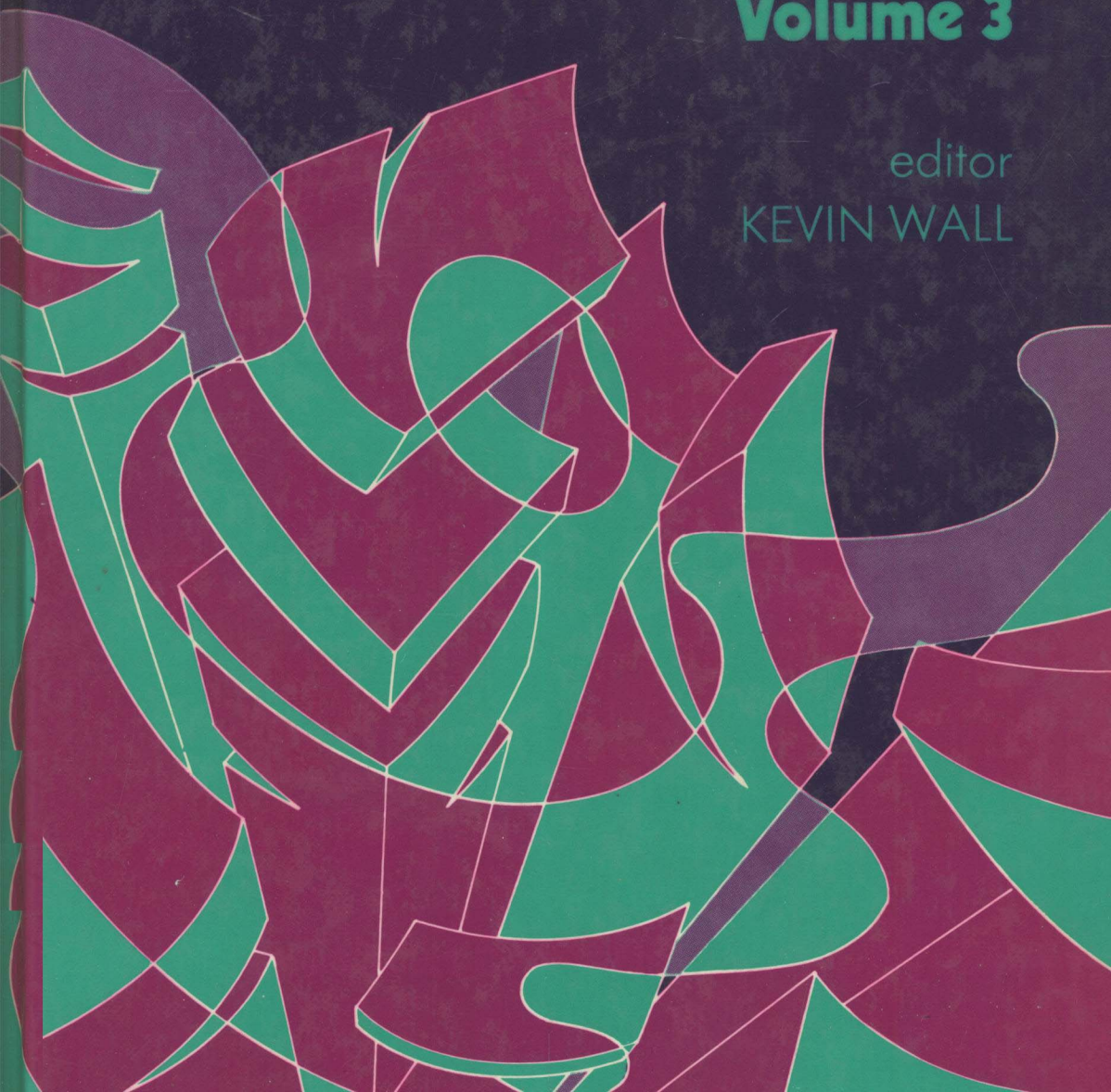


ELLIS HORWOOD · PUBLISHERS

MODERN CHLOR-ALKALI TECHNOLOGY

Volume 3

editor
KEVIN WALL



MODERN CHLOR-ALKALI TECHNOLOGY

Volume 3



MODERN CHLOR-ALKALI TECHNOLOGY

Volume 3

Editor:

K. WALL, B.Sc., Ph.D.
The Associated Octel Co. Ltd.
Ellesmere Port, South Wirral



Published for the
SOCIETY OF CHEMICAL INDUSTRY
London by



ELLIS HORWOOD LIMITED
Publishers · Chichester

First published in 1986 by

ELLIS HORWOOD LIMITED

Market Cross House, Cooper Street, Chichester, West Sussex, PO19 1EB,
England

The publisher's colophon is reproduced from James Gillison's drawing of the ancient Market Cross, Chichester.

Distributors:

Australia and New Zealand:

Jacaranda-Wiley Ltd., Jacaranda Press,

JOHN WILEY & SONS INC.

GPO Box 859, Brisbane, Queensland 4001, Australia

Canada:

JOHN WILEY & SONS CANADA LIMITED

22 Worcester Road, Rexdale, Ontario, Canada

Europe and Africa:

JOHN WILEY & SONS LIMITED

Baffins Lane, Chichester, West Sussex, England

North and South America and the rest of the world:

Halsted Press: a division of

JOHN WILEY & SONS

605 Third Avenue, New York, NY 10158, USA



© 1986 Society of Chemical Industry/Ellis Horwood Limited

British Library Cataloguing in Publication Data

Modern chlor-alkali technology Vol. 3. —

(Ellis Horwood series in industrial chemistry)

1. Chlorine

I. Wall, K. II. Society of Chemical Industry

665.8'3 TP248.C5

ISBN 0-85312-865-0 (Ellis Horwood Limited)

ISBN 0-470-20317-X (Halsted Press)

Phototypeset by Ellis Horwood Limited

Printed in Great Britain by Unwin Bros. of Woking

COPYRIGHT NOTICE

All Rights Reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, recording or otherwise, without the permission of Ellis Horwood Limited, Market Cross House, Cooper Street, Chichester, West Sussex, England.

Table of Contents

Introduction	17
K. Wall, The Associated Octel Co. Ltd.	

Section A The World Chlor-alkali business scene

1 The World of Chlor-Alkali Outlook 1975–1990

1.1 Introduction	20
1.2 Supply of Chlor-alkali	20
1.3 China	22
1.4 Eastern Europe	22
1.5 Production Technology Shifts	23
1.6 Production	25
1.7 Producers	27
1.8 Demand for Chlor-alkalis	27
1.8.1 Chlorine	29
1.8.2 Alkalis	29
1.9 Substitutability of Alkalis	29
1.10 World Trade Patterns	31
1.10.1 Caustic Soda	32
1.10.2 Soda Ash	32
1.11 Outlook	33
1.11.1 Chlorine	33
1.11.2 Caustic Soda	33

1.11.3 Soda Ash	34
1.12 Discussion	35
 *2 Chlor-alkali Industry of China	 36
Wang Zung Jie, President, China Chloralkali Industry Association	
 3 EEC Law and Policy Development	
C. Stanbrook, Barrister, Stanbrook and Hooper	
3.1 Introduction	39
3.2 Influencing Community Legislation	39
3.3 The Chlorine Industry and International Trade	40
3.4 Environment and Consumer Protection	41
3.5 Energy Costs.	43
3.6 Conclusions	43
 4 New Priorities for Chlor-alkali	
Vance Ward, Chairman, The Chlorine Institute Inc.	
4.1 References	48
4.2 Discussion	49
 Section B Aspects of Chlorine Safety	
5 First Report of the Toxicity Working Party:	
Toxic Effects of Chlorine	
Dr J. Withers, Loughborough, University of Technology	
5.1 Introduction	51
5.2 Effects on Humans	53
5.3 The Data Available from Animal Experiments.	54
5.4 The Comparative Acute Lethal Toxicity in Animals and humans.	55
5.5 Medical Aspects of Acute exposure to Chlorine-gas	57
5.5.1 Human effects from exposure to chlorine gas.	58
5.5.2 Medical treatment for human cases.	58
5.5.3 Treatment of the effects of chlorine exposure	58
5.5.4 Other measures.	59
5.5.5 Sequelae of acute chlorine exposure	59
5.6 Overview from Case Histories	59
5.7 Conclusion	61
5.8 References	63
(a) General references	63
(b) Specific references.	63
5.9 Appendix	69
5.10 Discussion	69

6 Corrosion and Erosion of Steel in Liquid Chlorine at Different Conditions of Velocity, Water Content and Temperature

M. W. J. Hammink and P. C. Westen, Akzo Zout Chemie, Nederland bv

6.1 Introduction	71
6.2 Phase Diagrams of $\text{FeCl}_3\text{-H}_2\text{O}$	72
6.3 Wall Thickness Decrease by the Dissolving of Iron Chloride	74
6.4 Wall Thickness decrease by Deliquesced Iron Chloride due to Electrochemical Corrosion	76
6.5 Erosion of the Iron Chloride Skin	79
6.6 References	80

7 Advances in Detection and Reliability of Atmospheric Chlorine Detection Systems

I. W. Rooney, Group Product Manager, Gas Detection, Draeger Safety Group Ltd.

7.1 Introduction	82
7.1.1 Draeger Safety Group	82
7.1.2 Chlorine	82
7.1.3 General	83
7.2 Chloralarm	83
7.2.1 Measuring principle.	83
7.2.2 Approvals	84
7.3 Test, Maintenance and Reliability	84
7.3.1 Electrolyte usage	84
7.3.2 Unique feature — dynamic test.	85
7.3.3 Control cards	86
7.3.4 Cost of maintenance	86
7.4 Suggestions for Installation	87
7.4.1 Sensor siting for atmospheric contaminants — open space — single tank — open air.	87
7.4.2 Sensor siting for atmospheric contaminants — confined space	88
7.4.3 Sensor siting for flow sampling	88
7.4.4 Suggested alarm sequence	89
7.5 Choosing Respiratory Equipment	89
7.5.1 Respiratory protection	89
7.5.2 Self-contained breathing apparatus.	93
7.5.3 Airline breathing apparatus	93
7.5.4 Escape breathing apparatus	94
7.6 References	94
7.7 Discussion	96

*8 Safety Considerations in the Design of Chlor-alkali Plants

I. F. White, G. J. Dibble, J. E. Harker and T. F. O'Brien,
Catalytic International Inc.

8.1 Summary	97
8.2 Introduction	97
8.3 Chlorine Processing.	98

8.3.1 Scrubbing and emergency venting	98
8.3.1.1 Seal pots	99
8.3.1.2 Other relieving devices	99
8.3.1.3 Scrubbing	100
8.3.1.4 High pressure vents	100
8.3.1.5 Materials	101
8.3.2 Cooling	101
8.3.3 Drying	102
8.3.4 Chlorine compression.	102
8.3.5 Liquefaction	103
8.3.6 Liquid chlorine handling	104
8.4 Caustic Soda Processing	106
8.5 Hydrogen Systems	107
8.6 Electrical Safety in Cellroom Design	108
8.6.1 Hazards to the human body	108
8.6.2 Cellrooms	109
8.6.3 Other hazards.	110
8.6.4 Operator training.	110
8.7 Safety equipment	110
8.8 Conclusion	111
8.9 Disclaimer	111
8.10 References	112

9 Chlor-Aid — The Intercompany Collaboration for Chlorine Engineers

B. Carr, Imperial Chemical Industries plc

9.1 Introduction	113
9.2 The Chlor-Aid Organization	115
9.3 Enlisting the Chlor-Aid Emergency Service.	115
9.4 Chlor-Aid Emergency Centres	116
9.5 Roles in a Chlor-Aid Emergency Response	117
9.6 Chlorine Emergency Techniques and Equipment	118
9.7 Training	118
9.8 The Chlor-Aid Committee	120
9.9 Conclusion	120
9.10 References	120
9.11 Discussion	120

Section C Development and Operation of Membrane Cells

10 The SCI Castner Medal Lecture:

Discovery and Development of Nafion®

Perfluorinated Membranes

W. Grot, E. I. du Pont de Nemours & Co.

10.1 Discussion	130
---------------------------	-----

11 Nafion® Perfluorinated Membranes —**Operation in Chlor-alkali Plants****J. H. Austin, E. I. du Pont de Nemours & Co.**

11.1	Introduction	131
11.2	Experience	133
11.3	Power Consumption	134
11.3.1	Current efficiency	134
11.3.2	Voltage	135
11.4	Performance Range.	135
11.4.1	Current density	135
11.4.2	Temperature	137
11.4.3	Caustic concentration	137
11.4.4	Brine impurities	138
11.4.5	Acid addition	140
11.4.6	Anolyte Strength	140
11.5	Ease of Use	142
11.6	Membrane Life	143
11.7	Future Trends	145
11.8	Conclusions.	146
11.9	Acknowledgements.	146
11.10	References	146

12 Operating Experience with the ICI FM21 Electrolyser**G. W. Cowell and C. Jackson, ICI plc**

12.1	Introduction	147
12.2	The FM21 Electrolyser	147
12.3	The FM21 Electrolyser Plants	149
12.4	The FM21 Electrolyser Systems	151
12.5	Assembly and Installation of the FM21 Electrolyser	152
12.6	Operational Procedures for the FM21 Electrolyser.	157
12.7	Performance of the FM21 Electrolyser	159
12.8	Membranes in the FM21 Electrolyser	159
12.9	Electrodes in the FM21 Electrolyser	159
12.10	Materials of Construction in the FM21 Electrolyser	160
12.11	Conclusions.	160

13 Operating Experience Gained with the Bipolar*Hoechst-Uhde Membrane Cell****Dr D. Bergner, Dipl-Ing K. Hannesen Aktiengesellschaft, Frankfurt/Main**

13.1	Introduction	162
13.2	Description of the Hoechst-Uhde Membrane Cell	163
13.2.1	Design of the cell elements	163
13.2.2	Arrangement of the cell elements in the electrolyzer	167
13.2.3	Contact between the elements.	167
13.2.4	Supply and withdrawal of the electrolytes and gases	167
13.2.5	Minimizing the leakage currents.	170

13.2.6	Arrangements of the electrolyzers in the electric circuit	171
13.3	Operation of the Hoechst-Uhde Membrane Cell.	171
13.3.1	Voltage/current curves	171
13.3.2	Electrolysis Plants using the Hoechst-Uhde membrane cells	173
13.4	Conclusions	173
13.5	References	175
14	Recent Developments in Ion-exchange Membranes for Chlor-alkali Electrolysis	
	Maomi Seko, Jukichi Omura and Mitsuo Yoshida, Asahi Chemical Industry Co. Ltd., Japan	
14.1	Introduction	178
14.2	Membrane Design Concept.	179
14.2.1	Exchange groups	179
14.2.2	Characteristics of multilayer membrane obtained by chemical conversion	181
14.2.3	Selection of ion-exchange capacity	183
14.2.4	Design anolyte concentration	183
14.2.5	Design catholyte concentration	184
14.2.6	Factors determining NaCl content in caustic soda	184
14.2.7	Influence or reinforcing material	187
14.3	Factors Causing Decline in Membrane Performance	188
14.3.1	Contamination by heavy metals	188
14.3.2	Physical damage to membrane	191
14.3.3	Physical relaxation under swelling and shrinkage	192
14.4	Conclusion	194
14.5	References	195
15	Operational Cell Technology	
	H. Ukihashi and K. Sato, Asahi Glass Co. Ltd.	
15.1	Introduction	196
15.2	Chlor-Alkali Plants using the Flemion Membrane Process	197
15.2.1	Operational results of filter-press cell plant	197
15.2.2	Operational results of AZEC plant	198
15.2.3	Performance of activated cathodes in an AZEC plant.	201
15.3	Application of Flemion in Various Electrolyzers	203
15.3.1	Membranes used for retrofitting cells	203
15.3.2	Operational requirements for obtaining longer membrane life	206
15.4	Progress of Flemion: Present and Future	208
15.5	Conclusion	208
15.6	References	208
15.7	Discussion	210

16 Membrane Cell Technology — An Optimum Design

N. Kawasaki, M. Murakami, M. A. Kazawa and T. Sato,
Toyo Soda Manufacturing Co. Ltd.

16.1	Introduction	212
16.2	Good Performance — High Current Efficiency and Low Cell Voltage.	212
16.2.1	Cell height.	213
16.2.2	Cell width	213
16.2.3	Back space.	214
16.2.4	Nozzle	214
16.3	Easy Operation and Maintenance — Simple Construction and Light Weight	215
16.4	Cheap Fabrication Cost and Long Life	216
16.5	Toyo Soda Membrane Cell	217

**17 The Eltech Membrane Gap Cell for the
Production of Chlorine and Caustic**

R. J. Horvath, Eltech Systems Corporation

17.1	Introduction	218
17.2	Membrane Gap Cell (MGC) Development Programme	218
17.2.1	Electrolyte IR	220
17.2.2	Structural IR	221
17.2.3	Cathode overpotential.	222
17.3	Some Design Aspects of the MGC Cell.	224
17.3.1	Electrode Design	224
17.3.2	Current distribution	225
17.3.3	Cell size	227
17.3.4	Cell gasketing	227
17.3.5	Hydraulic Design	228
17.3.6	Membrane damage	228
17.4	Commercial MGC Electrolyzer.	230
17.5	Performance	231
17.6	Applications	231
17.6.1	Diaphragm cell plants	233
17.6.2	Mercury cell plants	234
17.7	Summary	236

18 Adoption of Membrane Cells in India

R. D. Ahuja, V. K. Soni Shiram Fertilisers and Chemicals

18.1	Status of Caustic Soda in India	237
18.1.1	Introduction	237
18.1.2	Consumption pattern	237
18.1.3	Technology	239
18.2	Need for Membrane Cells	239
18.2.1	Savings in energy	240
18.2.2	Reduction in cost of production	240

18.2.3 Elimination of pollution	240
18.3 Adoption of Membrane Cells in India — Various Factors	244
18.3.1 Membrane replacement cost	244
18.3.2 Capital cost	245
18.3.3 Anode/cathode recoating	245
18.3.4 Optimum design	245
18.3.5 Quality of power supply	246
18.3.6 Brine purity/on-line analyser	247
18.3.7 Market conditions	247
18.4 Conclusions	247

Section D Chlor-Alkali Electrodes and Electrode Reactions

19 Precious-Metal Activated Cathodes for Chlor-Alkali Cells

D. E. Grove, Johnson Matthey Chemicals Ltd.

19.1 Introduction	250
19.2 Energy Requirements in Membrane Cells	251
19.3 Precious-Metal Coated cathodes	252
19.3.1 Introduction	252
19.3.2 Precious-metal coatings	253
19.3.3 Application	253
19.3.4 Nature of the coating	254
19.3.4.1 Thickness/porosity	254
19.3.4.2 Chemical	255
19.3.4.3 Physical	255
19.4 Measurement of Overpotential	257
19.5 Economics	259
19.6 Future Developments.	260
19.7 Conclusions.	261
19.8 Acknowledgements.	261
19.9 References	262

20 Titanium Anode Design

K. R. Kozoll, Conradty GmbH & Co. Metallelektroden KG

20.1 Discussion	292
---------------------------	-----

21 ICI Electrode Coatings for Membrane Cells

J. F. Cairns, A. M. Couper, D. A. Denton, Imperial Chemical Industries plc

21.1 Introduction	293
21.2 Mercury and Diaphragm Anodes	294
21.3 Membrane Cell Anodes	296
21.4 Diaphragm Cell Cathodes	299
21.5 Membrane Cell Cathodes	300
21.6 Conclusions	308
21.7 Discussion	308

22 The Oxygen Side Reaction in the Membrane Cell**Dr S. Kotouski and Dr B. Busse, Heraeus Elektroden GmbH**

22.1	Introduction	310
22.1.1	Economic background	310
22.1.2	Technical background	310
22.1.3	Scope of the paper	311
22.2	Investigation of Various Oxygen and Chlorate Sources	311
22.2.1	Reaction I	311
22.2.2	Reaction II	312
22.2.3	Reaction III	312
22.2.4	Reaction IV	313
22.2.5	Reaction V	315
22.2.5.1	Summary of the results obtained so far	315
22.2.5.2	Electrochemical oxidations cathode from chlorine generation	315
22.2.5.3	Further discussion of reaction V	320
22.2.6	Reaction VI	320
22.3	Influence of Anode Material	320
22.4	Influence of Operation and Cell Construction Parameters	322
22.5	References	325

Section E General Aspects of Chlorine Plant Design and Operation**23 Control of Sulfates in Membrane Cell Brine Systems****T. F. O'Brien, Stearns Catalytic Corporation**

23.1	Introduction	326
23.1.1	Background	326
23.1.2	The sulfate problem	327
23.1.3	Preparation of low-sulfate brines	327
23.2	Salt Selection	327
23.2.1	Natural salts	327
23.2.2	Processed salts	328
23.2.2.1	Purified vacuum salt	328
23.2.2.2	Recrystallized salt	328
23.2.2.3	Diaphragm cell evaporator salt	330
23.3	Removal of Sulfate from Brine System	331
23.3.1	Purging	331
23.3.1.1	Waste brine	331
23.3.1.2	Ion retardation	333
23.3.1.3	Hybrid plant operation	333
23.3.2	Chemical precipitation	336
23.3.2.1	Barium precipitation	336
23.3.2.2	Calcium precipitation	337
23.3.3	Crystallization	338
23.3.3.1	Sodium sulfate	339
23.3.3.2	Calcium sulfate	340

23.4	Rejection of Sulfate in Dissolver	341
23.4.1	Process conditions	341
23.4.2	Inhibition by minor additives	344
23.4.3	Stoichiometric suppression	345
23.4.3.1	Barium suppression	345
23.4.3.2	Calcium suppression	345
23.5	Examples	347
23.6	Acknowledgements	348
23.7	References	349

24 Development of a Modular Chlor-Alkali Plant Design

G. Dibble, Catalytic International Inc.

24.1	Summary	350
24.2	Introduction	350
24.3	Definition of Modular Concept	351
24.4	Basis of Approach	352
24.4.1	General criteria	352
24.4.1.1	Basic characteristics	352
24.4.1.2	Transportation	352
24.4.1.3	Standardization	353
24.4.2	Chlor-Alkali plant criteria	353
24.4.2.1	Plant capacity	353
24.4.2.2	Raw capacity	353
24.4.2.2	Raw materials and products	353
24.4.2.3	Module definition	354
24.4.2.4	Electrolyzer selection	355
24.4.2.5	Ancillary modules	355
24.5	Development of the Plant Design	355
24.6	Project Execution	357
24.7	Implementation of the Modular Plant Concept	360
24.8	Comparison of Conventional and Modular Plants	360
24.8.1	Cost	360
24.8.2	Schedule	362
24.9	Advantages of Modular Plant	362
24.10	Conclusion	363
24.11	Acknowledgements	364
24.12	References	364

25 Two methods for predicting shunt currents in stacks of bipolar plate cells

R. E. White, Texas A&M University,

H. S. Burney, R. N. Beaver, Dow Chemical, USA

25.1	Summary	365
25.2	Introduction	365
25.2.1	Undivided (no separator) cells	365

25.2.2	Divided cells.	370
25.3	Solution methods.	371
25.3.1	Linear circuit elements.	371
25.3.2	Nonlinear circuit elements.	373
25.4	Results and discussion.	376
25.4.1	Undivided cells.	376
25.4.2	Nonlinear circuit elements.	378
25.4.3	Divided cells.	380
25.5	Conclusions.	383
25.6	Acknowledgements.	384
25.7	References.	384
25.8	Appendix A. Application of Band (J) to solve for the Branch Currents in Fig. 3.	386
25.9	Appendix B. Finite difference equations for the the Branch Currents in Fig. 2.	389
25.10	Appendix C. Finite difference equations for the Branch Currents in Fig. 4.	390
26	Computer Based Data Acquisition for Chlorine Plants R. A. Crawshaw, Systems Designers plc	
26.1	Introduction.	394
26.2	Scenario.	394
26.3	Design Requirements.	395
26.4	Conclusion.	397
 Section F Hypochlorite and Chlorate Production		
27	The Use of a Multi-purpose High Mass Transport Cell for the Generation of Sodium Hypochlorite from Seawater. Dr. J. P. Millington, D. A. Hughes, The Electricity Council Research Centre, and J. Phelps, Steetley Engineering Ltd.	400
28	An On-stream Hypochlorite Generator with and without Pole Reversal of the Electrodes for Dilute Brine Electrolysis and Sea-water Electrolysis P. Fabian, W. Gerhardt, Haraeus Elektroden GmbH	
28.1	Introduction.	405
28.2	The Electrolytic Cell.	405
28.2.1	Description of the cell.	405
28.2.2	The current density distribution.	407
28.2.3	The electro-catalytic activation.	408
28.2.4	The performance of the cell.	409
28.2.4.1	Seawater electrolysis.	409
28.2.4.2	Electrolysis of dilute brines.	410
28.3	Examples of Applications of the Cell.	411
28.3.1	The chlorination of seawater swimming pools.	411

28.3.2. The chlorination of fresh-water swimming pools . . .	412
28.4. Conclusions	413
28.5. References	413
29 Elements of Chlorate Cell Design	
I. H. Warren and N. Tam, Chemitics International Co., Vancouver	
29.1 Introduction	414
29.2 Experimental	417
29.3 Results	419
29.4 Discussion and Conclusions	419
29.5 Acknowledgements	425
29.6 References	425
30 Hypochlorite and Chlorate Formation by Electrolysis of Dilute NaCl Solutions	
L. J. J. Janssen and E. Barendrecht, Eindhoven University of Technology	
30.1 Introduction	430
30.2 Reactions at the Anode and in the Anolyte	431
30.3 Experimental	432
30.3.1 Electrolysis cell and electrolyte flow circuits.	432
30.3.2 Electrolyte, procedure and analysis	432
30.4 Results	433
30.4.1 Current efficiencies	433
30.4.2 Mass transfer coefficient for hypochlorite	436
30.4.3 Chemical conversion of hypochlorite	436
30.5 Discussion	437
30.5.1 Rate-determining step for oxidation of chloride.	437
30.5.2 Rate-determining step for chlorate formation	438
30.5.3 Electrochemical rate constant for oxidation of chloride	441
30.5.4 Maximum hypochlorite concentration.	443
30.6 References	444
List of symbols and units	446
Index	449

* This paper was submitted but not presented at the 1985 Chlorine Symposium.