SILICATE SCIENCE

VOLUME VIII

INDUSTRIAL GLASS: GLAZES AND ENAMELS

WILHELM EITEL

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VOLUME VIII

INDUSTRIAL GLASS: GLAZES AND ENAMELS

1976

ACADEMIC PRESS New York San Francisco London
A Subsidiary of Harcourt Brace Jovanovich, Publishers

ACADEMIC PRESS, INC.
111 Fifth Avenue, New York, New York 10003

United Kingdom Edition published by
ACADEMIC PRESS, INC. (LONDON) LTD.
24/28 Oval Road, London NW1

Library of Congress Cataloging in Publication Data

Eitel, Wilhelm, (date)
Silicate science.

Bibliographical footnotes.
CONTENTS: v. 1. Silicate structures.—v. 2. Glasses, enamels, slags.—v. 3. Dry silicate systems. [etc.]
1. Silicates—Collected works. 2. Ceramics—Collected works. I. Title.
TA455.S46E5 546′.683′24 63-16981
ISBN 0–12–236308–6

PRINTED IN THE UNITED STATES OF AMERICA

To the Memory of

KAMILLO KONOPICKY

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Preface to Volumes VII and VIII

In general, Volumes VII and VIII are organized in the same manner as Volume II, Sections A and B. The numbering system used for paragraphs facilitates cross-referencing and index entries.

Advances made in silicate research from 1960 through 1970 are presented. Although much of the discussion is still based on the classic physical chemistry theories, an attempt has been made to introduce the essential solid state physics principles and to show how they can be applied to noncrystalline solids. The properties of many diverse vitreous materials are presented.

All of the international literature was examined in its original form by the author. Some came from the author's own collection of periodicals and books and some from The University of Toledo, the Toledo-Lucas County Public Libraries, and from the Library of the State of Ohio. The kind cooperation and help of the National Library Loan Service in obtaining rare literature are greatly appreciated.

When original texts were not available from any source, abstracts were used which, though critically chosen, sometimes lacked the information sought. Selected abstracts, however, have been included, but only when they could function as a guide to the reader's special endeavors.

These volumes complete this treatise. It is hoped that the information they supply will lead to fruitful research in the future.

The author is deeply grateful to Dr. W. C. Carlson, the previous President of The University of Toledo, to his successor Dr. G. R. Driscoll, and particularly to Dr. J. R. Long, previous Executive Vice President, and to his successor Dr. Robert S. Sullivant for their kind understanding and advancement of this enterprise during which the author enjoyed liberal hospitality as Professor Emeritus. The facilities of the Villa House of Cheltenham were placed at his disposal. The Board of Trustees of this University is sincerely thanked for providing financial aid for clerical help and for the administration of the Institute of Silicate Research.

Special gratitude is due Mr. P. T. Barkey, Director of the University Libraries, and his staff, especially to Mrs. I. J. Weis and to Mr. J. M. Morgan, for their help in supplying bibliographical material not only from the local libraries but from many

outside organizations. A debt of thanks goes to Mrs. B. M. Lorenzen and to Mrs. J. H. Kent, the author's personal secretaries, and to Mrs. B. G. Kirkpatrick who helped so much in preparing the many manuscripts and in keeping organized the tremendous amount of material to be examined through the many stages of proof. The accurate secretarial assistance of Mrs. M. Foster and Mrs. J. S. Barnes is greatly appreciated.

A good deal of energy was expended in securing and selecting the best available original illustrations for these volumes. We received invaluable aid from competent laboratories and special departments of The University of Toledo in reproducing, enlarging, and correcting the illustrations used, particularly from the staff of the University's Office Manager in Education, Mr. W. Douglas, and the Print Shop Manager, Mr. J. L. Clemens.

Our sincere thanks go to the numerous publishing organizations and editors who helped our enterprise by granting the necessary permissions to reproduce illustrations from their original literature.

Finally, it is the author's privilege and pleasure to express his deepest appreciation to Mr. Frederick K. McIlvaine for his editorial assistance in the form of valuable advice and discussions on the manuscripts for these volumes, essentially contributing to their readability.

Wilhelm Eitel

Acknowledgments

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Akadémiai Kiadó, Publishing House of the Hungarian Academy of Science, Budapest, Hungary
American Ceramic Society, Columbus, Ohio
Asahi Glass Co., Ltd., Yokohama, Japan
The British Ceramic Society, Stoke-on-Trent, England
Central Glass & Ceramic Institute, Calcutta, India
Deutsche Glastechnische Gesellschaft, E.V., Frankfurt am Main, Germany
Deutsche Keramische Gesellschaft, E.V., Bad Honnef/Rhein, Germany
Institut Du Verre, Paris, France
North-Holland Publishing Company, Amsterdam, Holland
Silicates Industriels, Brussels, Belgium
Società Technologica Italiana Del Vetro, Roma – Via Bissolati, Italy
Society of Glass Technology, Sheffield, England
Society of Mining Engineers of AIME, New York, N.Y.
VEB Verlag für Bauwesen, Berlin, Germany (DDR)
Verlag Brunke Garrels, Hamburg, Germany
Verlag Schmid GmbH, Freiburg, Germany

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Contents of Other Volumes

*General Introduction**

1. The present state of the art of glass manufacturing, or glass technology in the meaning proper for this text, is based on the developments of glass melting units over several centuries, from the primitive forms of pot furnaces of little capacity to modern tank furnaces that make possible the production of several hundred tons of glass a day. These furnaces are so well and richly described in the technological literature that we feel obliged to only make brief reference in this volume to the many possibilities for improvement and modification of the traditional forms and constructions beyond tank furnace to units equipped for glass fusion. These will not advance any essentially new principles beyond the classical reactions and operation for glass fusion from a "batch" consisting of the fundamental mixtures of mineral raw materials like quartz (sand), limestone, or dolomite, in combination with such chemicals as Na_2CO_3 or Na_2SO_4 as the simplest ingredients. Progress actually made in the last decades did not concern the basic concepts of the production from the batch in tank furnaces as the given tool of the industrial processes, but came in improvement of the heat economy of the furnace system, and acceleration of treatment of the batch to achieve homogenization and fining. These evolutions of the last decade will therefore be the subject of our introductory chapter.

2. A few remarks may be appropriate concerning the great and promising prospects offered by modern electric engineering through special modification of the usual glass fusion methods to gain essential advantages in the thermochemical balance aspects of corresponding new construction of electrical glass furnace. Such units create new possibilities for the manufacturing of special glasses which, because of their contents of highly corrosive or highly refractory batch components cannot be melted in the classical tank or pot furnaces. They require walls and linings of refractory ceramic materials which are much different and, in principle, new con-

*All volumes of "Silicate Science" have been published by Academic Press, New York. Vol. I, 1964; Vol. II, 1965; Vol. III, 1965; Vol. IV, 1966; Vol. V, 1966; Vol. VI, 1975; Vol. VII, 1976. Where a reference is listed by volume and paragraph number, this treatise is indicated.

tainer materials (refractories) such as noble metals of the Pt group, Wo, Mo metal, and the like. When high electrical current intensities must be applied in such cases, the fusion may be achieved in modern electric arc furnaces. Abundant literature on this process is available from the experience of electrometallurgy.

3. We will omit discussions of this wide and extremely specialized field of glass engineering, referring, however, to such excellent and comprehensive reviews as we have at hand. These include a publication by E. Plumat, P. Éloy, J. Duthoit, and J. Cl. Barbier† which not only outlines possibilities for evolution in glass fusion furnace construction, but also offers details for improvement of the efficiency of the different systems concerned. Later in this section we will call attention to important improvements in reactions of the batches, the homogenization and fining of the raw melts, and the behavior of the glass melts when refractories come into contact with the molten material. Plumat *et al.* give so many instructive examples for improvement to be proposed and others performed in the last 10 years that we feel justified in restricting consideration here to the physical and chemical reaction phenomena which normally occur in every glass tank furnace, and in electric furnaces of many shapes. This will be a rich source of information and recommendations for advancement. Studies of the more than one hundred references presented in Plumat's review are an excellent and adequate introduction of the student to patent literature on glass fusion units.

†*Glastech. Ber.* **40**, (11), 411–425 (1967).

Chapter I

Part A: Reactions of Glass Batch Mixtures at Elevated Temperatures

INTRODUCTION

4. As an instructive introduction to the physical–chemical basic reactions in batches for glass compositions of the common Na–Ca type we recommend the interesting report by K. Kautz and G. S. Stromburg[1] which starts from results essentially disclosed in reports by G. Tammann and W. Oelsen (1930), O. Knapp (1934), C. Kröger and J. Blömer (1958), and more recently by F. W. Wilburn, S. A. Metcalfe, and R. S. Warburton.[2] Most of these investigations were made by determination of reaction rates in the batches, measuring the temperature ranges for the appearance of definite phases which are different from those in the original batches, and are characteristic of partial reactions of the mixes. Kautz and Stromburg paid special attention to the changes in the raw materials, namely, quartz (sand), $CaCO_3$ (present as limestone, or in dolomite), and alkalies in the form of commercially pure Na_2SO_4. The nature of the new-formed compounds was examined by the classical methods of polarization microscopy techniques.

5. The application of a special gradient furnace[3] with an accurately controlled rate of heating and gas atmosphere is paradigmatic. The observed results were supplemented by the microscopic evaluation of thin sections and X-ray diffraction analysis of the crystalline phases. For the control of the water content in the batches and reaction products, infrared absorption spectroscopy proved to be an important help. Beside the α-III modification of Na_2SiO_3, CaO, and Na–Ca-double carbonate, the crystallization of $Na_4CaSi_3O_9$ was established, whereas $Na_2Ca_2Si_3O_9$, as de-

[1] *Glastech. Ber.* **42**, (8), 309–317 (1969); see also the comprehensive literature references presented by K. Kautz, *ibid.*, (6), 244–250.

[2] *Glass Technol.* **6**, (4), 107–114 (1965); see ¶ 16.

[3] Cf. K. Beyersdorfer and J. Hammer, *Ber. Deut. Keram. Ges.* **42**, (2), 44–49 (1965).

scribed by Kröger and Blömer was uncertain. From the glass technological viewpoint, it is significant that definite variations in the presence of the crystalline phases after the batch reactions were observed as a function of variable grain sizes on the reagents, the batch composition, and their moisture contents. There were characteristic differences between the products of the laboratory experiments and samples taken from industrial batches in the furnace process although, in most cases, the samples had been treated equally in the gradient temperature process. The experiments of Kautz and Stromburg, on the other hand, definitely confirm Kröger's conclusions on the importance of the presence of moisture in the furnace atmosphere and of "impregnation" effects; the existence of the latter was confirmed anew.

6. The *moisture content of glass sand* as an essential constituent of glass batch mixes, plays a very important role eventually as an accelerating agent for the fusion of the batch, and the fining of the glass melt. Its accurate determination and the constant survey for its presence are therefore some of the most important problems in glass manufacturing.[4] For all these reasons it is indispensable to organize periodically a regular and accurate survey of the moisture in commercial glass sands before they are introduced to batch feeding operation for which the nuclear methods using rapid neutrons in their interreaction with hydrogen cores (protons) are particularly attractive.[5]

A recent publication by V. Caimann[6] refers to more developed instrumentation for the current automatic survey of moisture determinations and digital-counter statistical evaluation for the plant control of glass sands, using a 100 (or better 300) $Ci-{}^{241}Am-Be$ source and an impulse-time counter (scintillometer) system. The accuracy for single measurements could thus be reproduced to ± 0.1 wt. % H_2O.

7. In order, as far as it is possible by simple technological measures, to reduce uncontrolled divergencies in the course of batch reactions in the early stages of their evolution in the tank furnace atmosphere, *granulation*, or *pelletizing*, of the batch mixtures by compacting treatments were again and again proposed, going back to recommendations of G. Keppeler (1929) and J. Löffler (1951). They now have been emphasized by S. Kirchhof[7] who constructed a rotating granulation panel which was adjustable to an optimum axial inclination of the pan, normally for an angle of 35° to 55° to have a reproducible efficiency comparable to that of the well-known

[4] Cf. the classical studies of batch reactions in many papers by C. Kröger *et al.*, *Glastech. Ber.* **29**, 275–289 (1956); **30**, 42–52 (1957); but also older literature, e.g., of F. Zsckacke, *et al.*, 1938.

[5] See older literature by E. Amrhein, A. Dietzel, and K. Metzner, *Ber. Deut. Keram. Ges.* **37**, (7), 311–315 (1960); H. Neuhaus, G. Hombeck, and W. Kühn, *Arch. Eisenhüttenw.* **82**, 1017–1026 (1962).

[6] *Glastech. Ber.* **45**, (6), 247–256 (1972).

[7] *Silikattechnik* **13**, (9), 325–329 (1962).