Ion Exchange for Pollution Control

Volume I

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FOREWORD

These volumes in the Uniscience series on Water Pollution Control Technology are a comprehensive report on applications of ion exchange to treatment of wastewater. They cover existing applications, and by extension of fundamental principles, they show the basis for innovative technology. The authors have been principals in the development of ion-exchange materials and process technology.

Our objective in these volumes and in subsequent volumes of the series is to provide a reference manual for design engineers, planners, and managers in industry and government. This is particularly important in the present critical period for implementation of water pollution control.

Richard Prober
Cleveland, Ohio
July 21, 1978

PREFACE

There are many books on ion exchange dealing with general subject matter and special topics such as the role of ion exchange in analytical, organic, and biochemical applications. While some aspects of ion exchange in pollution control were discussed in these texts, especially with reference to the removal of toxic heavy metals, the purification of metal plating baths, and the recovery of metal ions from metal plating rinse waters, the subject as a whole was never covered. In view of the emphasis in recent years on pollution control, the application of ion exchange in this endeavor has grown so a book on the subject itself is timely.

The aim of these volumes is not to cover all phases of ion-exchange theory, which may be found in in general texts, nor to cover every application in the literature, or to show an engineer ways on how to become an expert in the field so he could "do it all by himself". The main purpose of these books is to show the practical engineer what has been done in various types of applications of ion-exchange processes in pollution control, how to set up laboratory tests, the problems that may be encountered, to identify the individuals and organizations who are experts in the various phases of ion exchange, and most importantly, to emphasize the new developments in polymers with active sites that offer new approaches to wastewater treatment methods.

These books contain over forty chapters written by researchers and engineers from the industrial, academic, and research communities in the United States, United Kingdom, Australia, Canada, and Poland. The books are divided into six major sections:

General Aspects — Twelve chapters dealing with the ion-exchange process, ion exchangers, equipment, systems, and economic factors.

Inorganic Applications — Seven chapters dealing with the removal of heavy metals and ammonia and nitrate recovery from a variety of wastewaters.

Organic Applications — Contains four chapters on base recovery from spent sulfite liquors, decolorizing wood pulp bleaching effluents, and the use of polymeric adsorbents.

Other Applications — Seven chapters involving the treatment of effluents from nuclear and municipal treatment plants, agricultural wastewaters and the use of ion exchange for laboratory and analytical evaluations.

Uses of Polymers with Active Sites — Three chapters covering coagulants, dewatering agents, and dispersants.

New Developments — Ten chapters dealing with novel exchangers and processes developed in the last decade.

In addition, the volumes contain a bibliography of ion-exchange text books, a listing of ion exchanger and equipment manufacturers, and special tables of data. We have broadened the aspect of the subject to include polymeric polyelectrolytes as we feel it is an extension of ion exchange, and future developements in this field for wastewater treatment will increase with time.

The authors chosen to write the chapters in these volumes are well known for their contributions in the application of polymers with active sites to pollution control. Credit must be given to both the authors and the organizations they represent. The authors, in many instances, wrote their chapters on their own time.

We hope that these volumes will make a contribution to improving the quality of our environment and to saving our resources which grow scarcer every day.

Calvin Calmon
Harris Gold
Cambridge, Massachusetts
July, 1978

EDITOR-IN-CHIEF

Richard Prober is a principal engineer with GMP Associates, and Adjunct Professor of Chemical Engineering at Case Western Reserve University, Cleveland, Ohio.

Dr. Prober received his B.S. in chemical engineering in 1957 from the Illinois Institute of Technology. In 1958 he received his M.S. degree and in 1962 his Ph.D. degree in chemical engineering from the University of Wisconsin.

Dr. Prober's accomplishments include curriculum development for wastewater treatment plant operator training; development of low-flow dissolved oxygen models for the Cuyahoga River and Tinkers Creek, including direction of stream surveys to calibrate the models; development of process-design oriented B.S. and graduate level programs in wastewater engineering; and extensive research into process development of activated carbon treatment and treatment for industrial wastes containig cyanides.

His professional associations include the Water Pollution Control Federation, American Institute of Chemical Engineers, and the American Chemical Society. Dr. Prober has also served as Symposium Chairman for national meetings of the U.S. Environmental Protection Agency, American Institute of Chemical Engineers, and Wastewater Equipment Manufacturer's Association.

THE EDITORS

Calvin Calmon, Ph.D., has been in the field of industrial chemical research since he received his Ph.D. degree in physical chemistry from Yale University in 1938. (B.A. from Dartmouth College in 1934.) Except for a period of service from 1944 to 1947 as an officer in the U.S. Army, until his retirement in 1973, he worked continuously with various divisions of the Sybron Corporation. Until 1960 he was with the Permutit Company, where he was Head of Laboratories. He then joined Ionac Chemical Company as Director of Research, later became Vice President of Research and, on retirement, was Senior Vice President and Research Consultant to the Chemical Group of Sybron Corporation. In addition to this various consulting activities he is a limited partner in Water Purification Associates.

Most of his industral work, including about 65 technical publications and 19 patents, has been in water treatment, absorbents, ion exchangers, polymers, membmnes, and pollution control. In 1972 he received the Distinguished Service Award from the Environmental Chemistry Section of the American Chemical Society. In 1976 he received from the U.S. Environmental Protection Agency the Certificate of Appreciation for contributions towards the improvement of the environment.

He has served as Chief Research Scientist on contract projects for the Atomic Energy Commission, the Office of Saline Water, the National Aeronautics and Space Administration, and the U.S. Public Health Service. From 1962 to 1972 he served as Section Editor on Water for Chemical Abstracts, published by the American Chemical Society and is currently a scientific and technical merit reviewer for research demonstration grant applications submitted to the U.S. Environmental Protection Agency. With Dr. R. Kressman of England, he edited *Ion Exchangers in Organic and Biochemistry*. During World War II he was Chief of Biochemistry and Serology Sections of the Command Laboratory of the U.S. Army Forces of the Western Pacific. For his chemical work in developing the desalting kit for converting seawater to potable water, now used by all ocean-flying planes, he received a U.S. Government citation. He has received patents for a calcium sensor, improved condensate demineralizing, desalination, pollution control, and ion-exchange processes. He is a member of many technical societies and a Fellow of the American Association for the Advancement of Science.

Harris Gold, Ph.D., is a Partner with Water Purification Associates, Cambridge Massachusetts. He received a B.M.E. from the Polytechnic Institute of New York in 1958, a M.S.M.E. from Columbia University in 1959, and a Ph.D. from the California Institute of Technology in 1963.

From 1963 through 1974, Dr. Gold was with Avco Systems Division, Wilmington, Massachusetts, where he engaged in and directed theoretical and experimental research in heat and mass transfer in fluid flow systems. He was also responsible for the development of a continuous moving bed ion-exchange system for softening pretreatment. Since 1974, Dr. Gold has been with Water Purification Associates. His primary interests include the development of water management systems for power and fuel producing plants and the application of innovative water treatment technologies for industrial wastewater.

Dr. Gold has published many scientific papers and is the co-author of a recent book on the role of water in synthetic fuel production. He is a member of the American Institute of Chemical Engineers, the American Electroplaters Society, and the American Water Works Association.

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General Aspects

Chapter 1

THE ION-EXCHANGE PROCESS

C. Calmon

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I. INTRODUCTION

Ion exchange is a unit process usually involving the exchange of ions in solution with the counterions of insoluble polymers containing fixed anionic or cationic groups. If the exchange involves cations, the exchanger is a cation exchanger and the iogenic group which is fixed on the polymer is anionic, e.g., $-SO_3^-M^+$, $-CO_2^-M^+$, $-PO_3^=H_2^+$. The polymeric matrix of the exchanger can be a copolymer of styrene and divinylbenzene (DVB), phenol and formaldehyde, or natural polymers such as coal.

In the anion exchangers which undergo anion exchange, the fixed polar groups are usually amines, e.g., $-NH_2$, $-RNH$, $-R_2N$, $R_3N^+X^-$. The counterions which undergo exchange can be Cl^-, $SO_4^=$, NO_3^-, or organic anions such as $CH_3CO_2^-$.

The process, originally involving cations, was discovered in 1850 by Spence, Thompson,[1] and Way.[2] It was not applied until 1905 when Gans[3] showed that the process could be used for water softening and to remove iron and manganese from water. The success of the process was due to two factors: (1) Gans applied it to a system of low ionic concentration involving ions which are readily exchanged for innocuous ones and which are easily displaced from the exhausted resin by regeneration with ordinary salt and (2) the process was needed in the emerging electric power generation industry which required nonscaling waters for steam boilers. Similarly, the railroad and textile industries were expanding into many areas with poor water quality causing economic losses. As an example, the textile industry required waters free of hardness, iron, and manganese, as these were wasting soap and causing staining.

Although water softening is not often thought of as a pollution-control process, (1) it does make possible the use of a resource which otherwise could not be utilized, namely, waters of poor quality, (2) it replaces costly processes requiring a great deal of energy (e.g., evaporation), and (3) it helps in reducing waste, as in the case of textiles, the loss of soap, and in the case of boilers, required chemicals for removing scale. However, the subject of water treatment is detailed in many texts. In this book, the treatment of waste discharges are emphasized. In these cases, ion exchangers are used to concentrate trace ionic constituents which can be reused instead of being discarded or to prevent resources from becoming pollutants if discharged into streams or injected into the ground. Ion exchange also makes possible the control of discharges by reducing the waste volume so it can be discarded in controlled areas.

There are two problems associated with the treatment of waste discharges for disposal: (1) a concentrated solution may become diluted so the volume becomes too large for evaporation, or the ion concentration is so dilute that recovery or transporting of the solution to controlled areas becomes too costly and (2) concentrated solutions may become contaminated with trace pollutants resulting either in the discarding of these solutions or the application of costly treatment processes to purify the solutions by