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FUNDAMENTALS OF ADSORPTION

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Edited by

Motoyuki Suzuki Professor, University of Tokyo

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Motoyuki Suzuki (Editor)
Professor
Institute of Industrial Science
University of Tokyo
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Tokyo 106, Japan

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Editor's Biography

MOTOYUKI SUZUKI is Professor of Environmental Chemical Engineering at the Institute of Industrial Science, University of Tokyo. Born in Tokyo on February 7, 1941, he graduated from the Department of Chemical Engineering, University of Tokyo in 1963 and continued graduate studies there, finishing his doctorate in 1968. his dissertation entitled, "Transfer Processes in Solid Packed Beds" was conducted under the direction of Professor Daizo Kunii. Professor Suzuki spent two years (1969-1971) working with Professor J. M. Smith in the University of California, Davis, where he worked on chromatographic determination of rate parameters related to adsorption. After returning to Japan, he started his laboratory at the Institute of Industrial Science, University of Tokyo. In the meantime, he worked for seven years with Professor Kunitaro Kawazoe, one of the founders of adsorption research in Japan in the field of adsorption kinetics and regegneration of spent activated carbon. He also began woreking in environmental studies on water treatment by adsorption.

Dr. Suzuki received an award from the Society of Chemical Engineers, Japan for a Distinguished Paper in 1977, "Surface Diffusion of Volatile Organic s on Activated Carbons during Aqueous Phase Adsorption," and a Memorial Paper Award from the Industrial Water Association in 1979. He was given the Doctorem Honoris Causa from Veszprem University, Hungary in 1991 and was appointed Advisory Professor at Tongji University, Shanghai, China in 1992.

His publications total 130 reviewed papers plus 50 invited papers. he is the author of *Adsorption Engineering* published by Kodansha/Elsevier in 1990 and the coeditor of *Kasseitan-Kiso to Oyo (Activated Carbon-Fundamentals and Application)* published by Kodansha Ltd. in 1992. He was elected Vice President of the International Adsorption Society (1992).

PREFACE

The Fourth International Conference on Fundamentals of Adsorption was held in Kyoto, Japan, from May 17-22, 1992. This Conference followed the past three successful Conferences held in Schloss Elmau, Germany in 1983 (Co-Chairmen: A. L. Myers and G. Belfort), Santa Barbara, California USA in 1986 (Chairman: A. I. Liapis) and Sonthofen, Germany in 1989 (Chairman: A. B. Mersmann). The purpose of the Conferences is to provide a forum for chemists, chemical engineers, biochemists, environmental engineers and scientists/engineers in any other related fields to exchange ideas in the area of adsorption. The Fourth Conference was attended by 205 scientists/engineers from 28 countries, of which as a first occasion in the Asian area, 25 delegates were from Asian countries besides 84 from Japan.

Fortunately, the Conference was enjoyed by many participants for its high level scientific programs as well as local arrangements. Special thanks are due to Kenneth S. W. Sing (co-chairman) of Brunel, the University of West London (retired), Shivaji Sircar (co-chairman) of Air Product, U.S.A. and Yasushi Takeuchi (co-chairman) of Meiji University for their encouragement and help in every aspect of the organization of the Conference. I also appreciate the great help provided by the Scientific Advisory Board members: Matin Bülow of Central Institut für physikalische Chemie, GDR (currently with BOC, New Jersey), A.S.-T. Chiang of National Central University, Taiwan-China, G. Findenegg of Technische Universität Berlin, Germany, Seiichi Kondo of Fukui Institute of Technology, Japan, Hanju Lee of Yonsei University, Korea, A. I. Liapis of University of Missouri-Rolla, U.S.A., Y. H. Ma of Worcester Polytechnic Institute, U.S.A., Alan L. Myers of University of Pennsylvania, U.S.A., E. Richter of DMT-Gesellschaft für Forschung und Prüfung mbH, Germany, J. Rouquerol of CNRS, France, D. M. Ruthven of University of New Brunswick, Canada, R. P. Townsend of Unilever Research, U.K., Kazuo Tsutsumi of Toyohashi University of Teshnology, Japan, Klaus Unger of Johannes Gutenberg University, Germany, Pingdong Wu of Zhejian University, China.

About 180 abstracts were received in responce to Paper Call by May, 1991, when a Scientific Advisory Board members meeting was held in Tokyo. After careful review and discussion by the Board members, 63 papers were selected as oral presentations for three full days and two half day sessions, and about 100 were chosen as poster papers. Poster papers were displayed for two days, making discussions effective and intimate. After the Conference, reviewing of each paper submitted as full text was made by two reviewers. Besides the SAB members, the following scientists took part in reviewing the papers: Kazuyuki Chihara, Katsumi Kaneko, Masami Matsumura, A. V. Neimark, Morio Okazaki, Akiyoshi Sakoda, Hajime Tamon. Considering the results of the peer review and because of the page limit, only 96 of the 160 papers presented at the Conference are finally included in this Proceedings.

Two plenary lectures were selected so that audiences from industrial and fundamental areas can be familiarized with current progress. Shivaji Sircar from Air Products, U.S.A. and Morio Okazaki from Kyoto University gave pertinent lectures to fulfill this need.

During the Conference, Discussion Session on Pressure Swing Adsorption was held. More than one hundred individuals attended the session, where the state of the art was reviewed and problems to be solved in the future were introduced and discussed. A summary of the Discussion Session is given by D. M. Ruthven in this volume.

It should be noted that the International Adsorption Society was launched formally during the Conference by adopting the bylaws and electing the president and the board members. Alan L. Myers was elected President of the Society with M. Suzuki as tVice President. Chaim Aharoni, Joseph Ausikaitis, G. V. Baron, Diran Basmadjian, Brian Bolto, Douglas Levan, Yi Hua Ma, Alfons Mersmann, Douglas M. Ruthven, Kenneth Sing, William Steele, Yasushi Takeuchi, Daniel Tondeur, Pingdong Wu, Francis Meunier and Alirio Rodrigues were elected or nominated by the President as board members of the first term. Shivaji Sircar will serve as Treasurer and Kent Knaebel, the editor of "Adsorption News," is expected to take on the role of editor of a new journal, "Adsorption Science and Engineering."

Financial support for the Conference was provided through the Japan Adsorption Society (President: Yasushi Takeuchi) by its corporate members. Additional contributions were offered by Chiyoda Construction, Daiichi Fuel, Ebara-Infilco, Fuji-Davidson, Futamura Chemicals, Kawasaki Steel, Kobelco, Koken, Kuraray Chemical, Kurita, Kyowa Chemicals, Marutani-Kakoki, Midori Safety, Mitsubishi Chemicals, Mitsubishi Heavy Industries, Nihon Gaishi, Nihon Bel, Nihon Muki, Nihon Oxygen, Nittetsu Kakoki, Nippon Steel, Osaka Gas, Organo, Sanden, Sanko Chemical, Seibu-Giken, Sumitomo Heavy Industries, Takeda Chemicals, Teijin, Tokyo Yuki, Tosoh, and Toyo Engineering. Also National Science Foundation, Amoco, Air Products, Exxon, and UOP provided travel expenses for US academic participants. All this support is gratefully acknowledged.

Many people have played roles in the success of the Conference. I would like especially to thank the self-sacrificing efforts of Akiyoshi Sakoda for the arrangements and operation of the Conference in hia role as Secretary. Without his devotion, the Conference could not have been carried out so smoothly.

Local arrangements and operations were conducted by Drs. M. Okazaki, H. Tamon and M. Miyahara and their laboratory members at Kyoto University. Their efforts are greatly acknowledged. Also the assistance of Mss. Shinko Takahashi and Hiroko Masai and the encouragement given by Mr. Ippei Ohta of Kodansha Scientific Ltd. made possible the final publication of this volume on schedule.

In conclusion I would like to thank again all the participants and express my sincere appreciation for the efforts by the authors to make this volume a splendid addition to the existing literature in this field.

The next Confefence will be held in the United States in 1995. Douglas LeVan of the University of Virginia agreed to organize the Conference and the site is tentatively selected at Asilomar Conference Center in Monterey, California, where beautiful scenary will add flavor and excitement to the discussion on adsorption. I hope the next Conference will provide ever closer and constructive occasion for exchanging ideas, information and experiences among adsorption scientists and engineers.

Motoyuki Suzuki
Institute of industrial Science
University of Tokyo
Roppongi, Minato-ku
Tokyo
Japan

January 1993, Tokyo

CONTENTS

Dr. Shivaji Sircar received his Ph.D. in chemical engineering from the University of Pennsylvania, Philadelphia, PA, in 1970. After spending two years as a post-doctoral fellow at the same school, he joined Air Products and Chemicals, Inc. in Allentown, PA, in 1973, where he is currently employed as a Principal Research Associate.

During the last nlneteen years at Air Products, he has been involved in research and development of gas and liquid separations by adsorption. He is the inventor of many PSA gas separation processes, four of which have been commercialized by Air Products. His research interests include thermodynamics, kinetics, process development, mathematical modeling, and material development related to surface phenomenon and adsorption, both at the fundamental and applied levels. His experience also includes design and operation of bench, as well as pilot scale equipment for process and material testing, process optimization, and scale-up.

He is the author of thirty-seven U.S. and sixty-five international patents and ninety-one scientific publications. He has lectured extensively in professional conferences and is a member of the American Chemical Society and the American Institute of Chemical Engineers. He was honored by AIChE with the Professional Progress Award in 1988.

Fundamentals of Adsorption
Proc. IVth Int. Conf. on Fundamentals of Adsorption, Kyoto, May 17-22, 1992

Novel Applications of Adsorption Technology

Shivaji Sircar
Air Products and Chemicals, Inc., Allentown, PA 18195 U.S.A.

ABSTRACT
Three new applications of adsorption technology in the areas of air separation, hydrogen-hydrocarbon separation, and removal of pollutants from air are described. They use the concepts of pressure swing adsorption, selective surface flow and insitu sorption-reaction.

INTRODUCTION

Separation and purification of fluid mixtures by selective adsorption has found numerous applications in chemical, petrochemical, biochemical and environmental industries [1]. Figure 1 demonstrates the phenomenal growth in this area. It plots the number of worldwide adsorption patents issued every year during the last twenty years with the key words given in the figure. Japan, United States and Germany are in the forefront of this development.

Applications of adsorption technology will continue to grow in the foreseeable future because the technology has not reached its maturity limits as shown by Figure 2. It plots the estimated technology maturity against technology use for a number of established and emerging separation processes. Gas and liquid phase adsorption trail the more established separation processes like distillation, absorption and extraction by a significant distance.

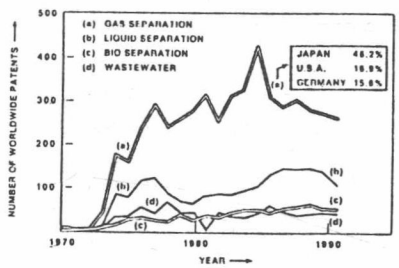

FIGURE 1: PATENT SURVEY (DERWENT)

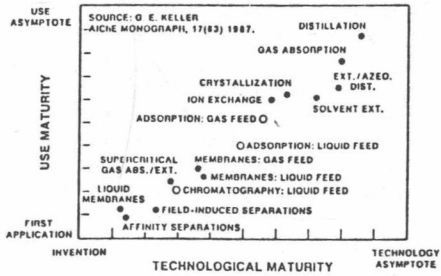

FIGURE 2: TECHNOLOGY MATURITY - USE

Another key element in the development of adsorption technology has been the availability of a very large spectrum of micro and mesoporous adsorbents with varying structures and surface properties. These include zeolites, activated carbons, aluminas, silica gels, ion exchange resins and polymeric adsorbents. New adsorbent structures or physico-chemical modification of existing materials are continuously being introduced.

The author believes that the endless choice of adsorbent materials and their

use in the design of innovative processes provide a very bright future for this technology as a separation tool. It should, however, be emphasized that a multidisciplenary integrated research and development between material and engineering sciences is called for.

The purpose of this paper is to describe three new applications of adsorption technology being developed by Air Products and Chemicals, Inc. They include:

(a) Air Separation by Fractionated Vacuum Swing Adsorption (FVSA) Process
(b) Bulk Hydrogen-Hydrocarbon Separation by Selective Surface Flow (SSF™) Adsorbent Membranes
(c) Removal of Trace Volatile Organic Contaminants (VOC) from Air by a Sorption-Reaction (SR) Scheme.

FRACTIONATED VACUUM SWING ADSORPTION (FVSA) PROCESS FOR AIR SEPARATION

Most alumino-silicate zeolites are polar adsorbents and they selectively adsorb N_2 from air over O_2 and Ar. Consequently, when dry air is passed through a zeolitic adsorbent column, which has been presaturated with an O_2 enriched gas, an effluent having a composition close to that of the presaturating gas is produced until N_2 breakthrough starts. The quantity of the effluent gas is in excess of the amount of the presaturating gas and the difference can be withdrawn as an O_2 enriched product gas. A typical O_2 product composition of 50-95 mole % can be produced by this method.

A N_2 enriched gas can then be produced by desorbing the adsorbed N_2 by lowering the column pressure. The N_2 composition of the mixed desorbed gas, however, depends on factors such as (a) N_2 adsorption capacity and selectivity of the zeolite from air at feed pressure, (b) levels of ad(de)sorption pressures, (c) adsorbent temperature changes during the ad(de)sorption processes, (d) kinetics of adsorption, and (e) amount of intra- and interparticle void gas in the column. The air-like void gas dilutes the composition of the desorbed gas. Typically, the desorbed gas is air-like at the beginning of the process and then it becomes more nitrogen enriched as the column pressure is lowered.

We examined the desorption characteristics of zeolite columns saturated with air at ambient pressure for four commercially available zeolites (NaX, 5A, Na-mordenite and CaX). Figure 3 shows the pure gas N_2 and O_2 adsorption isotherms for these zeolites at 30°C over a pressure range of 0-1.5 atm. It shows that both N_2 adsorption capacity and selectivity over O_2 increase in the order CaX > Na-mordenite > 5A > NaX zeolites. In particular, CaX zeolite shows significantly higher N_2 adsorption capacity and selectivity than the other zeolites. The dashed and solid lines in Figure 3 are best fit of the data by the Langmuir model. Table 1 gives the Langmuir parameters.

Table 1. Langmuir Parameters for N_2 and O_2 at 30°C

Zeolite	Saturation Capacity m, moles/kg	Interaction Parameter b_i (atm^{-1})		N_2/O_2 Selectivity (b_{N_2}/b_{O_2})
		N_2	O_2	
(a) Na-X	3.12	0.083	0.028	2.96
(b) Ca-NaA (5A)	1.41	0.370	0.092	4.00
(c) Na-Mordenite	1.47	0.602	0.126	4.78
(d) Ca-X	1.12	2.278	0.224	10.17

A very simple analytical mathematical model can be derived to evaluate isothermal desorption of an ideal binary gas mixture obeying Langmuir isotherms, if we assume that (a) local equilibrium prevails in the column and (b) axial mixing and pressure drops in the column are negligible.

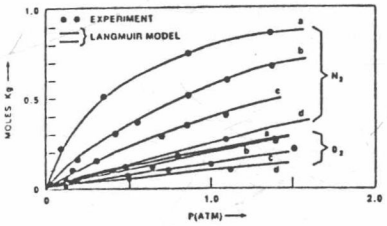

FIGURE 3: PURE N_2 AND O_2 ISOTHERMS

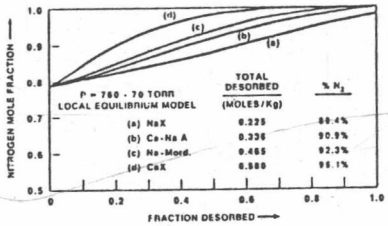

FIGURE 4: ISOTHERMAL DESORPTION OF AIR

Figure 4 shows the model isothermal air desorption characteristics of four adsorbents listed in Table 1. It plots effluent N_2 mole fraction as a function of fraction desorbed. The total amounts desorbed and the mixed desorbed gas compositions are also given in the figure. The figure shows that the rise in N_2 mole fraction in the desorbed gas with increasing amount desorbed gets sharper as the N_2 adsorption capacity and selectivity from air by the zeolite increases, as expected, but the mixed desorbed gas N_2 compositions are only between 88-95 mole% for these adsorbents. Such purity is not practically useful. A N_2 composition of above 98 mole% is required.

Figure 4 also shows that the zeolites NaX, 5A and Na-mordenite barely make 98% N_2 at the end of the desorption process. On the other hand, the CaX zeolite with the highest N_2 capacity and selectivity produces a decent amount of high purity N_2 at the lower pressure levels. This observation lead to the development of the Fractionated Vacuum Swing Adsorption process for simultaneous production of 80-90% O_2 and 98+% N_2 products from ambient air [2]. Figure 5 shows a flow sheet for the FVSA process. It consists of two parallel adsorbers packed with a layer of alumina at the feed end to remove water and CO_2 from ambient air followed by a layer of zeolite for air separation. It also contains two vacuum pumps, gas storage tanks, a nitrogen product compressor and necessary switch valves and gas headers. The cyclic process steps of the FVSA process are very simple. They consist of:

(a) Adsorption Step: where air at near ambient pressure (P_A) is passed through an adsorber which is presaturated with a 80-90% O_2-rich gas. The effluent is a 80-90% O_2 enriched gas which is partly stored and the balance is withdrawn as the product O_2. The step is continued until the N_2 mass transfer zone reaches the exit end of the column. The effluent is then vented until the column is saturated with air.

(b) Desorption Step I: where the column is evacuated countercurrently to an intermediate vacuum level and the effluent gas is wasted.

(c) Desorption Step II: where the adsorber is further evacuated countercurrently to the final desorption pressure (P_D) and the effluent is collected as the 98+% N_2 product gas which may be recompressed.

(d) Pressurization: where the column is countercurrently repressurized to near adsorption pressure level with a part of the O_2 enriched gas produced and stored during step (a). A new cycle is then started. The process of Figure 5 is designed in such a way that a continuous N_2 product is obtained. A typical cycle time for the process steps is

given in the Figure.

One of the advantages of this process is that the product N_2 is fairly dry because most of the water introduced into the adsorber during step (a) is desorbed during step (b) and that effluent is rejected.

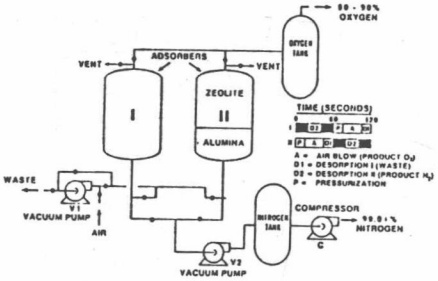

FIGURE 5: FLOWSHEET FOR FVSA

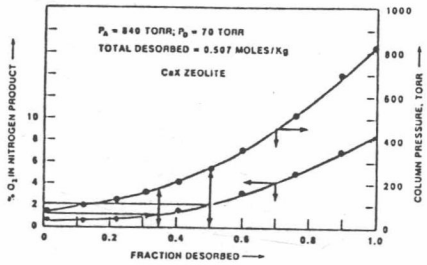

FIGURE 6: PERFORMANCE OF FVSA PROCESS

The FVSA process was tested in a bench scale unit using the CaX zeolite. Figure 6 shows a set of cyclic performance data. It gives the mole% of O_2 in the N_2 product by the process as a function of the fraction of total desorbed gas in step c. It also shows the column pressure corresponding to the fraction desorbed. It may be seen that about 34.0 and 50.0% of total desorbed gas can be collected as N_2 product of 99% and 98% N_2 purity, respectively.

Table 2. Performance of FVSA Process for Air Separation (CaX Zeolite)

Oxygen Product			Nitrogen Product		
Purity (%)	Recovery (%)	Capacity (moles/kg)	Purity (%)	Recovery (%)	Capacity (moles/kg)
90.0	24.2	0.04	99.0	30.0	0.17
			98.0	42.6	0.25

Table 2 summarizes the performance of this process for the operating conditions of Figure 6. The process can be successfully used to simultaneously produce a 80-90% O_2 product and a 98+% N_2 product from air.

SELECTIVE SURFACE FLOW MEMBRANE FOR HYDROGEN-HYDROCARBON SEPARATION

About 35 years ago, R. M. Barrer demonstrated the concept of selective surface flow of gases on an adsorbent material for separation of gas mixtures using a compressed plug of non-porous carbon [3]. Many other publications report this phenomenon [4-6]. In order to use this concept for practical gas separation, however, requires that a thin layer (<5μm) of a microporous adsorbent membrane be produced as shown by Figure 7. The figure also depicts the mechanism of gas separation through such a membrane.

Assume that a binary gas mixture is passed over one side of the adsorbent membrane at high pressure while maintaining a low pressure at the other side of the membrane. The more selectively adsorbed molecules (large circles) of the gas mixture will be preferentially adsorbed over the other (small circles) into the adsorbent pore at high pressure side and then migrate selectively on the pore surface to the low pressure side where they will desorb into the gas phase. Furthermore, if the pores of the adsorbent membrane are small in