



MODERN CHLOR-ALKALI TECHNOLOGY



MODERN CHLOR-ALKALI TECHNOLOGY

Editor:

M. O. COULTER

formerly Development Manager, BP Chemicals
Sandbach Works, Cheshire



Published for the
SOCIETY OF CHEMICAL INDUSTRY
London
by



ELLIS HORWOOD LIMITED
Publishers • Chichester

First published in 1980 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, New Zealand, South-east Asia:

Jacaranda-Wiley Ltd., Jacaranda Press,
JOHN WILEY & SONS INC.,
G.P.O. Box 859, Brisbane, Queensland 40001, Australia.

Canada:

JOHN WILEY & SONS CANADA LIMITED
22 Worcester Road, Rexdale, Ontario, Canada.

Europe, 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, N.Y. 10016, U.S.A.

British Library Cataloguing in Publication Data

Modern Chlor-alkali technology.

1. Chlorine industry

I. Coulter, M. O. II. Society of Chemical Industry

665'.83 TP245.C5 80-412-36

ISBN 0-85312-184-2 (Ellis Horwood Ltd., Publishers)

ISBN 0-470-27005-5 (Halsted Press)

Typeset in Press Roman by Ellis Horwood Ltd.

Printed in Great Britain by W. & J. Mackay Ltd., Chatham

COPYRIGHT NOTICE — ©Ellis Horwood Limited 1980

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.	13
M. O. Coulter, formerly of BP Chemicals Ltd., Cheshire, England	
SECTION A — The Design and Performance of Chlorine Cells and Brine Electrolysis Systems	
Chapter 1 The Development of an Improved Diaphragm for Chlorine Electrolysis	
C. M. KOOL, Akzo Zout Chemie Nederland, the Netherlands	
1.1 Introduction.	17
1.2 Boundary conditions	17
1.3 The process of diaphragm production	18
1.4 Plant performance	21
1.5 Future development.	22
1.6 Literature	25
Chapter 2 Evolutionary Developments in Hooker Diaphragm cells	27
J. V. WININGS and D. H. PORTER, Hooker Chemicals & Plastics Corp., Niagara Falls, N. Y., U.S.A.	
References	42
Chapter 3 Commercial Application of PPG Bipolar Electrolyzer Technology	
T. C. JEFFERY, P.P.G. Industries Inc., Lake Charles, L.A., U.S.A.	
3.1 General description of an electrolyzer and bipolar unit	44
3.2 Electrolyzer disassembly	44
3.3 Diaphragm deposition	45
3.4 Electrolyzer assembly.	45
3.5 Electrolyzer transport	46
3.6 Electrolyzer cutout	46
3.7 Operating electrolyzer	47
3.8 General plant	48

Chapter 4 Uhde Cell Technology – Technical and Economic Aspects

Dr. R. STRASSER and S. PAYER, Uhde GmbH, Dortmund,
West Germany

4.1	Amalgam cells.	52
4.2	Technology of the HU diaphragm cell	54
4.2.1	Design principles of the HU cell	55
4.3	Membrane cell technology.	58
4.4	Comparison of cell technologies.	60

Chapter 5 The Development and Operation of High Current Density Mercury Cells

J. H. COLLINS and J. H. ENTWISLE, ICI Mond Division,
Cheshire, England

5.1	Introduction.	63
5.2	The rocking cell	63
5.3	Concrete 'Long' cells with pumped mercury	65
5.4	Ebonite lined cells.	67
5.5	Steel base cells	67
5.6	25 m ² cells.	70
5.7	33 m ² cells.	71
5.8	Conclusion.	72
5.9	Acknowledgement.	73

Chapter 6 Ways to Save Energy in the Production of Chlorine and Caustic

R. DWORAK and K. LOHRBERG, Lurgi Chemie and Hutten-
technik GmbH, Frankfurt am Main, W. Germany

6.1	Part 1: Electrolysis according to the mercury process	75
6.2	Part 2: Electrolysis according the the diaphragm process.	78
6.3	Part 3: Electrolysis according to the membrane process	80

Chapter 7 The Samex Process for Brine Purification – An Indirect Solution to Mercury Pollution

E. D. NOGUEIRA, J. M. REGIFE, Tecnicas Reunidas, S.A.,
Madrid, Spain, and J. F. J. MELENDO, Investigation Quimica
Industrial

	Abstract	85
7.1	Introduction.	85
7.1.1	Industrial use of brines as raw material	85
7.1.2	Conventional brine purification procedure	87
7.2	A new approach	87
7.3	New brine purification process.	88
7.3.1	Organic solvent composition	88
7.3.2	Basic reactions	89

7.3.3	Process description	89
7.3.4	Stream compositions	91
7.4	Cost estimates.	91
7.5	Samex demonstration plant start-up	94

SECTION B – Coatings for Metal Anodes and Cathodes

Chapter 8 Dimensionally Stable Anodes and New Developments in DSA-Anode Coatings. 99

D. BERGNER, Hoechst Aktiengesellschaft, Frankfurt, W. Germany and KUEHN-VON BURGSDORFF, Heraeus Electroden GmbH, Freigericht, W. Germany

Chapter 9 Platinum/Iridium-coated Titanium Anodes in Brine Electrolysis

P. C. S. HAYFIELD, IMI Limited, Birmingham, England and
W. R. JACOB, IMI Marston Limited, Wolverhampton, England

9.1	Historical development of the Noble metal coated titanium NMT anode.	103
9.2	Previous publications	104
9.3	Choice of 70/30 platinum iridium ratio	105
9.4	Methods of coating deposition	106
9.5	Coating composition	106
9.6	Electrochemical characteristics of K-type 70/30 Pt/Ir.	108
9.6.1	Overpotential	108
9.6.2	Change of overpotential with time	111
9.6.3	Laboratory accelerated wear rate data	112
9.6.4	Durability of Pt/Ir coated titanium when electrolyzed in alkaline brine	113
9.7	Practical application.	113
9.7.1	Sodium chlorate manufacture	113
9.7.2	Chlorine manufacture.	115
9.7.3	Sodium hypochlorite – generation from seawater	117
9.7.4	Impressed current cathodic protection in seawater	118
9.8	Discussion	118
9.9	Conclusions	119
9.10	Acknowledgements	120
9.11	References	120

Chapter 10 Cobalt Spinel Based Chlorine Anodes

D. L. CALDWELL and M. J. HAZELRIGG, The Dow Chemical Company, Texas, U.S.A.

10.1	Introduction.	121
10.2	The cobalt spinel anode	121

10.3	Physical characterization.	122
10.4	Electrochemical evaluation	133

Chapter 11 Development of a New Anode for Chlor-alkali Production

SHUNJIRO SAITO, TDK Electronics Ltd., Chiba, Japan

11.1	Background of development	137
11.2	Features of palladium oxide electrodes	138
11.2.1	Superior polarization characteristics	138
11.2.2	Low oxygen concentration in anode compartment gas	138
11.2.3	Small electrolytic consumption	141
11.2.4	Applications to other uses.	144
11.3	Manufacturing capacity	144

Chapter 12 Commercial Application of Cathode Coatings in Electrolytic Chlorine Cells

T. A. LIEDERBACH, A. M. GREENBERG and V. H. THOMAS,
Diamond Shamrock Corp., Ohio, U.S.A.

12.1	Technology	145
12.2	Commercialization.	147
12.3	Cathode coating and cell renewal services.	147

SECTION C – Perm-Selective Membranes and Membrane Cells

Chapter 13 Fundamentals of Transport and Diffusion Through Chlor-alkali Cell Membranes

R. L. DOTSON, Olin Corp., Charleston, Tenn., U.S.A. and H. L.
YEAGER, University of Calgary, Canada

13.1	Introduction.	153
13.2	Transport in ion exchange membranes.	155
13.3	Experimental measurements	156
13.4	Relation of diffusion and electrical properties of chlor-alkali membranes.	167
13.5	Additional experiments	170
13.6	References.	170

Chapter 14 Fluorocarbon Membranes for Chlor-alkali Industry

D. E. MALONEY, E. I. du Pont de Nemours & Co., Inc., Delaware,
U.S.A.

14.1	300 Series Nafion [®] membranes	173
14.2	Amine-modified Nafion [®] perfluorosulphonic acid membranes	175
14.3	Performance with very pure brine.	178
14.4	Computerized data storage and correlation.	179

14.5	Summary	180
14.6	Acknowledgement	181
14.7	References	182

Chapter 15 Chlorine/Caustic Soda Production in a Permselective Membrane Electrolyzer Employing Series Catholyte Flow

R. H. FITCH, B. E. KURTZ and C. W. MERKH, Allied Chemical Corp., Solvay, N. Y., U.S.A.

15.1	Introduction	185
15.2	Description of equipment	185
15.3	Acquisition of data	187
15.4	Results	188
15.5	Conclusion	194

Chapter 16 New Development of the Asahi Chemical Membrane Chlor-alkali Process

MAOMI SEKO, Asahi Chemical Industry Co. Ltd., Tokyo, Japan

16.1	Summary	195
16.2	Introduction	195
16.3	Principle of electrolysis	196
16.4	The Asahi Chemical Membrane Process	197
16.4.1	Membrane	197
16.4.2	Metal anode	198
16.4.3	Electrolyzer	198
16.5	Brine treatment	201
16.6	Asahi Chemical heat recovery evaporator	201
16.7	Process flow sheet	202
16.8	Performance of the commercial plant	203
16.9	Advantages of Asahi Chemical's membrane chlor-alkali process	206
16.10	References	210

Chapter 17 Chlor-alkali Process with Flemion

MASAO NAGAMURA, HIROSHI UKIHASHI and OSAMU SHIRAGAMI, Asahi Glass Co. Ltd., Tokyo, Japan

17.1	Introduction	211
17.2	What is Flemion®?	211
17.3	Fundamental properties of Flemion®	213
17.4	Production of caustic soda	215
17.5	Production of caustic potash	216
17.6	Electrolyzer	220
17.7	Commercial plant	220

Chapter 18 The Tokuyama Soda Membrane Caustic-chlorine Process

K. MOTANI and T. SATA, Tokuyama Soda Co. Ltd., Yamaguchi,
Japan

18.1	Introduction	223
18.2	Characteristics of the technology	223
18.2.1	Principle of membrane electrolysis	223
18.2.2	Process flow	224
18.2.3	Electrolyzer	225
18.2.4	Ion-exchange membrane	228
18.2.5	Electrodes	231
18.2.6	Evaporator	231
18.2.7	Operation	232
18.2.8	Products	232
18.3	Economics of the technology	233
18.3.1	Energy consumption	233
18.3.2	Running cost	233
18.3.3	Investment cost	233
18.4	Summary	234

Chapter 19 Development of the Memmer Electrolyzer

E. HERMANA, A. S. INFANZON and M. BAILE, Investigacion
Quimica Industrial, S. A., Madrid, Spain

19.1	Introduction	235
19.2	Description	235
19.3	Performance	237
19.3.1	Operating voltage	237
19.3.2	Effect of temperature	239
19.3.3	Flow across the membrane	239
19.3.4	Brine depletion	240
19.3.5	Brine purity	241
19.3.6	Regeneration	246
19.4	Present situation	246
19.5	References	246

SECTION D—High Current Switches**Chapter 20 Recent Advances in Vacuum Switches**

P. WAYLAND and R. M. HRUDA, Westinghouse Electric Corp.,
New York, U.S.A.

20.1	Cell over-voltage affects switching	249
20.2	New slant on switching high voltage	252
20.3	Typical application	252

20.4	Higher energy switching	253
20.5	Combination of improvements	254
20.6	Brine spillage and corrosion	255
20.7	Summary and conclusions	256

Chapter 21 Recent Developments in Ultra High Current Switching Using Liquid Metal

M. R. KOWALCZYK, GEC Industrial Controls Ltd., Rugby,
England, A. J. WALKDEN and R. I. COOKE, GEC-Hirst Re-
search Centre, Wembley, England

21.1	Abstract	257
21.2	Introduction	257
21.3	Why Liquid Metals?	258
21.4	Gain switch	260
21.5	Operation of gain switch	264
21.5.1	Current making and carrying	264
21.5.2	Current breaking	264
21.6	Synchronization	267
21.7	Development testing	267
21.7.1	Laboratory experiments and tests	267
21.7.2	On-site trails	269
21.8	Conclusions	270
21.9	References	270

SECTION E – Safety and Environmental Protection

Chapter 22 Handling and Storage of Chlorine – The State of the Art 273

T. B. POSNER, Chemical Industries Association Ltd., London,
England and M. G. T. BURROWS, Consultant, Cheshire, England

Chapter 23 Hazard Assessment in the Chlor-alkali Industry

N. C. HARRIS, Imperial Chemical Industries Ltd., Cheshire,
England

23.1	Introduction	279
23.2	Criteria of acceptability	279
23.3	Allocation of criteria within a factory	280
23.4	Toxicity	280
23.5	Public boundaries	282
23.6	Hazard assessment	282
23.7	Atmospheric dispersion	283
23.8	Presentation of results	284
23.9	Review of chlorine emission studies	285

23.10 Other areas of hazard assessment 286

23.11 Other criteria 286

23.12 Emergency procedures 286

23.13 Transportation 287

23.14 The future of risk assessment. 288

23.15 Acknowledgement. 288

23.16 References 289

Introduction

M. O. COULTER

When this symposium was held, only 3 years had elapsed since the 1976 meeting on 'Diaphragm Cells for Chlorine Production' [1], which was also sponsored by the Electrochemical Technology Group of The Society of Chemical Industry. Such has been the pace of development, however, that ample new information was available for presentation and discussion, and the programme of 23 papers submitted for publication attracted an international gathering of some 280 delegates from 20 countries.

In recent years the most rapid advances have been made in the development of perm-selective membranes capable of withstanding the highly aggressive conditions in chlorine cells, and in the design of membrane cells. But continual improvement has also been taking place in the traditional mercury and diaphragm processes, both to minimise overall costs in the context of rapidly escalating fuel prices and to reduce the potential hazards to health and the environment.

The first 7 papers deal in the main with development of the traditional processes. They include information on improved diaphragms (not all based on asbestos), on the commercial performance of a bipolar diaphragm electrolyser and on a new method of brine purification employing liquid/liquid extraction of polyvalent ions with oil-soluble ion exchange agent, which avoids the production of solid waste contaminated with mercury. There are also comparisons of the competing cell technologies, information on a method of controlling the chlorate concentration in the circulating brine for membrane cells and a fascinating account of mercury cell development in one organisation from the Castner-Kellner rocking cell to their latest 400 kA design.

The next 5 papers are concerned with electrode coatings. Considerable research has been in progress on improved methods for coating titanium anodes and on alternative coating compositions to those based on ruthenium dioxide, the objectives being to reduce first cost or to improve durability and short-circuit resistance in mercury cells. The development of platinum/iridium coated titanium anodes, which have proved successful in chlorate manufacture and seawater electrolysis, is described. Attention has also been paid to reducing the cathode overvoltage in diaphragm and membrane cells by applying porous nickel coatings, a subject which is also referred to in one of the more general papers in the first section.

In their early days, membrane chlorine cells found acceptance principally for very small plants where the chlorine and caustic products could be used on site. However the papers in this section show that they are already becoming competitive for plants of medium size, especially at locations where particularly stringent pollution regulations are in force. The subjects covered in this section range from the fundamentals of membrane behaviour to data on plants in commercial operation of capacity up to 80 000 tonnes per annum of caustic soda. A novel development, approaching the stage of industrial scale testing, is a membrane electrolyser with vertical electrodes and a rising amalgam cathode; it is hoped that this will combine the advantages of membrane cells and horizontal mercury cells.

The maintenance of high current air-break switches in cell-rooms has long been a problem. The development of sealed vacuum-break and argon-filled liquid metal switches, which are described in the next two papers, is therefore particularly welcome. A multi-break scheme suitable for the higher switching potential of bipolar electrolyzers is included.

The two final papers deal with safety and environmental protection. Although the chlorine industry world-wide has not been entirely free from incidents, its safety record in relation to the tonnage produced, transported and handled is very creditable. These papers illustrate the contributions made in the UK to this record by guides to safe practice, developed by the industry in close collaboration with statutory bodies, and by the intelligent application of quantitative hazard analysis.

The Society's thanks are due not only to the contributors to this volume, but also to the opening lecturer [2], the Organising Committee [3] and the session Chairmen [4], whose efforts ensured the success of the symposium, and to BP Chemicals Limited for generous hospitality.

- [1] Diaphragm Cells for Chlorine Production. (Proceedings of a symposium held at The City University, London, England, 16-17 June 1976). London: Society of Chemical Industry 1977.
- [2] J. Wood. Olin Corporation, P.O. Box 248, Charleston, Tennessee, 37310, U.S.A. An Overview of the Coming Programme with an Update on Chlorine Gas Handling, (not for publication).
- [3] Dr. A. Pennell, BP Chemicals Limited (Chairman); Mr. W. E. Cowley, Associated Ocel Limited (Chairman, Electrochemical Technology Group, Society of Chemical Industry); Mr. D. Bell, BP Chemicals Limited (Organising Secretary); Mr. B. Lott, Associated Ocel Co. Limited; Dr. S. F. Mellish, ICI Limited; Mr. M. A. Warne, IMI Marston Limited.
- [4] Dr. A. Pennell; Mr. R. Schoberle, Solvay et Cie, Rus de Prince Albert 33, 1050 Bruxelles, Belgium; Mr. R. Mitchell, The Chlorine Institute Inc., 342 Madison Avenue, New York 10017, U.S.A.; Dr. S. F. Mellish; Mr. W. E. Cowley.

Section A

Design and performance of chlorine cells and brine electrolysis systems

