

ION EXCHANGE TECHNOLOGY

Edited by F. C. Nachod and Jack Schubert



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PREFACE

Despite the fact that ion exchange is now a unit operation, there exists no single text devoted to its technological and engineering aspects. The uses of ion exchange processes are now so widespread that it is of practical importance to make available a reliable source of information—both fundamental and applied—which is written primarily from the viewpoint and interests of technologists, engineers, and students in the engineering curriculum.

For the past several years one of the editors (J. S.) has given an evening lecture course on ion exchange at the University of Chicago while the other editor (F. C. N.) has taught the subject at Rensselaer Polytechnic Institute. Many of our students were either engineers or chemists employed in industries in which ion exchange operations were being utilized or contemplated. The available books, symposia records, or industrial bulletins on ion exchange only partially met their needs.

For the reasons given above we decided to arrange for the publication of a book on ion exchange which would serve both as a reference and as a text book for technologists and engineers. Admittedly, the present book with one noted exception is based mainly on ion exchange as practiced in the United States. However, our object was to produce a generally useful book which would deal with the fundamental problems, techniques, and operations of ion exchange such as mass transfer, equipment design, properties of ion exchange resins, and deionization. In addition, we felt it important to include chapters on two types of applications—those that are used industrially on a large scale, and those which have not yet reached large-scale use but have impressive potentialities. In both the fundamental and applied chapters we deemed it necessary that the successful aspects of ion exchange operation be included and, in addition, it seemed equally important to describe the problems and the inherent complexities encountered in the setting up of an ion exchange process. Wherever possible, we felt that the economic factors should be described realistically.

No single individual has the experience or background to cover the entire field of ion exchange as a unit operation. We were fortunate to obtain as authors of individual chapters experts who have a professional, practical, and intimate knowledge of their respective subjects. In nearly every chapter at least one of the authors is a professional engineer or

chemist with wide industrial experience in the particular operation under discussion.

It will be noted that the treatment of topics such as costs and resin stability recur in nearly all chapters. This apparent duplication is not only unavoidable but actually desirable because such factors must always be freshly evaluated in specific cases. As we mention in the first chapter, much time and effort can be saved by a familiarity with general fundamentals.

With an eye to the future we would be grateful to readers in industrial and academic circles for advice and criticism regarding this book.

We wish to acknowledge the splendid cooperation of each individual contributor and the patient and efficient help and consideration of the publishers.

Rensselaer, New York
Lemont, Illinois

F. C. NACHOD
J. SCHUBERT

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CHAPTER 1

INTRODUCTION

J. Schubert and F. C. Nachod

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1.1 The Business of Ion Exchange

The business of ion exchange grows bigger yearly. However, the true technological worth of ion exchange cannot be fairly measured in terms of the annual sales of ion exchange materials and equipment. For example, the use of a \$10,000 ion exchange unit may permit the operation of a process producing hundreds of thousands of dollars worth of product.

By itself, the annual business of ion exchange in the United States in 1954 in terms of sales of ion exchange equipment and materials has been conservatively estimated (M1) to exceed \$40 million dollars. Approximately 95% of the sales volume is concerned with water conditioning¹ (softening, demineralizing silica removal, and alkalinity reduction—in order of decreasing application (H2)). Probably 75% of the sales for water softening are for home water softeners. It has been estimated that in the softening of water by ion exchange the equivalent of 300 carloads of CaCO_3 per day is removed (M1). The remaining applications of ion exchange of various degrees of technological importance include sugar refining, metal recovery, acid and base recovery, catalysis, and chromatography of inorganic substances. Medicinal applications of ion exchange are still rather small, amounting to roughly \$100,000 annually in sales.

The chemicals consumed annually for regeneration purposes and in the manufacture of ion exchange resins are shown in Table 1.1. From these and other figures it would appear that total production of all

¹ It has been claimed that in 1946 the production of all grades of the Wofatit resins which were produced by I. G. Farbenindustriefabrik in Wolfen, Germany, amounted to 500–600 tons per month of which only one-fifth was used for water purification, the balance being used for special applications (M2, p. 9).

TABLE 1.1
Chemicals Consumed in Connection with Ion Exchanger Operations in the
United States*

Commodity	Consumption (tons/year)
Regenerative Chemicals	
Salt	200,000
Sulfuric acid	50,000
Soda ash	50,000
Caustic soda	15,000
Hydrochloric acid	5,000
Chemicals Used in Preparation of Ion Exchange Resin	
Styrene	2,500
Divinylbenzene	250
Sulfonating agents	10,000
Organic amines	250

* Rough estimates as of 1954 by Mindler and Paulson (M1).

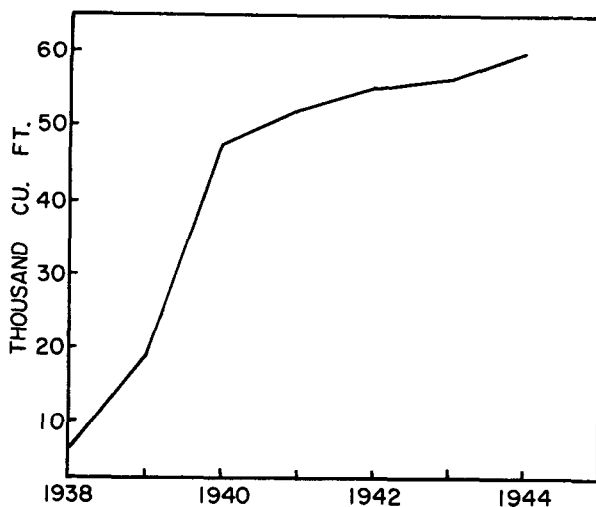


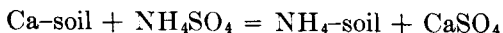
FIG. 1.1. Total production of Wofatit ion exchange resins by the I. G. Farbenindustriefabrik at Wolfen, Germany. (Taken from data in M1, p. 16.)

organic ion exchangers would be in the neighborhood of 300,000 cubic feet (wet weight) a year in the United States. It is of interest to note that the production of the Wofatit ion exchange resins constantly increased even during the exigencies of World War II to a high of 60,281 cubic feet (2,820,000 pounds) by 1944 (see Fig. 1.1). Carbonaceous exchangers (Permutit S) were produced in Germany at the rate of approximately

120,000 pounds per month. At this time only small amounts of anion exchangers were manufactured (M2, p. 6).

1.2 Historical Developments

The English agriculturist and entrepreneur H. S. Thompson (T1) was the first to observe and to publish descriptions of the phenomenon of ion exchange. Thompson found that the ammonium sulfate absorbed by soils could not be washed out by water and that much of the absorbed ammonium sulfate was converted to calcium sulfate. However, it was Way (W1), consulting chemist to the Royal Agricultural Society, to whom Thompson had disclosed his findings two years earlier, who thoroughly explored the phenomenon and demonstrated the underlying mechanism to be one of ion exchange involving the complex silicates present in the soil. As visualized by Way the process observed by Thompson could be formulated:



The first attempt to employ ion exchange for commercial purposes was made by Harm in 1896 (H1). In his patent, Harm claimed to have a successful process utilizing a naturally occurring cation exchanging silicate for removing sodium and potassium from sugar beet juice. However, successful large-scale applications of cation exchange were developed by Gans (G1) who synthesized inorganic materials of the type $\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10}$ in which the Na^+ was exchangeable. It should be noted that Way himself synthesized several inorganic silicates of a similar type.

Gans successfully applied his inorganic synthetic cation exchanger to water softening and sugar treatment on a technological scale. To a large extent his synthetic exchanger replaced the naturally occurring exchangers or zeolites as they are still called.

One decided shortcoming of the inorganic exchangers resided in the fact that they were acid sensitive and did not lend themselves to any exchange reactions in which hydrogen ions were taking part. It had been recognized (B1) that humus and other natural organic products exhibited exchange properties. An effort to improve these led to the use of sulfonated coals (L1, S4) which were rugged and inexpensive.

It is only in the past ten years that ion exchange has reached the point where it can or should be considered a unit process on a par with the traditional ones such as distillation, precipitation, and adsorption. The reason for this tremendous spurt in utilization of ion exchange processes stems directly from the discovery and appreciation of the potentialities of the ion exchanging properties of synthetic resins by Adams and Holmes (A1), English chemists then on the staff of the

Chemical Research Laboratory at Teddington. Adams was quite experienced in water treatment and at his instigation, Holmes synthesized both anion and cation exchange resins thus making it possible to de-ionize water in the cold for the first time.

The commercial production and improvement of synthetic resins by Holmes and the I. G. Farbenindustrie soon followed. The really modern era in ion exchange technology began in 1944 when D'Alelio of the General Electric Company's Pittsfield laboratories synthesized resins from preformed polystyrene (D1). These resins were the forerunners of the

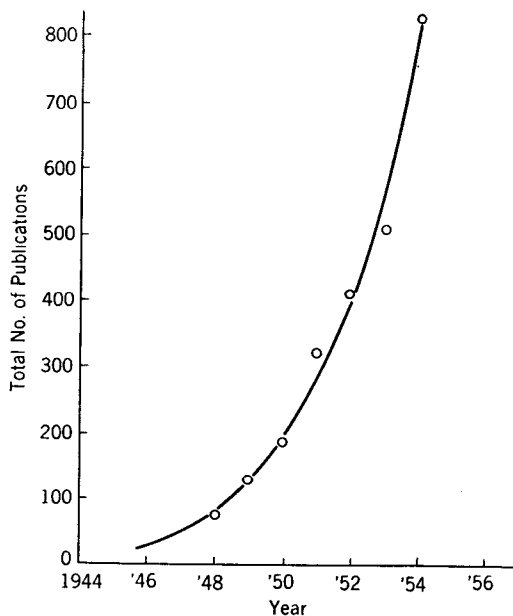


FIG. 1.2. Number of publications on ion exchange as a function of time.
(From *Chem. Eng.* **61**, 161 [1954]; reproduced by courtesy of the publishers.)

currently available line of polystyrene resins which, compared to earlier resins, possess greatly improved capacity and chemical and mechanical stability. Emulsion polymerization of swollen styrene and divinylbenzene followed by sulfonation yields stable polystyrene polysulfonates with "adjustable" cross-linking. The fact that perfect spheres are obtained gives a new impact to large-scale engineering use. Chloromethylation and ammination produce strongly basic quaternary ammonium type anion exchange resins, and copolymerization of methacrylic acid with divinylbenzene results in a cation exchange resin of lesser acid strength and high capacity. Tailor-made resins of high chemical and

mechanical stability in useful structural shapes such as membranes and rods are now available for large-scale engineering applications.

In recent years, a need has arisen for ion exchangers capable of withstanding the elevated temperatures associated with the purification of the water used as a moderator or coolant in nuclear reactors. To meet this need, it is probable that improved inorganic ion exchangers will be developed, unless radical improvements in the temperature stability of organic exchangers can be made.

An appreciable amount of literature, showing an almost hyperbolic rise (Fig. 1.2) dealing with the principles and practice of ion exchange has arisen to supply the increasing demand for information. Three books have appeared (K1, S1, N1), a fourth is shortly forthcoming (S3), and several others are in preparation. Several symposia on ion exchange have appeared here and abroad and the proceedings have been published. References to these appear in individual chapters in this book.

1.3 Applications of Ion Exchange

As mentioned earlier, Adams and Holmes pointed out several possible applications of ion exchange resins. These included (A1):

1. Removal of objectionable cations and anions from drinking and boiler feed water.
2. Production of de-ionized water.
3. Treatment of trade effluents, both for the purification of such liquors and for the economic recovery of small amounts of inorganic and organic substances.
4. Purification of organic and inorganic chemicals.
5. Applications to analytical chemistry.
6. Separation of ion mixtures.

Applications of ion exchange not discussed in this volume include determination of the properties of substances in solution such as the measurement of the stability of complex ions and other quantities which are reviewed elsewhere (S2), and medical uses such as in ulcer treatment for neutralization of excess acids by anion exchange resins and sodium removal from the body (M3).

The fundamental principles underlying all ion exchange applications are based on a few simple facts involving the exchange reactions:

1. Equivalence of exchange.
2. Selectivity or affinity preferences of the exchanger for one ion relative to another, including cases in which the differing affinities of the ions are modified by the use of complexing or chelating agents.
3. Donnan exclusion—the ability, under most conditions, of the resin to exclude ions but not, in general, undissociated substances.

4. Screening effect—the inability of very large ions or polymers to be absorbed to an appreciable extent (partly because of a slow rate of uptake).

5. Differences in migration rates of absorbed substances down a column—primarily a reflection of differences in affinity.

6. Ionic mobility restricted to the exchangeable ions and counter ions only.

7. Miscellaneous—swelling, surface area, and other mechanical properties.

The numerous ingenious applications that are made with ion exchangers derive from a knowledge both of the chemical and physical properties of ion exchangers and of the chemistry of substances in solution. Much time and effort can be saved by an acquaintance with these fundamentals—particularly when special applications are contemplated.

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CHAPTER 2

ION EXCHANGE RESINS

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I. INTRODUCTION

2.1 Scope of Chapter

The intelligent utilization of ion exchange resins and processes requires an understanding of a number of factors. These include: (1) the structure of the exchanger and its effect on the properties of the resin, (2) ion exchange equilibria, (3) kinetics, (4) certain basic handling and operational techniques such as backwashing, regeneration, etc., (5) the effect of operating conditions on performance and life expectancy, and (6) the limitations of the resins and ion exchange processes.

2.2 Historical Survey

A. EARLY DEVELOPMENT

The recognition of the phenomenon of ion exchange is generally attributed to Thompson (T1) and Way (W1), who reported in 1850 that when a soil is treated with either ammonium sulfate or ammonium carbonate most of the ammonia was adsorbed and calcium released. It was later proved by Eichorn (E1) that the adsorption of ions from ground waters by clays constitutes a reversible reaction. The ion exchange reaction enables soils to store a reserve of minerals for future availability by plants.

B. NATURAL PRODUCTS

Commercial development began about 60 years later when Gans (G1) synthesized materials from clay, sand, and sodium carbonate. However, natural zeolites such as greensand were the first to be extensively used on an industrial scale. The first applications of ion exchange were for the purpose of softening water where calcium was removed from the water and an equivalent amount of sodium released. Because of the limited exchange capacity of the natural zeolites, equipment had to be large and regeneration frequent when softening very hard water supplies. The natural zeolites were improved by various treatment methods and still find considerable use for softening water of low hardness.

C. SYNTHETIC CATION EXCHANGERS

Synthetic aluminosilicate zeolites were later prepared from aluminum sulfate and sodium silicate which had higher capacities than the natural products. They are still used to a limited extent for water softening purposes. The first cation exchanger capable of being regenerated with acid and operating at low pH was an organic type material prepared by sulfonating bituminous coal (S1, U1). In 1935 Adams and Holmes (A1)