

Schriftenreihe des IME

Band 65

**Yiqian Ma**

**Development of a hydrometallurgical process  
for the recovery of Zr, Hf, Nb from eudialyte**

Shaker Verlag  
Düren 2020

## Table of Contents

<b>Acknowledgement</b> .....	<b>i</b>
<b>Table of Contents</b> .....	<b>iii</b>
<b>Abstract</b> .....	<b>vi</b>
<b>List of Figures</b> .....	<b>ix</b>
<b>List of Tables</b> .....	<b>xiv</b>
<b>Abbreviations</b> .....	<b>xv</b>
<b>Extened Abstract</b> .....	<b>xvi</b>
<b>I Background</b> .....	<b>xvi</b>
<b>I.I State of the art of eudialyte processing</b> .....	<b>xvii</b>
<b>I.II The treatment of eudialyte concentrate in EURARE project</b> .....	<b>xviii</b>
<b>I.III Acid dry digestion</b> .....	<b>xx</b>
<b>I.IV Ion exchange</b> .....	<b>xx</b>
<b>II Experimental part</b> .....	<b>xx</b>
<b>II.I Material characterization</b> .....	<b>xx</b>
<b>II.II Design of the flowchart</b> .....	<b>xxii</b>
<b>II.III Experiments</b> .....	<b>xxiv</b>
<b>III Results and discussion</b> .....	<b>xxvi</b>
<b>IV Conclusions</b> .....	<b>xxxiv</b>
<b>1 Introduction</b> .....	<b>1</b>
<b>2 State of Technology</b> .....	<b>5</b>
<b>2.1 Background of Zr, Hf and Nb</b> .....	<b>5</b>
<b>2.2 Fundamental of Zr, Hf and Nb extraction</b> .....	<b>7</b>
<b>2.2.1 Zr and Hf extraction</b> .....	<b>7</b>
<b>2.2.2 The separation of Zr and Hf</b> .....	<b>9</b>

## Table of Contents

---

2.2.3	Niobium extraction .....	10
2.3	Leaching and E-pH diagram.....	11
2.4	Acid dry digestion .....	14
2.5	Solution coordination chemistry in hydrometallurgy .....	20
2.6	Metal precipitation and crystallization.....	25
2.7	Ion exchange.....	29
2.7.1	Mechanism and procedure of ion exchange.....	29
2.7.2	Thermodynamic equilibrium and kinetics of ion exchange .....	31
2.7.3	Ion exchanger and its applications in hydrometallurgy.....	35
2.8	The fundamental of eudialyte processing.....	37
2.8.1	Rare earth elements and eudialyte.....	37
2.8.2	State of art in eudialyte processing .....	39
2.8.3	The treatment of eudialyte concentrate in EURARE project .....	47
<b>3</b>	<b>Motivation, Hypothesis and Theoretical Foundation .....</b>	<b>55</b>
3.1	Motivation .....	55
3.2	Hypothesis.....	56
3.3	Theoretical foundation .....	57
3.3.1	Theoretical background of dry digestion and leaching .....	57
3.3.2	Aqueous chemistry analysis of the resulting leach solution .....	60
3.3.3	Zr recovery from sulfuric acid leach solution using selective precipitation .....	62
3.3.4	Recovery of Zr and Hf from sulfuric acid leach solution using ion exchange... ..	62
3.3.5	Preparation of Zr product.....	64
<b>4</b>	<b>Experimental Methodologies.....</b>	<b>65</b>
4.1	Design of hydrometallurgical process .....	65
4.2	Acid dry digestion and leaching of eudialyte residue .....	68
4.3	Recovery of Zr, Hf and Nb using selective precipitation .....	71
4.4	Selective recovery and separation of Zr and Hf using anion exchange resin .....	74
4.4.1	Batch adsorption experiments .....	74
4.4.2	Column test.....	75
4.4.3	Equilibrium studies.....	77
4.5	Preparation of Zr product.....	79
<b>5</b>	<b>Results and Discussion .....</b>	<b>81</b>
5.1	Characterisation of eudialyte and eudialyte residue from EURARE project .....	81

Table of Contents

---

5.2	<i>Acid dry digestion and leaching</i> .....	84
5.2.1	Preliminary results .....	84
5.2.2	Acid digestion.....	86
5.2.3	Leaching procedure .....	91
5.2.4	Morphology characterization and phase changes .....	95
5.3	<i>Precipitation</i> .....	99
5.3.1	Effect of pH on the precipitation of metal ions .....	99
5.3.2	Effect of the quantity of CaCl <sub>2</sub> on the basic zirconium precipitation .....	101
5.3.3	Effect of pH on the basic zirconium precipitation.....	102
5.3.4	Effect of temperature on the basic zirconium precipitation.....	103
5.3.5	Effect of time on the basic zirconium precipitation .....	104
5.3.6	Characterization of precipitates .....	105
5.3.7	Flowchart with metal balance .....	107
5.4	<i>Ion exchange</i> .....	108
5.4.1	Batch adsorption experiments .....	108
5.4.2	Column adsorption experiments.....	116
5.4.3	FT-IR studies .....	118
5.4.4	Adsorption modeling of Zr and Hf.....	119
5.4.5	Flowchart with metal balance .....	120
5.5	<i>Preparation of Zr products</i> .....	122
<b>6</b>	<b>Conclusions and Outlooks</b> .....	<b>125</b>
6.1	<i>Conclusions</i> .....	125
6.2	<i>Research outlooks</i> .....	127
<b>7</b>	<b>References</b> .....	<b>129</b>
<b>8</b>	<b>Appendix</b> .....	<b>140</b>