Therefore, a series of the experiments were carried out in order to determine the effect of TBP on the scandium extraction efficiency of DEHPA and co-extraction of the impurities. For this purpose, in these experiments, 1 vol% and 2 vol% of TBP were used with the constant quantity of DEHPA (5 vol%) in kerosene D80.

According to the results given in Figure 4.7, the increasing volume percentage of TBP in kerosene D80 with 5 vol% of DEHPA resulted in a decrease in the efficiency of the impurity co-extraction, decrease in distribution coefficients and increase in selectivity indexes. However, TBP is an expensive organic extractant and for this reason, although the increasing amount of TBP provided a decrease in the co-extraction, 1 vol% of TBP was chosen as the sufficient quantity of the modifier for the extraction. Thus, 5 vol% of DEHPA with 1 vol% of TBP in kerosene D80 was determined as the best condition for obtaining the obtaining scandium extraction efficiently with the presence of minimum amount of the impurity concentrations in the loaded organic phase, as shown in Table 4.5.

Table 4.5 Distribution coefficients and Selectivity indexes of each organic reagent used in the experiments.

Extractant	D_{Al}	D_{Co}	D_{Fe}	D_{Ni}	D_{Sc}	S_{Al}^{Sc}	S_{Co}^{Sc}	S_{Fe}^{Sc}	S_{Ni}^{Sc}
5 % DEHPA	0.0064	0.0077	0.0110	0.0076	22.31	3486	2897	2028	2935
5 % DEHPA + 1% TBP	0.0037	0.0055	0.0083	0.0075	48.24	13037	8771	5812	6432
5 % DEHPA + 2% TBP	0.0027	0.0041	0.0051	0.0054	48.24	17867	11766	9459	8933
5 % DEHPA	0.0064	0.0077	0.0110	0.0076	22.31	3486	2897	2028	2935
5 % DEHPA + 1% Isodecanol	0.0059	0.0067	0.0097	0.0069	31.57	5351	4712	3255	4575
5 % DEHPA + 2% Isodecanol	0.0046	0.0054	0.0077	0.0052	31.57	6863	5846	4100	6071

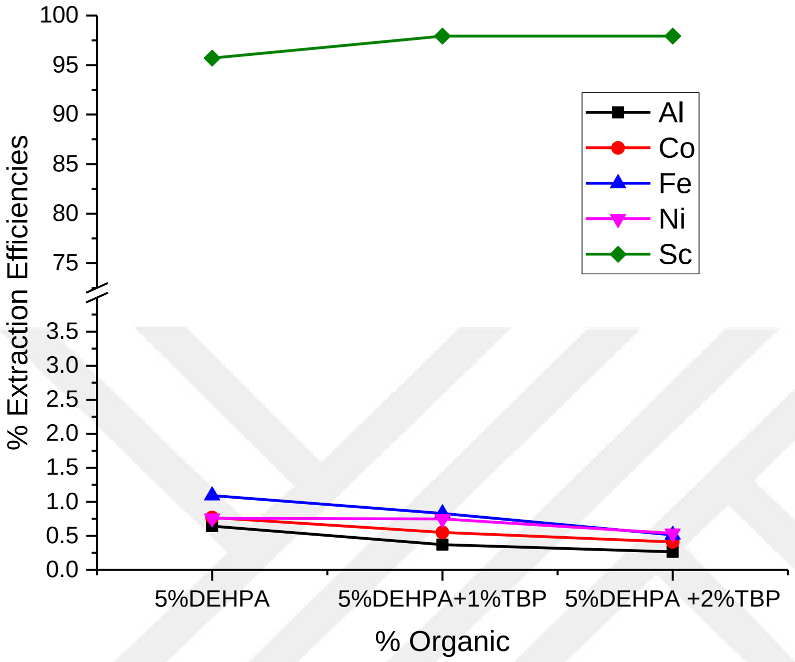

Figure 4.7 Extraction efficiencies of Sc, Fe, Co, Ni, Al with the increasing volume percentage of TBP with 5 vol% DEHPA in kerosene D80.

b) DEHPA and Isodecanol

Isodecanol was used as the alternative modifier in order to compare the effect of isodecanol and TBP on the extraction efficiency of scandium and co-extracted impurities. Isodecanol is a long chain alkyl alcohol with strong odor and its chemical formula is $C_{10}H_{22}O$**,** which is a chelating extractant. [50]

According to the experimental results given in Figures 4.7 & 4.8, as well as Table 4.5 both of the modifiers used decreased the quantity of co-extraction of the impurities and distribution coefficients but increased the selectivity indexes and prevented third phase as well as crud formation during the extraction processes. Moreover, there was not important difference in scandium extraction efficiencies between the organic phases in which TBP or isodecanol were present.

However, when TBP was used as the modifier in the extraction process, the impurity co-extraction was lower than the process in which isodecanol was used as the modifier. Furthermore, in solvent extraction systems, the used reagent should be odorless due to the requirement of safe working conditions and environmental concerns. Therefore, TBP was chosen as the modifier in this study due to lower impurity concentrations in the loaded organic phase and environmental concerns.

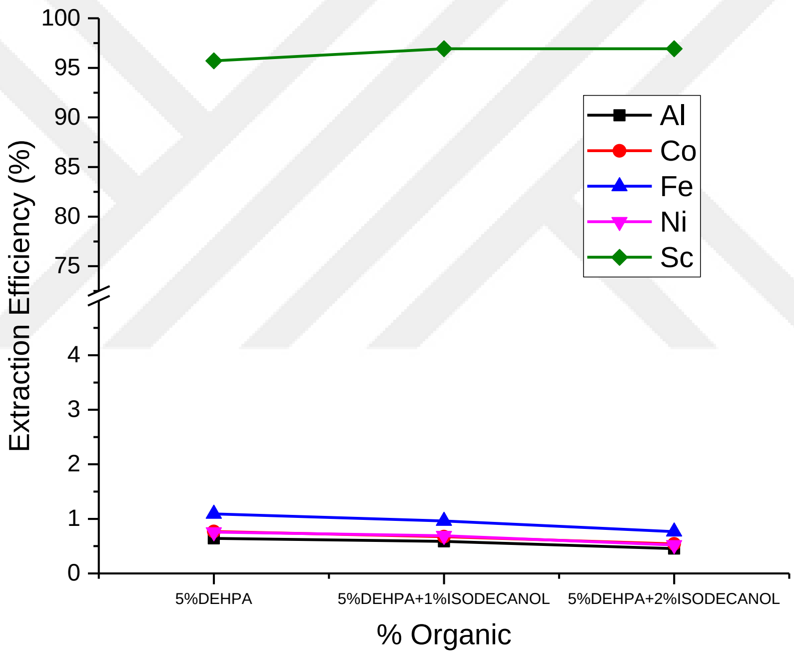

Figure 4.8 Extraction efficiencies of Sc, Fe, Co, Ni, Al with the increasing volume percentage of isodecanol with 5 vol% DEHPA in kerosene D80.

4.1.2. Aqueous Part

In this part of the study, the parameters that were generally related with the aqueous solution (PLS) were investigated. These parameters were the pH of the solution and the volume ratio of the aqueous phase to the organic phase (A/O). The pH of the pregnant leach solution is known as one of the important parameter, which affects the extraction efficiency directly and significantly in the solvent extraction processes.

In this part, the optimum pH value for PLS was tried to be determined for efficient scandium extraction with low impurity co-extractions.

In addition to this, the other parameter that was examined in this part was the volume ratio of the aqueous phase to the organic phase. The suitable A/O ratio was determined in these experiments. Moreover, by using the data of these experiments, which were done with the different A/O ratios, the necessary number of extraction stages was found for providing the maximum scandium extraction.

4.1.2.2.The Effect of the pH of Pregnant Leach Solution

The pH of the aqueous phase (PLS) is an essential parameter in the extraction and for this reason; the pH of the aqueous solution should be adjusted to lower values to reduce impurity concentration in the loaded organic phase, particularly iron. Therefore, in this part of the study, the pH of the aqueous phase was adjusted to different pH values with using H_2SO_4 and NaOH in order to investigate the effect of the pH on the extraction efficiencies. H_2SO_4 was used to increase acidity, while NaOH was added to increase the alkalinity of the solution.

At the end of the re-leaching of SNU and neutralization process, the pH of the obtained solution, PLS, was adjusted to 0.8. In this part, the experiments were carried out at different pH values, which were 0.5, 0.8, 1.0 and 1.5. In the all of the experiments, the aqueous solutions that had variable pH values were contacted with the organic phase whose composition was 5% DEHPA + 1% TBP + 94% D80.

According to the results given in Figure 4.9 and Table 4.6 with the increasing pH of the solution, the scandium extraction efficiency and scandium selectivity indexes decreased dramatically with the increasing concentration of the impurities in the loaded organic phase. The low pH values resulted in high scandium extraction efficiency with low impurity co-extractions and decreasing distribution coefficients for the impurities.

However, high amount of sulfuric acid was needed to adjust the pH of the pregnant leach solution (PLS) to 0.5. In addition to the acid consumption and corrosion problems created, extremely low pH values cause some difficulties in the scrubbing part. Also, according to the literature, the percentage of the scrubbed iron decreases considerably with the decreasing initial pH of the aqueous phase. [42] Therefore, due to the high acid consumption and scrubbing difficulties expected, initial pH of the pregnant leach solution was adjusted to pH= 0.8.

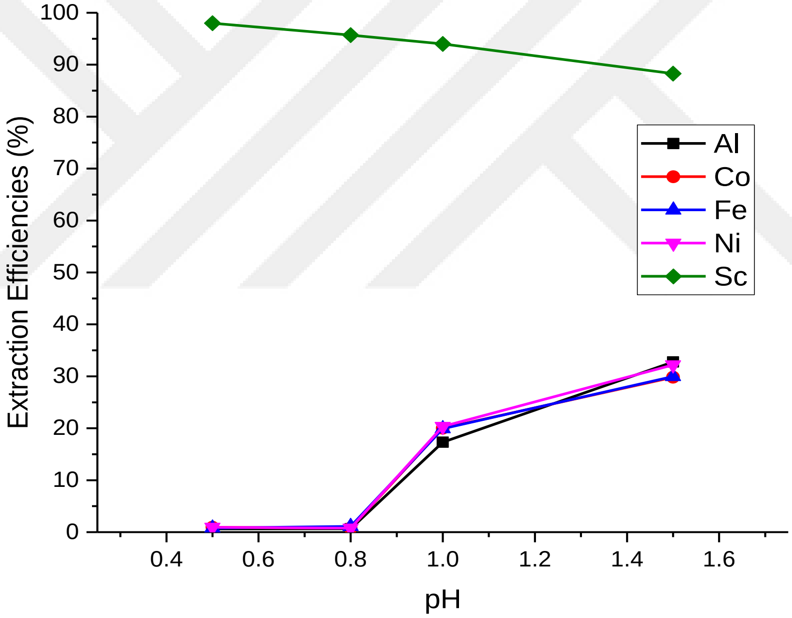

Figure 4.9 The effect of aqueous phase pH on the extraction process.

Table 4.6 Distribution coefficients and Selectivity indexes of the pregnant leach solution with different pH.

pH	D_{Al}	D_{Co}	D_{Fe}	D_{Ni}	D_{Sc}	S^{Sc}_{Al}	S^{Sc}_{Co}	S^{Sc}_{Fe}	S^{Sc}_{Ni}
0.5	0.0063	0.0094	0.0078	0.0095	48.75	7617	5417	6093	5417
0.8	0.0064	0.0077	0.0110	0.0076	22.31	3486	2897	2028	2935
1.0	0.2091	0.2500	0.2493	0.2551	15.56	74	62	62	61
1.5	0.4872	0.4250	0.4284	0.4750	7.53	15	18	18	16

4.1.2.3.The Effect of A/O Ratio

The organic phase with the composition of 5% DEHPA + 1% TBP + 94% D80 kerosene and the aqueous phase (pH=0.8) were contacted with each other with different Aqueous to Organic phase ratios (A/O) in order to determine the necessary number of the extraction stages and the suitable phase ratio for the scandium extraction. All of the experiments were carried out at the room temperature and for 10 minutes of mixing duration.

In the solvent extraction method, the volume ratio of aqueous to organic phase is an important parameter in order to concentrate and purify the desired metal ions present in the unit volume of the solution. In order words, if a high volume of the aqueous phase is contacted with a suitable organic extractant that has smaller volume than the aqueous phase, the desired metal ions can be extracted selectively from the aqueous to the organic phase. Because of this process, the desired metal ions are concentrated and purified in the loaded organic phase. [37,38,39]

Therefore, in this study, the different volume ratios of the aqueous to organic phases were tested in order to obtain higher scandium extraction efficiency with lower impurity co-extractions and to determine the necessary number of the extraction stages for the scandium extraction. According to the results given in Figure 4.10, the aqueous to organic phase ratio was determined as A/O: 10/1.

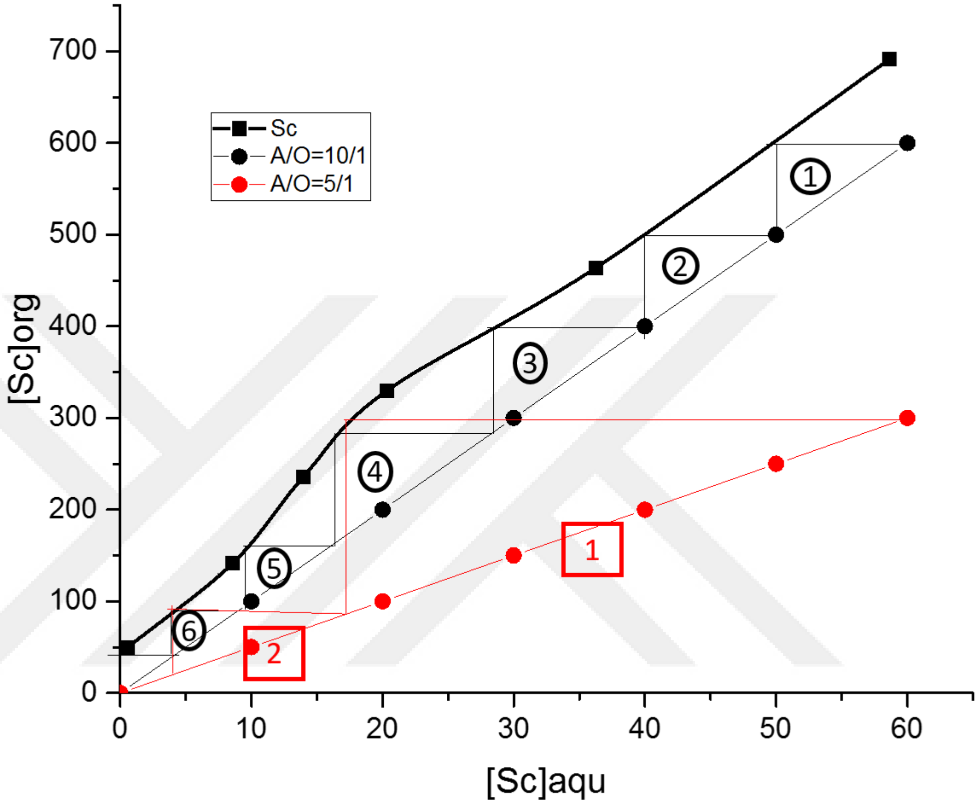

Figure 4.10 The effect of A/O ratio on scandium extraction.

According to the McCabe-Thiele Method given in Fig 4.10, when the aqueous to organic phase ratio was 10/1, six times repeating of extraction step is sufficient to extract almost all of the scandium from the pregnant leach solution. On the other hand, twice repeating is enough for extraction of scandium with the high extraction efficiency when the aqueous to organic phase ratio was 5/1. Therefore, it can be said that depending the number of repetition of the extraction step, A/O can be chosen either 10/1 or 5/1.

Furthermore, in spite of the increasing repetition of the extraction steps with the increasing A/O ratio, the process becomes more economic, when the aqueous to organic phase ratio increases due to decreasing consumption of the organic extractant. Thus, in this thesis, the aqueous to organic phase ratio was chosen as 10/1 in consideration of the economic aspects.

4.2. Scrubbing of Iron from the Loaded Organic Phase

The aim of this part was to determine the suitable scrubbing reagent for removing impurities, particularly iron from the loaded organic phase.

For using in the scrubbing experiments, initially the loaded organic phase stock was prepared according to the previously determined conditions. For this purpose, the organic phase composition of 5 vol% DEHPA + 1 vol% TBP + 94 vol% kerosene D80 was used. Moreover, the pH of pregnant leach solution was adjusted to 0.8. The extractions to prepare the loaded organic phase were done with the volume ratio of A/O=10/1 for 10 minutes mixing duration at the room temperature**.**

After the loaded organic phase was prepared, scrubbing experiments were started to be carried out at the room temperature and with the phase ratio O/A: 1/1, for 10 minutes mixing duration with the different scrubbing reagents in order to find the most suitable reagent for removing iron from the loaded organic phase. Therefore, sulfuric acid, hydrochloric acid and oxalic acid were tested with the different molarities in order to achieve scrubbing with the maximum efficiency and the minimum scandium loss as possible. After determining the proper reagent for removing iron from the loaded organic phase, the different volume ratio of the organic to aqueous phases were tried to determine the appropriate volume ratio for the scrubbing process and to find the necessary number of scrubbing stages for this process. The molarities of the used reagents were chosen with respect to the information provided in the literature. [40,41,42] The experimental conditions are given in Table 4.7.

Table 4.7 The conditions of the scrubbing experiments that were conducted with the variable molarities of the different reagents.

Name of the used scrubbing reagents		**Used molarities of the reagents**	**O/A ratio**	**Temperature**	**Mixing duration**
Sulfuric Acid	H_2SO_4	3M, 4M, 5M, 6M	1/1	Room Temp.	10 min.
Hydrochloric Acid	HCl	3M, 4M, 5M, 6M	1/1	Room Temp.	10 min.
Oxalic Acid	$C_2H_2O_4$	0.25M, 0.50M, 0.75M	1/1	Room Temp.	10 min.

4.2.1. Scrubbing with Sulfuric Acid - H_2SO_4

In this part, H_2SO_4 was used in different molarities that were varied from 3M to 6M in order to investigate the scrubbing behavior of sulfuric acid. Moreover, if this reagent was found to be suitable for the process, then the appropriate molarity of the reagent for scrubbing of iron from the loaded organic phase with the minimum scandium loss was determined.

According to the results given in Figure 4.11, it was concluded that sulfuric acid was not a suitable reagent for the scrubbing process. Although, the scandium loss was negligible in these experiments, the quantity of the scrubbed iron was not enough for the removal of the impurities from the loaded organic phase. Moreover, the scrubbing efficiencies were extremely low, as shown in Figure 4.11.

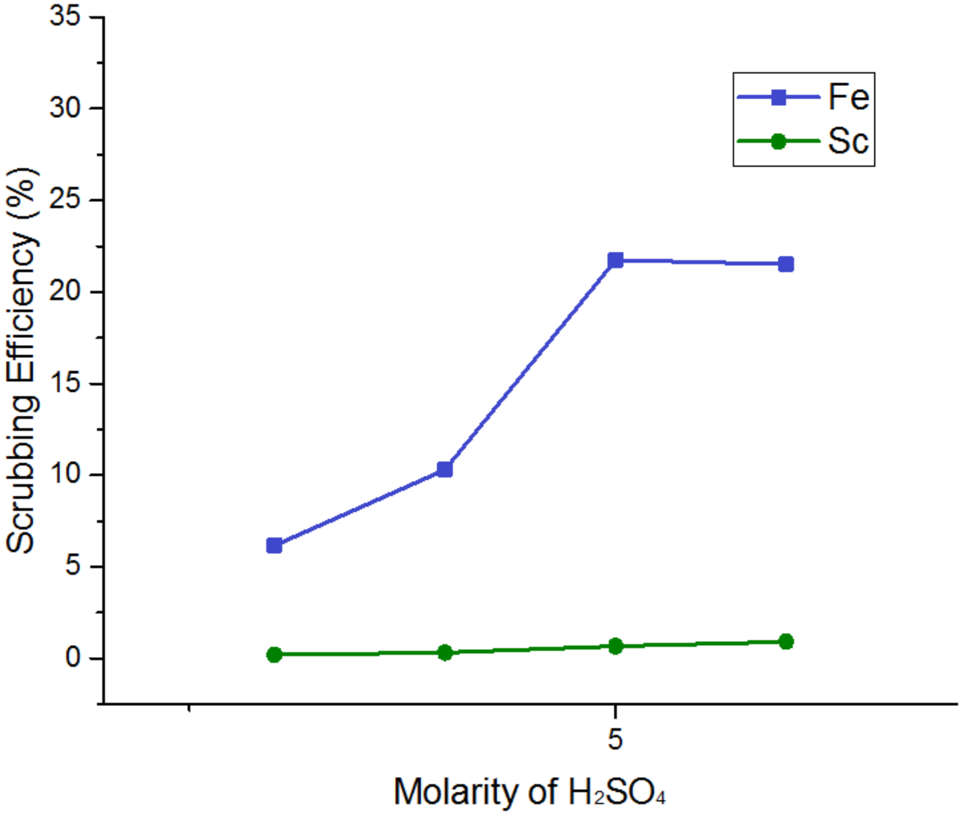

Figure 4.11 Scrubbing with the different molarities of H_2SO_4.

4.2.2. Scrubbing with Hydrochloric Acid - HCl

Hydrochloric acid was contacted with the loaded organic phase in different molarities in order to investigate the scrubbing of iron ions present in the loaded organic phase. The experiments were conducted with the volume ratio of O/A: 1/1 at the room temperature for 10 minutes mixing duration.

According to the results given in Figure 4.12, it can be stated that hydrochloric acid was a better scrubbing reagent than sulfuric acid. When hydrochloric acid was used as the scrubbing reagent, the highest amount of iron removal from the loaded organic phase with the minimum scandium loss would be achieved with 4M hydrochloric acid in the scrubbing process, as indicated in Figure 4.12.

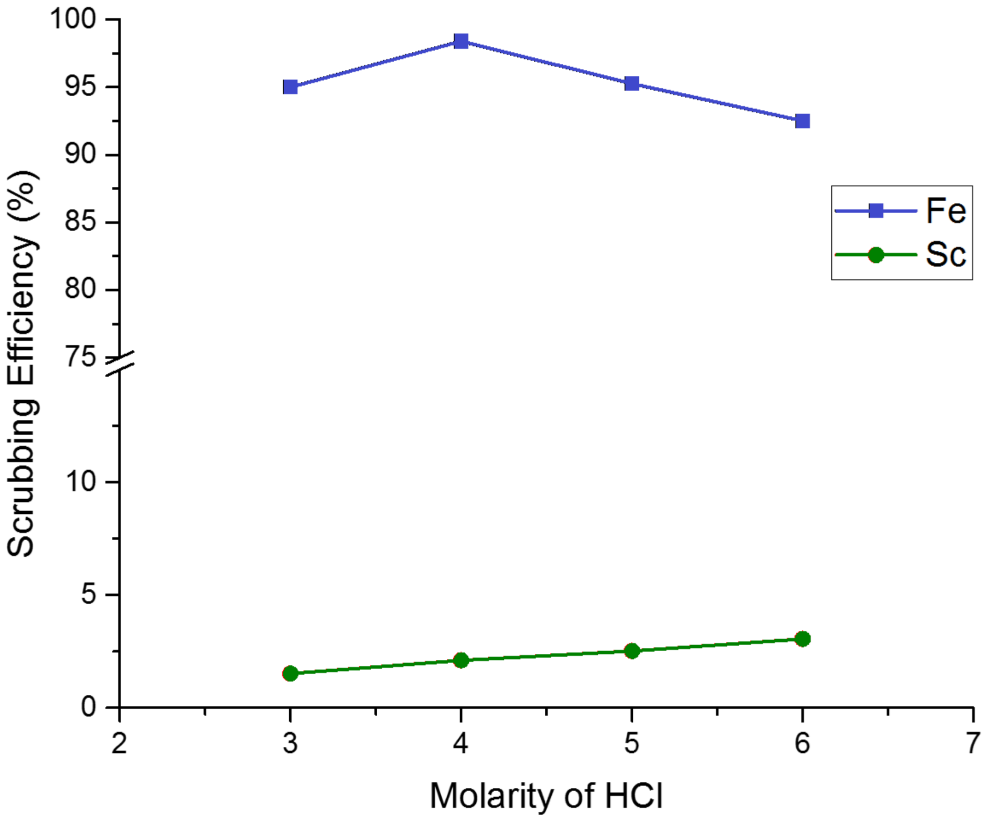

Figure 4.12 Scrubbing with the different molarities of HCl.

4.2.3. Scrubbing with Oxalic Acid – $C_2H_2O_4$

Finally, oxalic acid was used as the scrubbing reagent in order to remove impurities present on the loaded organic phase.

All of the experiments were conducted with O/A: 1/1 at the room temperature and 10 minutes mixing duration. Different molarities of oxalic acid were used in order to determine the suitable amount of oxalic acid in the scrubbing process.

According to the results given in Figure 4.13, when oxalic acid was used as the scrubbing reagent, the maximum efficiency of iron scrubbing from the loaded organic phase with the minimum scandium loss was achieved with 0.75 M oxalic acid that is the solubility limit of this reagent in the aqueous phase. Although, the scandium loss increased with the increasing molarity of oxalic acid, this loss was negligible as seen in Figure 4.13.

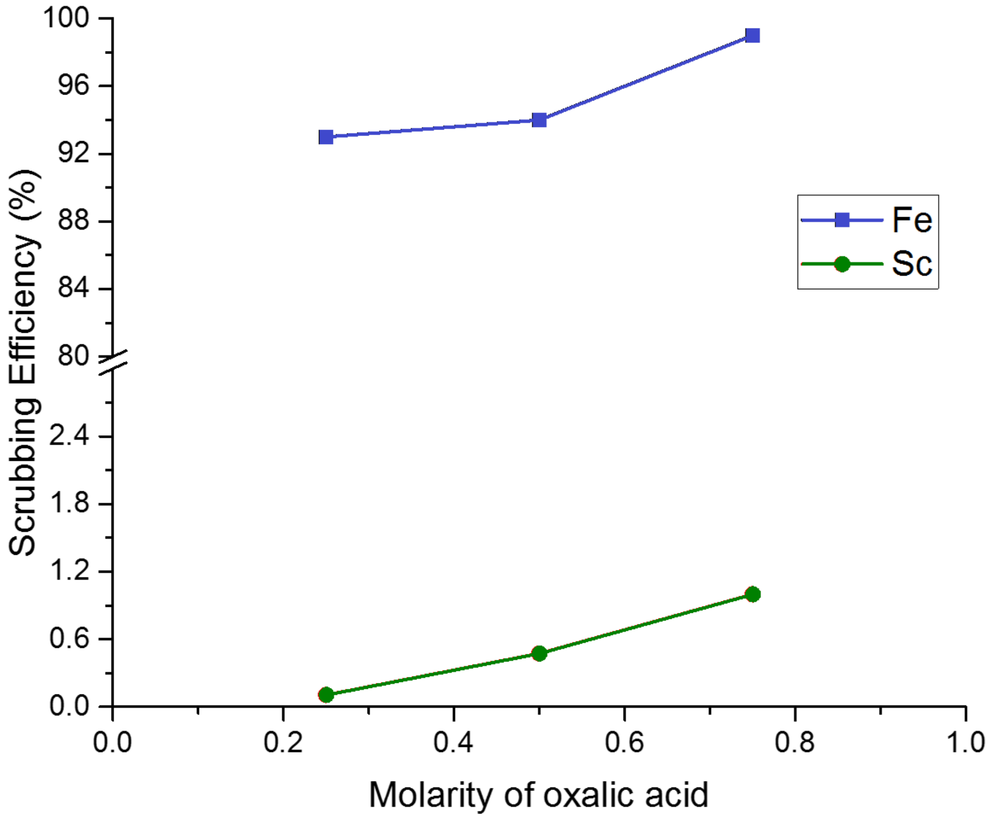

Figure 4.13 Oxalic acid scrubbing with different molarities.

Furthermore, the comparison of the scrubbing behaviors of HCl and oxalic acid indicated that, while using a lower concentration of oxalic acid (0.75M) was sufficient for the iron removal from the loaded organic phase, higher molarity of hydrochloric acid was necessary for removing impurities (4M HCl). Therefore, oxalic acid was chosen as the appropriate scrubbing reagent for removing the maximum amount of iron from the loaded organic phase.

4.2.4. The Effect of the O/A Phase Ratio

In the scrubbing part, the amounts of aqueous and organic phases were the other important parameter for providing the maximum impurity removal from the loaded organic phase. In this part, generally, the volume ratio of phases is adjusted with respect to the volume of the organic phase and hence, this ratio for scrubbing is shown as the organic to aqueous phase ratio (O/A), which is opposite to the extraction process.

Therefore, the ratios of O/A: 1/1, 3/1, 5/1, 7/1, 10/1 and 15/1 were studied in order to find the appropriate ratio for the scrubbing process and to determine the necessary number of the scrubbing stages for achieving the highest amount of the impurity removal, which is iron.

According to the findings given in Figure 4.14 and McCabe-Thiele Method, the decided organic to aqueous phase ratio was O/A: 3/1. Since when organic to aqueous phase ratio increases, the slope of the McCabe-Thiele graphs also increases and this means that, more repetition of scrubbing stage is necessary for removing the remaining impurities in the loaded organic phase. On the other hand, if the O/A ratio is chosen as 3/1 in this system, only one-step of scrubbing is enough to remove impurities from the loaded organic. Therefore, the suitable O/A phase ratio for scrubbing process was determined as 3/1 with respect to McCabe-Thiele Method.

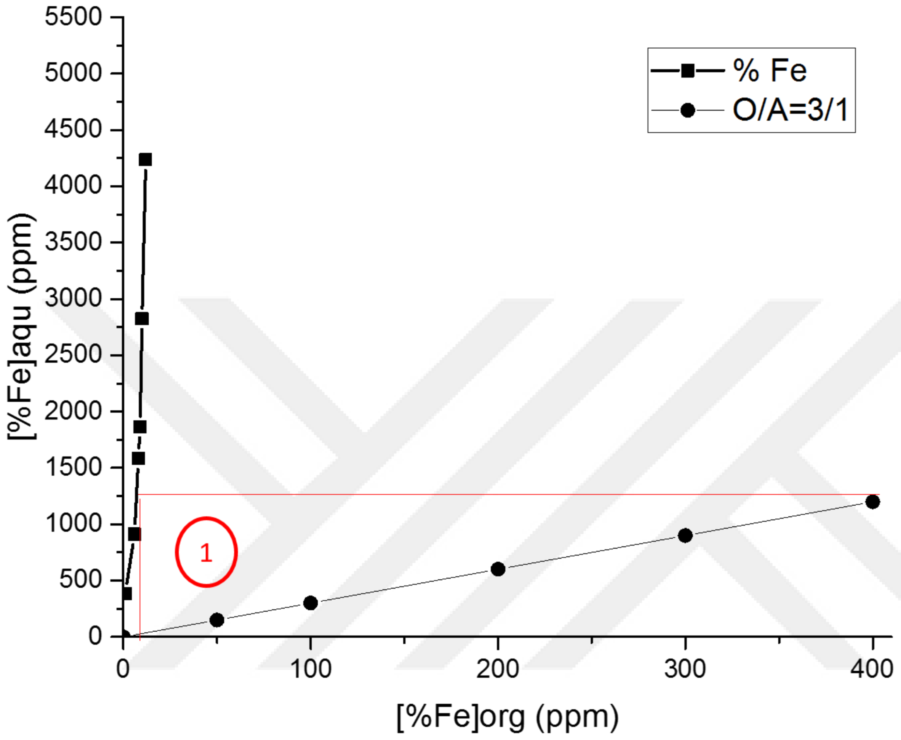

Figure 4.14 The effect of the O/A ratio on the scrubbing process.

To conclude, the best condition for scrubbing part was determined as 0.75 M oxalic acid with O/A: 3/1 and the ICP-OES analysis result of the scrubbed loaded organic phase is given in Table 4.8

Table 4.8 The ICP-OES analysis result of the loaded organic phase before and after the scrubbing process (ppm).

Elememts	Al	As	Ca	Co	Cr	Cu	Fe	Mg	Mn	Na	**Ni**	**Sc**	**Zn**
Loaded Organic	5	<1	<1	<1	<1	<1	1252	<1	<1	<1	<1	463	<1
Scrubbed Loaded Organic	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	459	<1

CHAPTER 5

CONCLUSION

In this study, the main aim was to find the suitable organic extractant and scrubbing reagent for the solvent extraction process that was done for obtaining scandium as a by-product from the pregnant leach solution of the nickel-cobalt laterite ores. For this purpose, the different experiments were carried out and the findings in these could be summarized as;

1. In order to find the appropriate organic extractant for the scandium extraction, the different organic reagents which were Ionquest 801 (Bis(2-ethylhexyl) phosphate), DEHPA (Di(2-ethylhexyl) phosphoric acid), Cyanex 272 (Bis(2,4,4-trimethylpentyl) phosphinic acid), Cyanex 923 (Trialkylphosphine oxide) and a Primene JMT were tried in the first part. Consequently, according to the experimental findings, it was decided that DEHPA was the most suitable organic extractant for the scandium extraction. This organic reagent had the lowest impurity co-extractions from the pregnant leach solution that was obtained after re-leaching and neutralization processes of the secondary neutralization precipitate derived during the HPAL process of the nickel-cobalt laterites. Moreover, the quantity of DEHPA to be used in the scandium solvent extraction was chosen as 5 vol% in kerosene.
2. After determining the proper organic extractant for the scandium extraction, the effect of the diluent on its extraction efficiency was examined. For this purpose, the different types of kerosene such as D80 and D60 whose flash points are respectively, 80°C and 60°C were tried in the extraction processes.

According to the results, since D80 kerosene provided low co-extraction of the impurities during the extraction process and it has higher flash point that means safer working conditions, it was decided that D80 kerosene was more suitable than D60 kerosene.

3. Then, the effect of the modifiers on the scandium extraction was investigated and TBP as well as isodecanol reagents were used for this purpose. It was noticed that both isodecanol and TBP prevented the third phase and crud formations and decreased the concentration of co-extracted impurities in the loaded organic phase. Furthermore, according to the results, it could be stated that the modifiers had not any significant effect on the extraction efficiency of scandium. However, the concentration of the impurities in the loaded organic phase decreased more when TBP was used instead of isodecanol as the modifier in the process. Therefore, it can be said that due to environmental concerns such as odor, the concentration of the co-extracted impurities and working conditions, isodecanol was not the suitable reagent for the solvent extraction process. Moreover, since both TBP and isodecanol are expensive reagents, the volume percentage of the used modifier should be chosen as low as possible. In consideration of these factors, TBP was chosen as the modifier in this study and it was used as 1 vol% with 5 vol% DEHPA in 94 vol% D80 kerosene.
4. So, before investigating the effect of the pH of the pregnant leach solution and A/O phase ratio on the scandium extraction process, the suitable organic phase mixture had been determined as 5 vol% DEHPA + 1 vol% TBP in 94 vol% kerosene D80.
5. The effect of the pH of the pregnant leach solution on the scandium extraction efficiency and the concentration of the co-extracted impurities were examined in the following part of the study. For this purpose, the different pH values, which were 0.5, 0.8, 1.0 and 1.5, was tried to determine the optimum value for the extraction process. According to the experimental findings, it was concluded that the higher values of the pH was not suitable for the scandium extraction due to the increasing co-extracted impurity concentrations in the loaded organic phase after the extraction.

On the other hand, the extremely low pH values are not suitable due to high acid consumption in the process. Therefore, the pH of the pregnant leach solution was fixed at 0.8 for providing the scandium extraction from the aqueous solution.

6. The proper volume ratio of the aqueous to organic phases was also investigated in the extraction part of the study. For this purpose, the different A/O ratios were tested to determine the best A/O ratio for the scandium extraction with high efficiency and low impurity co-extractions. Furthermore, the number of the necessary extraction stages was determined as a result of these experiments by using McCabe-Thiele Method. According to the findings, the phase ratio was chosen as A/O: 10/1.
7. In the scrubbing part, the iron was the most critical impurity present in the loaded organic phase due to its similar behaviors with the scandium ions and its high concentration in the organic phase obtained after the extraction process. In this part, different scrubbing reagents were tested in different molarities in order to find the most suitable reagent with the appropriate molarity for removing iron from the loaded organic phase. These scrubbing experiments were carried out at the room temperature with the phase ratio O/A: 1/1 and for 10 minutes mixing duration. Moreover, in these experiments the loaded organic phase stock, which was prepared with respect to the determined conditions in the previous extraction part of the study, was used. As a result, 0.75 M oxalic acid was determined as the most appropriate scrubbing reagent for removing iron from the loaded organic phase with the minimum scandium loss.
8. After determined the suitable scrubbing reagent for this process, the proper O/A ratio was investigated. Consequently, the conditions for scrubbing process were determined as O/A: 3/1 phase ratio at the room temperature by using 0.75M oxalic acid as the scrubbing reagent.

In conclusion, it can be stated that the solvent extraction is an essential process for the scandium extraction and recovery from the pregnant leach solution of the nickel-cobalt laterite ores. In this process, the selection of the organic extractant and scrubbing reagent are very critical issues in order to obtain highly purified scandium enriched solution at the end of the solvent extraction. The purity of the product is a very critical for scandium production in the world and meeting of this requirement highly depends on the applied processes, particularly solvent extraction process. Therefore, in this study, reaching the highest scandium extraction efficiency with the minimum impurity co-extraction was aimed in order to achieve the highest purity product at the end of the all processes. The following steps such as stripping of the scrubbed organic phase and precipitation of scandium from the strip solution are being planned to be investigated in the future.

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APPENDIX A

EXTRACTION EFFICIENCIES

- **DEHPA**

DEHPA%	Al%	Co%	Fe%	Ni%	Sc%
2	0.06	0.03	0.61	0.05	89.13
3	0.08	0.33	0.67	0.30	91.30
4	0.13	0.67	0.85	0.63	93.48
5	0.64	0.77	1.09	0.76	95.71
6	0.76	0.90	1.47	0.86	96.83

- **CYANEX 272**

CYANEX 272 %	Al%	Co%	Fe%	Ni%	Sc%
2	0.057	0.03	0.46	0.47	2.17
3	0.47	0.10	1.47	0.56	6.52
4	1.09	0.33	2.10	0.76	10.69
5	1.75	0.37	2.90	0.97	15.22
6	2.43	0.50	3.94	1.05	19.56

- **CYANEX 923**

CYANEX 923	Al%	Co%	Fe%	Ni%	Sc%
3	0.01	0.01	0.25	0.16	10.87
4	0.03	0.33	0.53	0.19	15.22
5	0.07	0.37	0.94	0.21	23.91
6	0.09	0.67	1.39	0.32	30.43
7	0.10	0.70	2.06	0.33	30.43

- **IONQUEST 801**

IONQUEST 801%	Al%	Co%	Fe%	Ni%	Sc%
3	0.01	0.01	0.38	0.19	2.17
4	0.04	0.33	0.80	0.21	10.87
5	0.09	0.37	0.97	0.26	15.87
6	0.34	0.67	1.51	0.40	21.74
7	0.40	0.70	2.94	1.34	26.09

- **PRIMENE JMT**

PRIMENE JMT %	Al%	Co%	Fe%	Ni%	Sc%
3	0.82	0.01	0.34	0.10	88.13
4	1.19	0.33	2.19	0.25	89.13
5	1.44	0.67	2.60	0.93	91.30
6	1.91	0.70	4.33	1.09	92.48
7	2.50	1.00	5.63	1.25	93.58

- **DEHPA + TBP**

	Al%	Co%	Fe%	Ni%	Sc%
5 % DEHPA	0.64	0.77	1.09	0.76	95.71
5 % DEHPA + 1% TBP	0.37	0.55	0.83	0.75	97.93
5 % DEHPA + 2% TBP	0.27	0.41	0.51	0.54	97.93

- **DEHPA + ISODECANOL**

	Al%	Co%	Fe%	Ni%	Sc%
5 % DEHPA	0.64	0.77	1.09	0.76	95.71
5 % DEHPA + 1% Isodecanol	0.59	0.67	0.96	0.69	96.93
5 % DEHPA + 2% Isodecanol	0.46	0.54	0.77	0.52	96.93

- **The pH effect**

pH	Al%	Co%	Fe%	Ni%	Sc%
0.5	0.63	0.93	0.78	0.94	97.99
0.8	0.64	0.77	1.09	0.76	95.71
1	17.31	20.00	19.93	20.34	93.99
1.5	32.76	29.82	29.96	32.20	88.28