ION EXCHANGE TECHNOLOGY

Editors:
D. NADEN, B.Sc.(Joint Hons)
Research Project Manager
Davy McKee Research and Development
Stockton-on-Tees Cleveland, UK

and

M. STREAT, B.Sc.(Tech.), Ph.D.
Reader in Process Engineering
Imperial College of Science and Technology
University of London

Published for the
SOCIETY OF CHEMICAL INDUSTRY
London, by

ELLIS HORWOOD LIMITED
Publishers · Chichester

First published in 1984 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
Ion exchange technology.
1. Ion exchange
I. Naden, D. II. Streat, M.
660.2'9723 TP156.16

Library of Congress Card No. 84-10145

ISBN 0-85312-770-0 (Ellis Horwood Limited)
ISBN 0-470-20089-8 (Halsted Press)

Typeset by Ellis Horwood Limited.
Printed in Great Britain by R.J. Acford, Chichester.

Table of Contents

Foreword 11

PART 1 – WATER TREATMENT

Ion exchange in water purification: Where do we stand? 14
J. Brown and N. J. Ray, CEGB, Ratcliffe, UK

Production and use of high purity water in the micro-electronics industry 25
T. Mottershead, Ferranti Electronics Ltd., Oldham, UK

Deionisation of boiler feedwater: Silica removal by counter-current regenerated anionic systems 37
E. Zanganiaris and G. H. Beasley, Rohm & Haas, France

Anion exchange resin kinetics in mixed bed condensate polishing 50
J. T. McNulty, Rohm & Haas, USA

The choice of ion exchanger for British Nuclear Fuels Ltd's Site Ion Exchange Effluent Plant 66
M. Howden and J. Pilot, BNFL and Davy McKee, UK

The oxidative pretreatment of organic matter in natural waters 74
K. Tittle, G. Knowles and J. D. Tyldesley, CEGB, N.W. Region, UK

Partial demineralisation of water by ion exchange using carbon dioxide as regenerant 85
W. Hoell and B. Kiehling, Kernforschungszentrum Karlsruhe, Germany

The regeneration of weak and strong cation exchange resins with an aqueous solution of SO_2 93
R. Raiter, D. Glasser and A. W. Bryson, Durban Corpn. and University of Witwatersrand, South Africa

Ammonium form cation resin operation of condensate purification plant 106
M. Ball, M. A. Jenkins and R. J. Burrows, CEGB, Ratcliffe, UK

Condensate polishing with the Ammonex procedure – 1984 119
G. J. Crits, Crane Co., USA
Experience data with Liftbed and Rinsebed processes 127
F. Martinola and G. Siegers, Bayer AG, Leverkusen, Germany
New Regenerant saving methods for producing ultra-pure water 138
V. Kadlec and P. Hubner, CKD DUKLA, Prague, Czechoslovakia
A new continuous packed-bed ion exchange system applied to treatment of mine water 144
A. Himsley and J. A. Bennett, Himsley Engineering, Toronto, Canada
The use of bead cellulose anion exchangers for ultra-pure water production 153
Z. Matejka and J. Eliasek, Institute of Chemical Technology, Prague, Czechoslovakia
The effect on the capacity of strong base anion exchange resins of the ratio of chloride to sulphate in the feed water 160
J. D. Nolan and J. I. Irving, Duolite International, UK

PART 2 – FUNDAMENTALS

A useful method for summarizing data in ion exchange 170
E. Hogfeldt, The Royal Institute of Technology, Sweden
Ion exchange selectivity and activity coefficients as functions of ion exchange composition 179
V. S. Soldatov and V. A. Bichkova, BSSR Academy of Sciences, USSR
Thermodynamic aspects of chelating ion exchange resins 189
K. G. Ashurst, MINTEK, South Africa
A new approach to ion exchange kinetics 201
L. Liberti, D. Petruzzelli, G. Boghetich and R. Passino, IRSA–CNR, Bari, Italy
Microcalorimetric measurements of enthalpies of ion exchange in aluminosilicate minerals and soils 213
K. W. T. Goulding and O. Talibudeen, Rothamsted Experimental Station, UK
EXAFS spectroscopy: a breakthrough in monitoring metal–support interactions in ion-exchange materials? 222
L. Alagna, T. Prosperi and A. A. G. Tomlinson, CNR, Rome, Italy
The development of a computer model, AMM LEAK, for sodium leakage from NH_4^+/OH^- from mixed beds. 231
J. C. Bates and T. D. Johnson, CEGB, UK
Simulation of membrane processes using network thermodynamics. . . . 242
R. Paterson and Lutfallah, University of Glasgow, UK

The rate of ion interdiffusion in complex-forming ionites for various convex and concave isotherms 257
T. D. Semenovskaya, A. I. Kalinitchev and E. V. Kolotinskaya, USSR Academy of Sciences, USSR

Nickel recovery by electrodialysis: a study of the membrane couple characterisation 266
C. Fabiani, M. DeFrancesco and L. Bimbi, Rome, Italy

Thermodynamics of ion exchange in microcrystals of hydrous oxides . . 276
R. Paterson and H. Rahman, University of Glasgow, Scotland

Hydrodynamics and mass transfer in a counter-current ion exchange pilot plant plat column 284
A. P. van der Meer, D. N. M. M. Weve and J. A. Wesselingh, Delft University of Technology, The Netherlands

Density relationships between gel and macroporous ion exchange resins 295
F. X. McGarvey, Sybron Chemical Corp., USA

Ion replacement by interactions of minerals in electrolyte solutions . . . 304
P. Kaushansky, Weizmann Institute, Israel

Structure of Nafion and its transport properties 314
C. Heitner-Wirguin, Hebrew University, Jerusalem, Israel

pH waves in anion exchange columns 322
B. J. Bennett and F. G. Helfferich, Pennsylvania State University, USA

The kinetics of ion exchange sorption in ternary systems 331
J. Plicka, J. Cabicar, K. Stamberg and M. Fabián, Technical University of Prague, Czechoslovakia

Thermal degradation of chemically modified silica and selected ion exchangers by TG – DTA – MS investigations 337
A. Kettrup and K.-H. Ohrbach, University of Paderborn, FRG

New techniques in ion exchange surface electrochemistry 343
J. D. Reid, O. R. Melroy, W. E. Bronner, P. Vanysek and R. P. Buck, University of North Carolina, USA

PART 3 – SPECIAL APPLICATIONS

Chemical processing: acid–base–salt systems 354
R. Blumberg, Miles Labs, Inc., USA

Direct hydration of propylene to isopropyl alcohol 360
W. Neier, Deutsche Texaco A.G., FRG

Difference in reactivities with effect of polarity of the solvent in the aldol condensation of citral with acetone under basic ion exchange catalysis 367
V. Subramoni, V. K. Rajeevan and B. Rajendra Prasad, Keala State Drugs and Pharmaceuticals Ltd., India

A new approach to large-scale sugar beet deionisation: 'New Demineralisation/Demi Process' . . . 381
G. Rousseau, Générale Sucrière, France
Interaction between a resin containing Dibenzo 18 Crown 6 and organic molecules . . . 391
A. F. Danil de Namor and E. Sigstad, University of Surrey, UK
Ion exchangers and adsorbent resins for the purification of proteins . . . 400
H. A. Chase, University of Cambridge, UK
Chemical disinfection by means of speciality ion exchange resins . . . 407
M. B. Kril, G. E. Janauer, G. Wilber and B. Kresge, SUNY-Binghamton, USA
The SMR process – a new ion exchange process to demineralise cheese whey with recovery of regenerant . . . 421
H. Jönsson, Swedish Dairies Association, Malmö, Sweden
Aminomethylated styrene/DVB copolymers: new applications for an existing technology . . . 430
G. Kühne and P. M. Lange, Bayer AG, Leverkusen, FRG
Bifunctional styrene/DVB catalysts . . . 436
P. M. Lange, Bayer AG, Leverkusen, FRG
Ion exchange resin catalysts having improved catalytic activity and enhanced thermal stability . . . 440
G. Beasley, Rohm & Haas, France, and I. J. Jakovac, Rohm & Haas, USA
Preparations, examination and parameter optimisation of cation exchangers in ion-chromatography . . . 450
P. Hajós and J. Inczédy, University of Chemical Technology, Hungary
Cation exchange resin – catalysed Ritter reaction of isobutylene with acetonitrile: a remarkable role of bound water . . . 458
N. Kalyanam and S. Sivaram, Indian Petrochemicals Corp., India
Separation of glucose and fructose: effects of resin characteristics on separation . . . 463
H. Welstein and C. Sauer, Duolite International, USA
Shock test for the determination of the resistance of ion exchange resins to osmotic and hydromechanical stress . . . 472
K. Hochmüller, BASF AG, FRG

PART 4 – ION EXCHANGE DEVELOPMENTS

A new method of halomethylation . . . 484
A. Deshe and A. Warshawsky, Weizmann Institute, Israel
Poly(vinylimidazole) – a versatile matrix for the preparation of chelating resins . . . 490
B. R. Green and E. Jaskulla, MINTEK, South Africa

The efficiency of aqueous aromatic eluants in the chromatographic separation of ions 500
H. Hershcovitz, G. Halevi and G. Schmuckler, Institute of Technology, Haifa, Israel
New developments in the chemistry of XFS 4195 and XFS 43084 chelating ion exchange resins 509
R. R. Grinstead, Dow Chemical Co., USA
Ion exchange in ferrierite, a natural zeolite 519
Z. B. Ahmad and A. Dyer, Salford University, UK
Controlled release by polyelectrolyte microcapsule membranes 533
Ming-Fu Tsai and M. Levy, Weizmann Institute, Israel
The present status of continuous ion excahnge using magnetic microresins 542
E. A. Swinton, B. A. Bolto, R. J. Eldridge, CSIRO, Australia.
P. R. Nadebaum AUSTEP, P. C. Coldrey, ICI, Australia
New developments in the use of ion exchangers and adsorbents as precoat filters 563
R. Kunin (consultant), A Tavares, R. Forman and G. Wilber, Graver Company, USA
Thermally regenerable polymeric crown ethers. II. synthesis and application in electrodialysis 579
A. Warshawsky, I. Rubinstein and O. Kedem, Weizmann Institute, Israel
Complex equilibria and the analytical ion exchange properties of divalent transition metals 585
J. M. Riviello, Dionex Corp., USA
Ion exchanger phase spectrophotometry for a sensitive determination of metals 595
H. Waki, Kyushu University, Japan

PART 5 – HYDROMETALLURGY

Hydrometallurgical processes for the separation of platinum group metals (PGM) in chloride media 604
A. Warshawsky, Weizmann Institute, Israel
Selective recovery of some platinum groups and precious metals using copolymers with covalently bound 1, 3, 4-thiadiazole-2, 5-dithiol groups and dithiocarboxylate groups 611
M. J. Hudson, Reading University, UK
The separation of noble metals by ion exchangers containing s-bonded dithizone and dehydrodithizone as functional groups 618
M. Grote and A. Kettrup, University of Paderborn, FRG

Unconventional weak-base anion-exchange resins useful for the extraction of metals, especially gold 626
B. R. Green and A. H. Potgieter, MINTEK, South Africa

The recovery of gold from cyanide liquors in a countercurrent contactor using ion exchange resin 637
A. Mehmet and W. A. M. Te Riele, MINTEK, South Africa

Silver–Copper separation by continuous ion exchange parametric pumping 653
G. Grevillot and D. Tondeur, CNRS–ENSIC, France

Comparative engineering and process features of operating continuous ion exchange plants in Southern Africa 661
F. L. D. Cloete, University of Stellenbosch, South Africa

The simulation and process design of NIMCIX contactors for the recovery of uranium 668
M. A. Ford, MINTEK, South Africa

The recovery of by-product uranium from wet phosphoric acid solutions using selective ion exchange resins 679
S. Gonzalez-Luque and M. Streat, Imperial College, UK

Development of an in-pulp contactor for metals recovery 690
D. Naden, E. Bicker, G. Willey and D. Lunt, Davy McKee, UK

The removal of thorium isotopes from nitric acid liquors 698
H. Eccles, BNFL Springfields Works, UK

The use of supported liquid membranes in the treatment of mining effluents 709
D. Hebden and J. J. Smit, Chamber of Mines, and Potchefstroom University, South Africa

Recovery of tungsten from hydrometallurgical liquors by ion exchange 715
J. Martins, C. Costa, J. Loureiro and A. Rodrigues, University of Porto, Portugal

A comparative study of some chelating ion exchange resins for applications in hydrometallurgy 724
J. Melling and D. W. West, Warren Spring Lab., UK

Uranium recovery from phosphoric acid with selective resins 736
S. Belfer, E. Korngold and Y. Egozy, Ben-Gurion University, Israel

Foreword

In recent years, we have been reminded that the first ion exchange conference was organised by the Society of Chemical Industry in the William Beveridge Hall, London University, 5–7 April 1954. The Proceedings of that conference were entitled 'Ion Exchange and its Applications' and was published in 1955. On re-reading the papers presented almost exactly thirty years ago, we are immensely impressed by the quality and range of work and also by the vision of some of the distinguished authors at that time. The conference was hardly international, since of the twenty papers presented, sixteen originated from speakers in the UK and the remainder from one or two European countries. However, the range of applications presented was considerable, for example the application of ion exchange in water treatment processes, synthetic fibre processes, metallurgical industries, drugs and pharmaceuticals, wine treatment and therapeutic applications in the field of medicine. Developments such as continuous ion exchange were anticipated and the paper by Hutcheon still deserves to be read by those of us interested in the historical background to this fascinating subject. Several contributors to the first meeting are still extremely active today, and it is a pleasure to pick out the names of Dr Roger Kressman and Dr Tom Arden, both of whom are active participants at this fourth SCI organised conference.

The second conference was organised at Imperial College, London in July 1969 and was truly international in character. Approximately 60 papers were published in the Proceedings in a wide variety of subject areas, though ion exchange resin developments, water treatment and ion exchange equipment developments were are at the forefront of interest. The concept of continuous ion exchange was fashionable and many papers proposed new contactor designs and flowsheet applications.

In 1976 the third conference entitled 'The Theory and Practice of Ion Exchange' was organised at Churchill College, Cambridge University. The subject matter was somewhat narrower than at the previous meetings in an attempt to bridge the gap between academic endeavour and industrial practice. This aim was achieved in a number of ways; many practical problems were highlighted and the advent of novel solutions to several hydrometallurgical problems started to emerge.

In the intervening eight years, the ion exchange industry has gone through difficult times, though research has continued undaunted. This is reflected in the present conference whereby the number of papers to be presented has increased substantially, though the topic areas are reduced. The most important area of application and research is clearly the field of water treatment, and it is noticeable that some topics have now settled into a state of publishable equilibrium. Examples are resin developments and hydrometallurgical processes. No attempt was made to restrict the scope of the conference and it is significant that some areas of work, such as inorganic materials, sugar processing and effluent treament, no longer enjoy such predominance.

All papers presented at this conference are published in these Proceedings and we have not discriminated between oral and poster presentations. It is intended that the papers as a whole represent the state of the art in ion exchange technology in July 1984.

The joint editors would like to express their gratitude to the members of the organising committee, namely Morton Carlyle, Michael Hudson, Roger Kressman, Michael Slater, and Michael Verrall, for their tireless work in processing manuscripts and assisting in the preparation of this book.

DAVID NADEN
MICHAEL STREAT
February 1984

PART 1

WATER TREATMENT

Ion exchange in water purification
Where do we stand?

J. BROWN and N. J. RAY, Scientific Services Department, Midlands Region, Central Electricity Generating Board, Ratcliffe on Soar, Nottingham, UK

1. INTRODUCTION

In a little over two decades, ion exchange technology has gained a virtual monopoly of use for the determineralisation of make-up water supplies to power station boilers within the CEGB. It has displaced traditional methods based on distillation or precipitation and, as yet, has not been seriously challenged by newer technologies such as reverse osmosis. Moreover, the confidence that has grown in ion exchange has led to its direct use for condensate purification of the main feedwater circuit of units which are particularly sensitive to impurities in boiler water. These are mainly the once-through nuclear boilers and certain sea-cooled conventional stations where full flow condensate polishing plants are employed. It is in the context of condensate purification that more stringent standards of performance have progressively been demanded from mixed-bed ion exchangers, but without matching improvements in the technology available.

In the period during which final water purification by ion exchange has become the norm, resin manufacturers have developed new types of resins and many new variants of existing types. In addition, the plant manufacturers have offered various innovations aimed at improving overall performance, some of which have gained general acceptance following the resolution of early problems. Over this period, also, a wealth of experience has clearly been acquired in the operation of ion-exchange systems. However, these developments have not been matched by improvements in knowledge of the basic processes involved, and some of the major problems of using resins which were apparent in the early 1960s are still apparent today and a number of new ones have appeared. In particular, the lifetimes of anion resins in service are still unpredictable and the fouling of such materials still presents significant limitations. Moreover, there are uncertainties in the manufacturing process itself as evidenced by the receipt of resins which are not within specification. From a mechanical point of view, inadequacies in the separation and re-mixing of resins in different parts of the regeneration/exhaustion cycle have assumed greater importance as the need for higher standards of treated water has become apparent in certain applications.

The plant provided is not particularly robust or reproducible in terms of routine day-to-day plant operation using semi-skilled operatives and work in resin separation techniques has intensified to improve this situation. It has also led to a reopening of the debate on whether mixed beds or separate cation and anion units are the best choice for certain condensate purification applications.

As a result of the limitations outlined we continue to use ion exchange processes for the most part in an empirical way, and this calls for a high degree of vigilance and monitoring. The object of this paper is to illuminate these points and to consider what the prospects are for materially improving the situation. In this field, as in others, the CEGB has elected to become an 'informed user' by developing its own expertise and test procedures while leaving actual resin development to the manufacturers. The paper will, therefore, also include commentary on the progress that has been made in characterising resins to improve selection for specific applications, particularly in the production of ultra-pure water.

2. THE DETERIORATION OF ANION RESINS IN SERVICE

2.1 Background

Leaving aside for the moment specific problems such as fouling, anion resins inevitably deteriorate in service from a combination of progressive hydrolysis of the thermodynamically unstable basic groups, general loss of groups, and more obscure ageing processes leading to loss in rate of exchange, possibly by self-fouling. The lifetime that might be expected is a function of the resin type and the water being treated, and type II strongly basic resins, developed for higher regeneration efficiency, are particularly prone to rapid deterioration (Fig. 1). In practice, however, the resins are used at low regeneration levels and useful operational lifetimes are obtained by progressively increasing the amounts of regenerant used, to maintain output despite resin deterioration, albeit at a cost.

The physical chemistry of the ageing process and the rate of deterioration under controlled conditions have been studied and, in theory, it should be possible to predict an upper limit to the resin life. The actual rate may be a function of the particular matrix, its temperature history in operation and of time. In our experience it is apparently not directly related to frequency of regeneration and exhaustion. However, even if the dependence on these individual factors were sufficiently well known, the continual variations in service conditions would make it difficult to compute the probable residual life of the resin at any particular point in time without a prohibitive amount of monitoring. Consequently, we fall back on the direct measurement of the effects of deterioration in terms of quality and actual throughput to some overriding break point. This deterioration is then confirmed by actual capacity measurements on samples of the resin to ensure that the observed decline in performance is not the result of maloperation of the plant rather than the state of the resin itself.

The incentive to improve this data base/methodology is small when other problems are added to the picture. The most obvious and complex of these is fouling of the resins by certain classes of organic compounds which may be present in the water being treated.

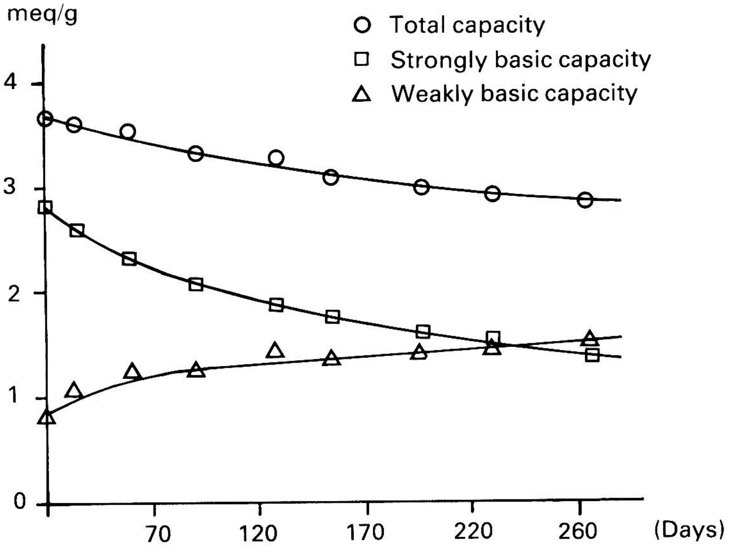

Fig. 1 – Deterioration of type II anion resin.

2.2 Organic fouling

Twenty years ago the principal organic fouling problem was that arising from the presence of high-molecular-weight organic acids in town waters derived from upland surface sources. As town mains water has become more expensive and its availability for power generation purpose has decreased, other sources of raw water have become increasingly important. In particular, many plants treating river water have been commissioned. This development has increased the risk and diversity of organic fouling because industrial rivers may contain numerous unidentified natural and synthetic organic materials often in only trace quantities. The isolation and identification of these compounds which is seen as an essential precursor to any controlled basic studies of the fouling process would be extremely difficult and little progress in this direction has been made, although there have been some non-specific studies based on the measurement of total organic carbon. This is a significant and continuing limitation because, as will be seen later, in high flow-rate plants the effects of quite moderate accumulations of organic material become important and vary considerably with the origin of the organic contamination.

Macroporous resins were originally developed to resist organic fouling rather than for their high strength (which at the time was very much an incidental benefit and not strictly required for most make-up applications). It was postulated that the larger pore size of these resins allowed large organic molecules to diffuse into and out of the exchanger surface more easily thus increasing the rate of uptake during the service cycle and minimising the chance of retention during regeneration. Additionally the microspheres within the bead were highly crosslinked and this conferred a high selectivity for organic matter. Nevertheless, in practice, macroporous resins in the OH-form have not proved to have any outstanding advantage in either respect over gel resins and tend now to be selected for applications where the advantage of high strength outweighs the lower capacity. Studies carried out during the development of acrylic-polymer-based resins suggested that these materials, although having lower selectivity for large organic molecules, would react faster than the polystyrene types [1]. The inference that acrylic resins might be superior to other types for the removal of organic matter from water has not been confirmed in practice, but they may offer a compromise, balancing rate of intake and ease of removal. In this overall context, it should be remembered that selectivity data are derived from long-term equilibrium studies and will not necessarily reflect the dynamic situation in the plant.

In treating low-grade raw waters, a great deal of the organic material is removed from the water by the pretreatment plant before it reaches the resins, but TOC studies on River Trent water have shown that significant amounts of uncharacterised organic compounds pass forward, some of which are retained by and foul the resins (Table 1). A small amount of material, presumably un-ionised, is not taken up by the resin and passes forward into the boiler feedwater. However, recent experience with acrylic resins in the main anion stage of treatment shows these to strike a satisfactory balance between uptake and release of organic matter.

Table 1.
Typical total organic levels across de-ionisation plant treating River Trent water.

Sample point	Total organic carbon mg kg^{-1}	Removal %
River water	16	0
After pre-treatment stage	7	56
Main anion outlet	2 – 3	81 – 87
Mixed bed outlet	1	93