

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

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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 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 developments 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 containing 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 industrial work, including about 65 technical publications and 19 patents, has been in water treatment, absorbents, ion exchangers, polymers, membranes, 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.

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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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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., $-\text{SO}_3^-\text{M}^+$, $-\text{CO}_2^-\text{M}^+$, $-\text{PO}_3^-\text{H}_2^+$. 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., $-\text{NH}_2$, $-\text{RNH}$, $-\text{R}_2\text{N}$, $\text{R}_3\text{N}^+\text{X}^-$. The counterions which undergo exchange can be Cl^- , SO_4^{2-} , 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 Gans³ 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

removal of these trace ions. Today, ion-exchange processes can economically solve these two problems.

However, it must be recognized that the ion-exchange process can be a polluting process itself if the eluting solution is not recovered and is promiscuously discarded into sewers and streams or injected into the ground. A great deal depends on the value of the recovered product. In other words, economics is an important factor in encouraging plants to use recovery processes.

II. HISTORICAL BACKGROUND

The use of the ion-exchange process for pollution control, especially in the field of metal-ion recovery, was already suggested very early. However, there were limitations due to the fact that only cation exchangers were available and these were stable only in neutral solutions so that the regeneration or elution had to be done with neutral salts. Gans³ initially tried to recover gold from seawater with manganese zeolite; instead, he succeeded with water softening. However, he recommended salt conversion which is basic to heavy metal recovery.

Patents were taken out for recovery of gold, silver, radium, nickel, and ammonia from solutions.^{4,5,6,7,8} Austerweil and Jeanpost⁸ recovered copper from a solution with a greensand exchanger and then recovered the copper by elution with a salt. Syркин and Krynkin⁹ recovered copper from a cuprammonium waste liquor by means of an inorganic exchanger in the ammonium form.

However, the limitations of the then available inorganic exchangers are quite evident as there were almost no actual industrial applications until the appearance of cation exchangers, namely, the sulfonated coal products and the sulfonate containing synthetic polymers, which could be used on the hydrogen cycle.

The first pilot plant for recovery of copper from cuprammonium waste liquors was built in Germany in 1939; the full-scale plant was built in 1941. Both copper and water were recovered for reuse. Copper recovery was over 90%. Ammonia was also recovered for recycling. Griessbach¹⁰ reviewed the capacities for copper recovery with the various ion exchangers available in 1939 as given in Table I.

Anion exchangers for picking up metal ions were applied in Germany prior to 1945, e.g., the recovery of silver from photographic film rinses. The capacity of one exchanger was 8 g of silver per liter of anion exchanger prepared from *m*-phenylenediamine, polyethylenediamine, and formaldehyde.¹⁰

Most of the preliminary work on showing that ion exchange is a valuable unit process for valuable metal-ion recovery was done by 1946. The ion exchangers were highly improved and becoming more varied. Publications on ion-exchange techniques appeared with greater frequency, so a wider number of scientists became acquainted with them and began to apply these to wastewater problems. The number of manufacturers of ion exchangers also increased. In order to sell more of the exchangers, a great deal of application work was done which was publicized in technical journals. The work

TABLE I
Capacities of Various Ion Exchangers for Copper

Exchanger	Breakthrough capacity (wt %)	Maximum capacity (wt %)
Greensand	2—3	—
Carbonaceous	7—10	9—13
Synthetic resin (phenolic)	9—12	10—20
Improved synthetic resin	16.4	—

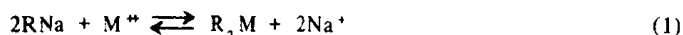
of the Atomic Energy Commission on rare-earth recovery and separation combined with theoretical considerations also opened new vistas, especially when the ion exchangers made from copolymers of styrene and divinylbenzene appeared on the commercial market. These exchanges proved superior to all the previous ion exchangers.

III. THE PROCESS

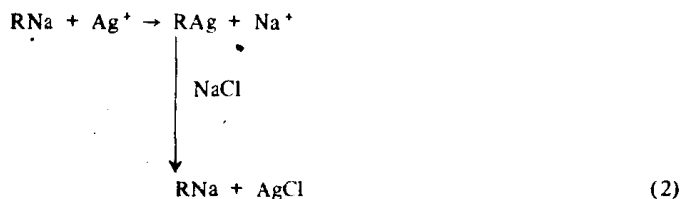
A. Reactions

As it was pointed out previously, the ion-exchange process usually involves ions in solution. The ions can be inorganic or organic. Nonelectrolytes are adsorbed and eluted.¹¹ Certain nonelectrolytes can also be exchanged via a process known as ligand exchange.¹² Ion exchangers have also been applied as filters for particulate and colloidal material removal. Reactions with solid electrolytes are well known. All of these will be discussed in this book. However, ion-exchange processes are best known when applied to ions in solutions. The size of the ions are important as very large ions may be excluded from the exchanger because the pores within the exchanger may be too small for the ions to diffuse into the matrix of the exchanger.

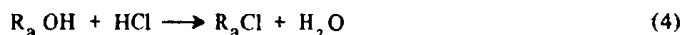
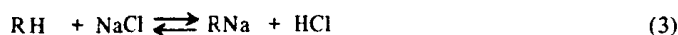
Generally, exchange reactions are reversible. The degree of reversibility for a given time at a given regenerant dosage will depend on the affinity the exchanger has for the ion. Some ions form ion pairs with the fixed polar groups and, therefore, are very tightly held. The result is that these ions are not readily released upon regeneration. The most common ion exchange reaction is softening of water in which Ca^{++} , Mg^{++} , Fe^{++} , and Mn^{++} are exchanged for sodium ions which are innocuous. When exhausted the ion exchanger is regenerated with common salt, NaCl . The reaction can be represented by the following equation:



where R represents the resin matrix and M^{++} the divalent ion. The reaction is reversed with a strong solution of sodium chloride. The reaction to the right holds for exchangers containing sulfonic or carboxylic groups. In the case of exchangers containing carboxylic groups, the reverse reaction cannot be attained with an economic dosage of NaCl and in a time usually used for ion-exchange reactions. However, if a precipitate is formed, then the reverse reaction is easily attained with carboxylic type exchangers, e.g., when the carboxylic acid is in the silver form, the affinity of divalent ions and silver by a carboxylic exchanger is extremely high:



The availability of ion exchangers in the acid form (H) and anion exchangers in the basic form (OH) made possible deionization, as shown by Equations 3 and 4:



To regenerate the salt form of the anion exchanger, R_aCl , caustic (NaOH), is used:

