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 RCSG 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.

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 2 M HNO_3 and 7 M HNO_3 aqueous solutions have been developed respectively. ^{95}Zr 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 $HClO_4$ 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 (ϵ_{544} = 1.69×10^4 dm^3 $mole^{-1}$ cm^{-1} at 26 ± 2 °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 (ß) 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 ^{o}C) whereas, negilible effect on the extraction of zirconium was noted upto 50 ^{o}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

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

INDEX OF TABLES

CHAPTER SEVEN

INDEX OF FIGURES

CHAPTER SIX

CHAPTER SEVEN