

EXPLOITATION OF THE NATURAL RESOURCES OF PAKISTAN
FOR THE RECOVERY OF METALS USED IN NUCLEAR REACTORS

A Thesis Submitted

to

THE UNIVERSITY OF THE PUNJAB

For The Degree of

DOCTOR OF PHILOSOPHY

in

CHEMISTRY

by

MUHAMMAD HALEEM KHAN

INSTITUTE OF CHEMISTRY,
UNIVERSITY OF THE PUNJAB,
LAHORE (PAKISTAN)

1992

ACKNOWLEDGEMENTS

I am deeply grateful to my Research Supervisor, Professor Dr. Muhammad Ali Khan, Head Nuclear Chemistry, Institute of Chemistry, University of the Punjab, Lahore, for his never ending kindness, continuous help, invaluable guidance, long discussions, sympathetic behaviour and constant encouragement throughout this study.

I am grateful to Dr. Moosa Hasany, Principal Scientific Officer for his advice and assistance during my stay at the Pakistan Institute of Nuclear Science & Technology, 'PINSTECH', Islamabad.

My thanks to Dr. N. M. Butt, Director, 'PINSTECH', Islamabad and M. Y. Mughal, Director Mineral Centre, 'AEMC', Lahore, for allowing me to use research facilities available in these Institutions.

I owe thanks to Mr. Akbar Ali, Senior Scientific Officer, PINSTECH for his advice, guidance, encouragement and willingness to discuss my problems at any time. The author also thanks Mr. M.N. Cheema, CSO, Head RCSI for his helpful counseling and allowing me to use research facilities.

I am also grateful to Azad Jammu and Kashmir University Authorities for granting the study leave to complete this work and University Grants Commission for the award of scholarship.

A deep appreciation is felt for the support and encouragement of my parents over the years. I am highly thankful to my wife, Kousar, whose understanding and cooperation are the essential driving forces for my studies. I owe thanks to my brothers, Dr. M. Zareen Khan and Dr. Tariq Hussain for their moral support.

I wish to express my thanks to the technical staff of Nuclear Chemistry Div. 'NCD', Student Information Div. 'SID', and Reactor Operation Group, 'ROG', PINSTECH for their help.

I would like to thank my friends, Munir Ahmed, M. M. Saeed Sohail Ahmed, and M. Saeed who helped and encouraged me to complete this work in one way or the other.

Finally, I would also like to thank Mr. M. Tariq, Mr. Khan Bahadur, Mr. M. Riaz, Mr. Sajad Khan and Mr. Basharat Hussain for their co-operation and help.

15/11

DEDICATION

TO

MY SON

'MR. KAMI'

ABSTRACT

To evaluate the feasibility of the material used in nuclear reactor technology, seventy one metal bearing ore samples were collected from various localities of Pakistan. These were analyzed by employing various instrumental analytical techniques such as atomic absorption, visible spectrophotometry, x-ray fluorescence, flame photometry, radiometry and inductively coupled plasma-emission spectrometry 'ICP'. The concentrations of uranium, thorium and zirconium were found upto 0.190%, 10.5 % and 3.3% respectively. Calcium, magnesium, sodium, potassium, iron, aluminium and silica were the major ore constituents, while manganese, strontium, barium, zinc, hafnium and lead were present at trace levels in these samples.

The solvent extraction methods for the extraction of thorium and zirconium from their ore leached solutions using 30% and 40% (v/v) di-n-butylsulfoxide (DBSO) in xylene from 2M HNO₃ and 7 M HNO₃ aqueous solutions have been developed respectively. ⁹⁵Zr radiotracer was used to follow the extraction of zirconium while, a spectrophotometric method has been developed and employed for the determination of thorium using 0.05%(w/v) thorin in 3 M HClO₄ acid solution as chromogenic reagent. Absorbance was measured at 544 nm. Thorium-thorin complex was found quite stable for more than two months. Beer's law is obeyed from 1-26 µg/g of thorium in perchloric acid solution with molar absorptivity of ($\epsilon_{544}^{\circ} = 1.69 \times 10^4 \text{ dm}^3 \text{ mole}^{-1} \text{ cm}^{-1}$ at $26 \pm 2^{\circ} \text{ C}$). Optimal conditions for solvent to metal ion concentration, equilibration time and

temperature were established. The effect of various cations and anions on the extraction of these metals were also studied. Separation factors (β) for these metals with respect to other mineral impurities present in the local ores were also calculated and discussed. The stoichiometric compositions of the extracted complexes of thorium and zirconium with DBSO were determined by slope analysis and found to be 1:2 and 1:1 respectively. The process of thorium extraction was found exothermic in the temperature range studied (30-55 °C) whereas, negligible effect on the extraction of zirconium was noted upto 50 °C. Thermodynamic functions such as free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) changes for thorium extraction have been determined. Deionized water and 1% ammonium bifluoride aqueous solution were found very effective for the back-extraction of thorium and zirconium respectively. The percent purity for extracted thorium was found to be > 98% whereas, for zirconium it was noted >96%.

The recycling capacity of the organic solvent for thorium and zirconium have been checked and found to be quite satisfactory. On the basis of data obtained at laboratory scale extraction studies, pilot plant schemes for the extraction and refining of these metals from their ores have been worked out. On the basis of analytical data, different areas of the country such as Dera Ghazi Khan, Isakhel and Rajanpur for uranium, Badar and Landhi for thorium and Sonmiani, Mekran coast for zirconium have been identified and suggested for ore exploitation.

TABLE OF CONTENTS

	Page
ACKNOWLEDGEMENTS	
DEDICATION	
ABSTRACT	i
CHAPTER ONE – INTRODUCTION	
1.1 THE ECONOMIC DEVELOPMENT AND ENERGY CRISIS IN PAKISTAN	1
1.2 ENERGY RESOURCES	6
1.2.1 Energy Sources and Power Growth in Pakistan	7
1.3 RATIONALE FOR THE WORK PRESENTED IN THIS THESIS	13
1.4 THESIS LAYOUT	14
CHAPTER TWO – NUCLEAR REACTOR TECHNOLOGY	
2.1 NUCLEAR REACTOR TECHNOLOGY	15
2.2 NUCLEAR REACTORS	16
2.2.1 Nuclear Reactor Fuel	20
2.2.2 Fuel Breeding Reactor Technology	21
2.2.3 Fuel Cladding Material	24
2.3 THE CHEMISTRY OF NUCLEAR REACTOR MATERIALS	25
2.3.1 Thorium	25
2.3.2 Thorium Occurrence	26

2.3.3	Thorium Chemistry and Isotopic Abundance	28
2.3.4	Nuclear Properties of Thorium	29
2.3.5	Neutron-Induced Transmutation Chains of Thorium	31
2.3.6	Applications of Thorium in Breeder Reactors	32
2.4	URANIUM ORES AND MINERALS	32
2.5	ZIRCONIUM AS REACTOR STRUCTURAL MATERIAL	33
2.5.1	Occurrence and Separation of Zirconium	36
CHAPTER THREE - EXTRACTION AND REFINING OF METALS		
3.1	EXTRACTION AND REFINING OF METALS	38
3.2	THE LIQUID-LIQUID EXTRACTION	39
3.2.1	Process of Solvent Extraction	44
3.2.2	Types of Extraction Processes	46
3.3	EXTRACTION EQUILIBRIUM IN CHELATE EXTRACTION SYSTEM	50
3.4	ION ASSOCIATION COMPLEXES	53
3.4.1	Extraction Equilibrium in Ion-Association Process	54
3.5	EXTRACTION BY SOLVATION PROCESS	55
3.6	TYPES OF EXTRACTION TECHNIQUES	56
3.7	FACTORS OF PRIME IMPORTANCE IN SOLVENT EXTRACTION TO METALLURGICAL PROCESSING	58

CHAPTER FOUR – PROCUREMENT AND ANALYSIS OF THORIUM,
URANIUM AND ZIRCONIUM BEARING ORES
FROM VARIOUS LOCATIONS OF PAKISTAN

4.1	INTRODUCTION	65
4.1.1	Analysis of the Ores	66
4.2	EXPERIMENTAL	68
4.2.1	Procurement of Ore Samples	68
4.2.2	Ore Sampling Areas	69
4.2.3	Preparation of Ore Samples	71
4.2.4	Dissolution of Ore Samples	73
4.3	QUALITATIVE ANALYSIS OF ORE SAMPLES	75
4.4	QUANTITATIVE ANALYSIS OF THORIUM, URANIUM AND ZIRCONIUM BEARING ORE SAMPLES	79
4.4.1	Apparatus	79
4.4.2	Reagents and Solutions	79
4.4.3	Standard Stock Solutions for Spectrophotometric Determination of Th, Ti, U, Zr and P	85
4.4.4	Atomic Absorption Grade Stock Standard Solutions	86
4.5	GENERAL DETERMINATION PROCEDURES	88
4.5.1	Spectrophotometric Determination of Thorium in Various Thorium-bearing Ore Samples	88
4.5.2	Spectrophotometric Determination of Uranium in the Ore Samples	90
4.5.3	Spectrophotometric Determination of Zirconium-bearing Ore Samples	92
4.5.4	Determination of Titanium in Various Thorium, Uranium and Zirconium Bearing ore	94

4.5.5	Determination of Silica in Thorium, Uranium and Zirconium Bearing Ore Samples	95
4.5.6	Spectrophotometric Determination of Phosphates in Uranium and Zirconium Bearing Ore Samples	96
4.5.7	Determination of Various Impurities in Thorium, Uranium and Zirconium Bearing Ore Samples	97
4.5.8	Determination of Sodium and Potassium in Various Ore Samples Containing Thorium, Uranium and Zirconium	99
4.6	PRECISION AND ACCURACY IN DETERMINATION OF VARIOUS MINERALS CONSTITUENTS IN ORE SAMPLES	100
4.7	RESULTS AND DISCUSSION	115
CHAPTER FIVE - SPECTROPHOTOMETRIC METHOD FOR THE DETERMINATION OF THORIUM FROM ORE SAMPLES		
5.1	INTRODUCTION	127
5.2	EXPERIMENTAL	130
5.2.1	Apparatus	130
5.2.2	Reagents and Solution	130
5.2.3	General Determination Method	132
5.3	OPTIMIZATION OF THORIUM DETERMINATION PARAMETERS	133
5.3.1	Absorption Spectra of Thorin in Perchloric Acid	133
5.3.2	Absorption Spectra of Thorium-thorin Complex in Perchloric Acid	134
5.3.3	Effect of Acid Concentration on Thorin-perchloric Acid Solution	134
5.3.4	Effect of Acid Concentration on Thorium-thorin complex	134

5.3.5	Effect of Reagent Concentration on Standard Curve	136
5.3.6	Preparation of Standard Curve for Thorium Determination	136
5.3.7	The Effect of Cations on Thorium Determination	138
5.3.8	The Effect of Anions on Thorium Determination	138
5.4	DETERMINATION OF THORIUM IN (NBL) STANDARD ORE SAMPLES	138
5.5	RESULTS AND DISCUSSION	145
CHAPTER SIX - STUDIES ON THE SOLVENT EXTRACTION/ SEPARATION OF THORIUM FROM NITRIC ACID SOLUTIONS BY DI-n-BUTYL SULF- OXIDE IN XYLENE AS AN EXTRACTANT		
6.1	INTRODUCTION	155
6.1.1	Organic Sulfoxides as Extractants	157
6.2	EXPERIMENTAL	161
6.2.1	Apparatus	161
6.2.1	Reagents and Solutions	161
6.2.3	General Procedure for the Extraction and Determination of Thorium	161
6.3	OPTIMIZATION OF THE PARAMETERS FOR THORIUM EXTRACTION	165
6.3.1	Effect of Nitric Acid Concentration on Thorium Extraction	165
6.3.2	Effect of Solvent Concentration on Thorium Extraction	166
6.3.3	The Effect of Shaking Time on Thorium Extraction	166

6.3.4	Effect of Salting-out Agents on the Extraction of Thorium	167
6.3.5	The Influence of Thorium Concentration on its Extraction	167
6.3.6	The Effect of Cations on Thorium Extraction	169
6.3.7	The Effect of Anions on Thorium Extraction	171
6.3.8	The Effect of Temperature on the Extraction of Thorium	173
6.4	EXTRACTION BEHAVIOUR OF IMPURITIES	175
6.4.1	Extraction Behaviour of Lead Aluminium, Calcium, Magnesium and Strontium	176
6.4.2	Extraction Behaviour of Titanium	177
6.4.3	Extraction Behavior of Sodium and Potassium	178
6.5	GENERAL PROCEDURE FOR THORIUM EXTRACTION/ SEPARATION FROM ITS ORES	179
6.6	ACCURACY AND PRECISION OF THORIUM EXTRACTION METHOD	180
6.7	STOICHIOMETRIC COMPOSITION OF THORIUM-DBSO COMPLEX	182
6.8	EXTRACTION OF THORIUM WITH 30% DBSO IN XYLENE FROM HYDROCHLORIC ACID SOLUTIONS	184
6.9	RESULTS AND DISCUSSION	188
CHAPTER SEVEN - SOLVENT EXTRACTION/SEPARATION OF ZIRCONIUM FROM NITRIC ACID SOLUTION WITH DIBUTYLSULFOXIDE IN XYLENE AS AN EXTRACTANT		
7.1	INTRODUCTION	210

7.2	EXPERIMENTAL	215
7.2.1	Apparatus	215
7.2.2	Reagents and Solutions	
7.2.3	General Extraction Procedure	216
7.3	OPTIMIZATION OF PARAMETERS FOR THE EXTRACTION OF ZIRCONIUM	217
7.3.1	Effect of Nitric Acid Concentration	218
7.3.2	Effect of Non-equilibrated Solvent on Zirconium Extraction	218
7.3.3	Effect of Pre-equilibrated Solvent on Zirconium Extraction	219
7.3.4	Effect of Equilibration Time on Zirconium Extraction	219
7.3.5	Salting-out Effect on the Extraction of Zirconium	219
7.3.6	The Influence of Metal Concentration on Its Extraction	220
7.3.7	The Temperature Effect on the Extraction of Zirconium	220
7.3.8	The Effect of Cations on the Extraction of Zirconium	222
7.3.9	Effect of anions on the Extraction of Zirconium	222
7.4	STOICHIOMETRIC COMPOSITION OF ZIRCONIUM-DBSO COMPLEX	225
7.5	TEST FOR THE EFFICIENCY OF SOLVENT EXTRACTION METHOD	225
7.6	RESULTS AND DISCUSSION	231
	SUMMARY	248
	REFERENCES	253

INDEX OF TABLES

		Page
CHAPTER ONE		
Table 1.1	World's crude oil and natural gas reserves	3
Table 1.2	Current position of energy growth and consumption in Pakistan	5
Table 1.3	Source-wise energy distribution in Pakistan	10
Table 1.4	World nuclear power and its contributions	12
 CHAPTER TWO		
Table 2.1	Principal fissionable nuclides	22
Table 2.2	Important minerals of uranium and their composition	34
Table 2.3	World's recoverable reserves and resources of Uranium	35
 CHAPTER THREE		
Table 3.1	Classification of extraction reagents	51
 CHAPTER FOUR		
Table 4.1	Locality, source of procurement and the informations regarding the ore samples	70
Table 4.2	Qualitative analysis of Thorium, Uranium and Zirconium bearing ore samples	77
Table 4.3	Operating conditions used for XRF measurements	78
Table 4.4	Ore sample decomposition and analytical methods employed for the chemical analysis of Thorium, Uranium and Zirconium bearing ores	80

Table 4.5	Instrumental conditions used for the atomic absorption spectrophotometric measurements	98
Table 4.6	Instrumental/operating conditions used for the determination of Sodium and Potassium by flame photometric method	101
Table 4.7	Analysis of elements in standard reference materials	103
Table 4.8	Chemical analysis of Thorium and Uranium bearing ore samples from Parachinar area	104
Table 4.9	Chemical analysis of Thorium and Uranium bearing ore samples collected from Nangarnai and Hunza	105
Table 4.10	Chemical analysis of Uranium, Thorium and Phosphate bearing ore samples from Rustam area	106
Table 4.11	Chemical analysis of Uranium and Thorium bearing ore samples from Tarbela area	106
Table 4.12	Chemical analysis of Uranium bearing ore samples from Kabul Khel area	107
Table 4.13	Determination of Uranium in the ore samples from Isa Khel and Rajan Pur area	108
Table 4.14	Determination of Thorium in the ore samples from Badar and Landi area	108
Table 4.15	Chemical analysis of Zircon bearing beach sand samples obtained from Sonmiani	109
Table 4.16	Chemical analysis of Zircon conc. sand from NMD, PINSTECH	110
Table 4.17	Concentration range of Thorium, Uranium and Zirconium in the ore samples analysed	111
Table 4.18	Concentration of Thorium, Uranium and Zirconium in some representative ore samples determined by various analytical techniques	112

Table 4.19	Concentration range of various elements found in Thorium, Uranium and Zirconium bearing ore samples	113
Table 4.20	Concentration of Thorium, Uranium and Zirconium oxides reported in the ores of various countries	114
CHAPTER FIVE		
Table 5.1	Effect of perchloric acid conc. on the absorbance of Thorin solution in perchloric acid	135
Table 5.2	Effect of perchloric acid conc. on the absorbance of Thorium-thorin complex	137
Table 5.3	Effect of cations on the spectrophotometric determination of Thorium in perchloric acid	139
Table 5.4	Effect of anions on the spectrophotometric determination of Thorium in perchloric acid	140
Table 5.5	Thorium contents in standard NBL ore samples	142
Table 5.6	Determination of Thorium in Thorium bearing ore samples (HRCB-2) by employing various analytical techniques	143
Table 5.6	Comparison of various spectrophotometric methods employed for Thorium determination	144
CHAPTER SIX		
Table 6.1	Effect of Sodium and Aluminium nitrate as salting-out agents on the extraction of Thorium	168
Table 6.2	The influence of Thorium conc. on its extraction employing 30% DBSO in xylene from nitric acid solution	170
Table 6.3	The effect of cations on the extraction of Thorium with DBSO from nitrate solution	172

Table 6.4	Effect of various anions on Thorium extraction by employing DBSO in xylene from nitric acid solution	174
Table 6.5	Extraction of Thorium from Thorium bearing standard (NBL) ore sample	181
Table 6.6	Accuracy and precision of method developed for Thorium extraction by employing 30% DBSO in xylene	183
Table 6.7	Extraction of Thorium as a function of hydrochloric acid concentration	185
Table 6.8	Separation factor for various metal ions with respect to Thorium extd. into 30% DBSO in xylene from 2 M HNO ₃ solution	186
Table 6.9	Various systems used for Thorium extraction and its subsequent detn. by spectrophotometric method	187

CHAPTER SEVEN

Table 7.1	Effect of Aluminium nitrate as salting-out agent on the extraction of Zirconium from 7 M HNO ₃ solution	221
Table 7.2	Effect of temperature on the extn. of Zirconium with DBSO in xylene from nitric acid solution	223
Table 7.3	Effect of cations on the extn. of Zr(IV) with DBSO from HNO ₃ sol.	224
Table 7.4	Effect of various anions on the extn. of Zr(IV) with DBSO from HNO ₃ solution	226
Table 7.5	Determination of accuracy and precision of Zirconium extraction method	229
Table 7.6	Performance of various stripping solution for Zirconium back extn.	229
Table 7.7	Separation coefficients for various metal ions with respect to Zirconium	230

INDEX OF FIGURES

Following Page

CHAPTER ONE

Figure 1.1 Energy consumption versus per capita
income for various countries 4

CHAPTER TWO

Figure 2.1 Schematic side view of swimming
pool reactor 17

Figure 2.2 The heat transport system of a
pressurized water reactor 18

Figure 2.3 Fuel control and fuel zoning in
light water breeder reactor (LWBR) 24

Figure 2.4 Principal reactions in conversion of
Thorium-232 to Uranium by neutron
capture and radioactive decay 31

Figure 2.5 Generation of Uranium-232 in a Thorium
fueled nuclear reactor 31

CHAPTER THREE

Figure 3.1 The general process of solvent extn.
as applied to metallurgical processing 59

CHAPTER FOUR

Figure 4.1 Location map showing various metal
bearing ores in Pakistan 66

CHAPTER FIVE

Figure 5.1 Absorption spectra of Thorin solution
and Thorium-thorin complex in 3 M HClO₄ 133

Figure 5.2 Effect of Thorin conc. in 3 M HClO₄
on the absorbance of Thorium-thorin
complex 136

CHAPTER SIX

Figure 6.1	Extraction of Thorium with 30% DBSO as a function of nitric acid conc.	166
Figure 6.2	Effect of DBSO conc. on the extn. of Thorium from 2 M HNO_3 solution	166
Figure 6.3	Influence of shaking time on the extn. of thorium with DBSO from 2 M HNO_3 sol.	167
Figure 6.4	Distribution ratio of Thorium as a function of temperature	173
Figure 6.5	Extraction equilibrium constant of Thorium as a function of temperature	173
Figure 6.6	Extraction of various metallic impurities with DBSO from HNO_3 sol.	176
Figure 6.7	Extraction behavior of various metal impurities with 30% DBSO from HNO_3 soln.	177
Figure 6.8	Log-log relationship of distribution ratio of Thorium and DBSO conc.	184
Figure 6.9	Schematic flow diagram for Thorium extraction from ore.	209

CHAPTER SEVEN

Figure 7.1	Extraction of Zirconium with 40% DBSO in xylene as function of nitric acid concentration	218
Figure 7.2	Influence of DBSO concentration on % extraction of Zirconium from 7 M nitric acid.	218
Figure 7.3	Influence of shaking time on the extn. of Zirconium from 7 M nitric acid using 40% DBSO in xylene	219
Figure 7.4	Effect of Zirconium on its extraction from 7 M nitric acid using 40% DBSO in xylene	220
Figure 7.5	Log-log relationship of distribution ratio of zirconium and DBSO conc.	225
Figure 7.6	Extraction of Zirconium with 40% DBSO in xylene as a function of hydrochloric acid concentration	230