TABLE OF CONTENTS

Chapter 1. Introduction

1.1	Current socioeconomic situation	1
1.1.1	Resources of metals in the world	1
1.1.2	Environmental and health effects of heavy metals	8
1.2	The potential of electrodialysis for the recovery of	
	heavy metals	11
1.2.1	Principle of electrodialysis	11
1.2.2	Advantages and challenges of electrodialysis applied to	the
	treatment of metal containing effluents	15
1.3	Ion-exchange membranes	18
1.3.1	Structure and properties of ion-exchange membranes	18
1.3.2	Ion transport and concentration polarization	22
1.3.3	The potential of the overlimiting current regimes	29
1.3.4	Transport of heavy metal ions	30
1.4	References	34

Chapter 2. Objectives and scope

2.1	Objectives and scope	41
2.2	Structure of this Thesis	42

Chapter 3. Experimental techniques

3.1	Introduction	47
3.2	Ion-exchange membranes used in the Thesis	48
3.3	Visualization and characterization of the structu	re of
	ion-exchange membranes	50

3.3.1	Scanning electron microscopy	50
3.3.2	Raman spectroscopy	50
3.4	Ion uptake experiments	51
3.5	Electrochemical characterization of the ion tra	ansport
	through the membranes	55
3.5.1	Experimental setup and procedure	56
3.5.2	Chronopotentiometry	57
3.5.3	Calculation of the transport number	61
3.5.4	Current-voltage curves	64
3.6	Galvanostatic electrodialysis experiments	67
3.6.1	Experimental setup and procedure	67
3.6.2	Atomic absorption spectrometry	70
3.6.3	Figures of merit of an electromembrane reactor	71
3.7	References	73

Chapter 4. Results and discussion

4.1	1 Transport of metal ions present in single salt solutio	
	through cation-exchange membranes	75
4.1.1	Introduction	75
4.1.2	Structure and ion exchange equilibrium properties of Nafic	on
	membranes	76
4.1.2.1	Characterization of the membrane structure	76
4.1.2.2	Ion sorption equilibrium properties	78
4.1.3	Transport of monovalent ions	81
4.1.3.1	Chronopotentiometric response	81
4.1.3.2	Calculation of the transport number of Na * ions through N	afion
	117 membranes	88
4.1.3.3	Current-voltage characteristics	91
4.1.4	Transport of divalent ions	94
4.1.4.1	Chronopotentiometric response	95
4.1.4.2 Calculation of the transport number of Ni ²⁺ ions thro		afion
	117 membranes	100
4.1.4.3	-	102
4.1.5	Transport of ions of trivalent metals	105
4.1.5.1	Chronopotentiometric response	106

		CONTENTS
4.1.5.2	Current-voltage characteristics	116
4.1.6	Conclusions	123
4.2 (Competitive transport of metal ions present in	
	nulticomponent mixture solutions through ca	
	exchange membranes	127
4.2.1	Introduction	<i>,</i> 127
4.2.2	Competitive ion transport between protons and met	-
4.2.2	Case of study: H^+ vs. Ni^{2+}	129
4.2.2.1	Introduction and applicability	129
4.2.2.2	lon sorption experiments	131
4.2.2.3	Chronopotentiometric response	134
4.2.2.4	Current-voltage characteristics	141
4.2.2.5	Calculation of the transport number of Ni ²⁺ ions throu	
	117 membranes	146
4.2.3	Competitive ion transport between metal ions of diff	erent
	valence. Case of study: Na(I) vs. Fe(III)	150
4.2.3.1	Introduction and applicability	150
4.2.3.2	lon sorption experiments	152
4.2.3.3	Chronopotentiometric response	155
4.2.3.4	Current-voltage characteristics	162
4.2.4	Conclusions	167
4.3 I	nvestigation of the mechanisms of overlimitir	ig mass
	ransfer	171
4.3.1	Introduction	_ / _ 171
4.3.2	Mechanisms of overlimiting mass transfer	_/_ 174
4.3.2.1		174
4.3.2.2	Exaltation effect	176
	Gravitational convection	, 177
4.3.2.4	Electroconvection	178
4.3.3	Study of the overlimiting currents by means of	
	chronopotentiometry and current-voltage curves	181
4.3.3.1	Dynamics of ion transport in membrane systems ope	rated at
	overlimiting currents	181
4.3.3.2	Steady state of membrane systems operating at over	rlimiting
	currents	184
4.3.4	Overlimiting currents originated by water splitting pr	oducts 185

4.3.5	Overlimiting currents originated by enhanced convective	
	phenomena	196
4.3.5.1	Electroconvection and gravitational convection	196
4.3.5.2	Role of M ⁺ⁿ ions on coupled convection	205
4.3.5.3	Role of H^+ ions on coupled convection	210
4.3.6	Conclusions	215
4.4 E [.]	ffects of the electrolyte composition and the cu	urrent
re	egime on the performance of electrodialysis	218
4.4.1	Introduction	218
4.4.2	Effect of the electrolyte composition on the membrane	
	behavior at underlimiting currents	221
4.4.2.1	Electrodialysis performance with different compositions a	at a
	constant current	221
4.4.2.2	Electrodialysis performance at 75% i _{lim} for each solution	
	composition	228
4.4.3	Effect of the current regime	232
4.4.4	Assessment of the convenience of applying overlimiting	
	currents	239
4.4.5	Conclusions	244
_		

4.5 References

246

Chapter 5. Conclusions

5.1	Conclusions	259
5.1.1	Transport of single salt solutions	259
5.1.2	Transport of multicomponent mixtures	261
5.1.3	Mechanisms of overlimiting currents	263
5.1.4	Galvanostatic electrodialysis experiments	264

ABSTRACT	267
RESUMEN	269
RESUM	271