OKLAHOMA GEOLOGICAL SURVEY
Charles J. Mankin, *Director*
CIRCULAR 79

THIRTEENTH ANNUAL FORUM ON THE GEOLOGY OF INDUSTRIAL MINERALS

Themes: Gypsum, Silica-Rich Sediments,
Natural Brines, and Energy in the
Industrial-Minerals Industry

KENNETH S. JOHNSON and JUDY A. RUSSELL, *Editors*

Proceedings of the 13th annual meeting of the Forum on the Geology of Industrial Minerals held May 12-14, 1977, in Norman, Oklahoma. Sponsored by the Oklahoma Geological Survey and The University of Oklahoma

Forum Co-chairmen:

KENNETH S. JOHNSON and CHARLES J. MANKIN

The University of Oklahoma
Norman
1978

This publication, printed by the Transcript Press, Norman, Oklahoma, is issued by the Oklahoma Geological Survey as authorized by Title 70, Oklahoma Statutes 1971, Section 3310, and Title 74, Oklahoma Statutes 1971, Section 3310, and Title 74, Oklahoma Statutes 1971, Sections 231-238. 1,500 copies have been prepared for distribution at a cost to the taxpayers of the State of Oklahoma of $7,426.

Type faces:	Text in 8- and 10-pt. Century Schoolbook, leaded 1 pt. Heads in 10-pt. bold Century Schoolbook Captions in 8-pt. Helvetica, leaded 1 pt. Table heads in 10-pt. large and small caps Century Schoolbook
Presswork:	Miehle TP-29 Perfector
Binding:	Sewn with softbound and hardbound cover
Paper:	Text on 70-lb. Mountie Matte Cover (hardbound) on Gane 8117LV red cloth on 160-pt. binder's board Cover (softbound) on 65-lb. Hammermill gray, antique finish

FOREWORD

The Forum on the Geology of Industrial Minerals is an annual meeting during which representatives of industry, government, and universities can discuss the problems of geology, exploration, evaluation, and production of our important industrial minerals (stone, sand, clay, gypsum, salt, and other nonmetallic rocks and minerals). Each year the Forum is held in a different state, and in 1977 Oklahoma was privileged to be the host of the 13th Forum. A total of 116 people from throughout the United States, Canada, and England attended the meeting.

The Oklahoma Geological Survey and The University of Oklahoma jointly sponsored the Forum, held in Norman at the Oklahoma Center for Continuing Education on the campus of The University of Oklahoma. Technical sessions emphasizing gypsum, silica-rich sediments, natural brines, and energy in the industrial-minerals industry were held on May 12–13. A one-day field trip following the meeting was conducted to the Arbuckle Mountains to examine the geologic setting and history of the Arbuckles, to visit the silica-sand pit (Ordovician, Oil Creek Sandstone) and processing plant operated by Pennsylvania Glass Sand Corp., and to visit the granite quarry (Precambrian, Troy Granite) operated by Century Granite Company.

Special thanks are due the Society of Economic Geologists Foundation, Inc., for its grant of $500.00 to help in printing this Forum Proceedings volume.

The lists that follow show (1) Forum steering committee for 1976–77, (2) registrants for the 13th Forum, and (3) hosts and publications of past Forums.

—Kenneth S. Johnson
Charles J. Mankin

FORUM STEERING COMMITTEE 1976-77

Nonvoting members (future hosts)
Al L. Hornbaker
James A. Martin
George S. Austin
Donald D. Carr

W. Robert Power — Cochairmen, 1976
Sam M. Pickering

Kenneth S. Johnson — Cochairmen, 1977
Charles J. Mankin

Barrett Williams (term ends 1977)
Richard C. Runvik (1978)
Lance Meade (1979)
William E. Cutcliffe and/or
Jim Davis (Cochairmen elect)

REGISTRATION LIST FOR THE 13TH ANNUAL FORUM

Catherine A. Adeleke, Conoco
Robert K. Alberts, American Aggregates
Hank Allen, Martin Marietta
Robert H. Arndt, U. S. Bureau of Mines
Brenda L. Atkins, Conoco
Curtis H. Ault, Indiana Geological Survey
George S. Austin, New Mexico Bureau of Mines & Mineral Resources
Kerry D. Bartlett, U. S. Gypsum Co.
Alan Bates, The Carborundum Co.
Robert L. Bates, Ohio State University
Enid S. Bergstrom, *Rock Products*
Gene R. Block, Ottawa Silica Company
H. Lyn Bourne, Consulting Geologist
Frank W. Bowdish, Nevada Bureau-Mines & Geology
Lawrence L. Brady, Kansas Geological Survey
M. D. Buckner, Dow Chemical Company
Raymond R. Burchett, Nebraska Geological Survey
Alden B. Carpenter, University of Missouri
Donald D. Carr, Indiana Geological Survey
Robert S. Cathcart, Medusa Cement Company
Armin L. Clark, Murray State University
Marion Clark, Oklahoma Geological Survey
Wendell Cochran, *Geotimes*
A. Gene Collins, U. S. Energy Research & Development Administration
James Corff, Sooner Rock & Sand Co.
John C. Corff, Sooner Rock & Sand Co.
Howard M. Cotten, Amoco Production Research
Rosemary Croy, Oklahoma Geological Survey
William E. Cutcliffe, Dunn Geoscience Corp.
Vi Duong Dang, Brookhaven National Lab
George H. Didawick, Pennsylvania Glass Sand Corp.
Fred H. Dorheim, Iowa Geological Survey
L. J. Duersmith, The J. E. Baker Company
Ned A. Finney, Land Consultants—Exploration
David Foster, Oklahoma Geological Survey
Harold B. Foxhall, Dow Chemical Company
S. A. Friedman, Oklahoma Geological Survey
G. Robert Ganis, Dunn Geoscience Corp.
Thomas M. Garland, U. S. Bureau of Mines
Serge Gonzales, Earth Resource Associates
John M. Grosshans, Anglo American Clays Corp.
Betty Ham, Oklahoma Geological Survey
Ron Hardy, Kansas Geological Survey
Claire Hardy
Steve E. Hendricks, U. S. Gypsum Co.
John W. Hipple, Dow Chemical Company
April J. Hoefner, University of Oklahoma
Rudolph K. Hogberg, Ernest K. Lehmann & Assoc.
Drew Holbrook, Arkansas Geological Commission
Peter P. Hudec, University of Windsor
Richard A. Hunnisett, Pennsylvania Glass Sand Corp.
Pat Jackson, Wendling Quarries, Inc.
Kenneth S. Johnson, Oklahoma Geological Survey
R. T. Johnson, Dowell
Duane B. Jorgensen, U. S. Gypsum Co.
James H. Joseph, *Industrial Minerals Journal*
William W. Kephart, Brockway Glass Co.
Keith B. Ketner, U. S. Geological Survey
Claren Kidd, Oklahoma Geological Survey
E. R. Kiehl, Celotex Corp.
Harold J. Kleen, Independent Geologist
William A. Kneller, Eitel Institute of Silicate Res.
Allen R. Krueger, Alpha Aggregates
Dean F. Kruse, Calvert Mines, Inc.
Dan B. Leak
Richard K. Leininger, Indiana Geological Survey
Richard A. Lucas, The France Stone Co.
Kenneth V. Luza, Oklahoma Geological Survey
Henry R. McCabe, McCabe-Woody & Co.
Eugene E. McClellan, Florida Bureau of Geology
Lee McCulley, Fuel Dynamics Inc.
Alice McGuire, Sooner Rock & Sand Co.
Sid McIlveen, Ozark-Mahoning Co.
Vic H. Malone, Medusa Cement Co.
Charles J. Mankin, Oklahoma Geological Survey
James A. Martin, Missouri Geological Survey
John M. Masters, Illinois Geological Survey
Lance P. Meade, Pluess-Stauffer
Michael C. Moore, Indiana Geological Survey
Reza Moussavi-Harami, Oklahoma Geological Survey
Pauline Moyd, Geological Survey of Canada
Richard H. Olson, Consultant
Mark Orgren, University of Oklahoma
Ronald L. Parratt, Stauffer Chemical Co.
H. Wesley Peirce, Arizona Bureau of Mines
Robert Powell, Oklahoma Geological Survey
W. Robert Power, Georgia State University
Williard F. Quirk, The Carborundum Co.
Henry E. Reed, Burlington Northern, Inc.
John F. Roberts, Oklahoma Geological Survey
Jimmie L. Rogers, Central State University
William D. Rose, Oklahoma Geological Survey
Richard C. Runvik, U. S. Gypsum Co.
Ken Santini, Arizona Portland Cement Co.
Walter E. Seibert, Jr., Chemical Bank of New York
Nelson R. Shaffer, Indiana Geological Survey
Richard A. Sheppard, U. S. Geological Survey
Lawrence E. Shirley, U. S. Bureau of Mines
Thomas E. Shufflebarger, Pennsylvania Glass Sand Corp.
Harry O. Sorensen, Michigan Geological Survey
Alfred C. Spreng, University of Missouri
Meyer Steinberg, Brookhaven National Lab
John W. Stevens, Dow Chemical U.S.A.
James Stewart, White Pigment Corporation
Charles Stone, Arkansas Geological Commission
Fred A. Teeters, Dow Chemical U.S.A.
Bobby J. Timmons, Fl. Rock Ind.
Michael L. Trout, Phillips Petroleum Co.
Barbara Uehling, University of Oklahoma
G. Oliver Vagt, Energy Mines & Resources
Dan H. Venard
William A. Walden, Michigan Geological Survey
Bryan L. Watts, HFCO Coal Co.
Edward B. Westphal, U. S. Gypsum Co.
Barrett J. Williams, Southern Railway System
Norman F. (Bill) Williams, Arkansas Geological Commission

HOSTS AND PUBLICATIONS OF PAST FORUMS

Year, Place, Theme	*Host*	*Publication*	*Source*
First, 1965 Columbus, OH. Industrial limestone and dolomite	Dept. of Geology, Ohio State Univ.	Ohio Journal of Science, 1966, v. 66, no. 2, p. 97-191.	Ohio Academy of Science, 445 King Ave., Columbus, OH 43201
Second, 1966, Bloomington, IN. Cement raw materials	Indiana Geol. Survey and Indiana Univ.	A symposium on geology of cement raw materials, 197 p.	Out of print
Third, 1967, Lawrence, KS. Exploration and development	State Geol. Survey of Kansas and Univ. of Kansas	Kan. Geol. Survey, Spec. Distrib. Publication 34, 174 p.	State Geological Survey of Kansas, University of Kansas, Lawrence, KS 66044
Fourth, 1968, Austin, TX. Chemical materials, depositional models	Bureau of Economic Geology and Univ. of Texas at Austin	Proc. 4th Forum on Geology of Ind. Mins., 1968, 174 p.	Bureau of Economic Geology, Box X, University Station, Austin, TX 78712
Fifth, 1969, Harrisburg, PA. Sand and gravel, urbanization, land use	Pennsylvania Topographic & Geologic Survey	Pa. Geol. Survey, Mineral Resources Rept. M64, 278 p.	Bureau of Publications, 10th & Market Sts., Harrisburg, PA 17125
Sixth, 1970, Ann Arbor, MI. Chemical, industrial, construction materials	Mich. Geol. Survey, Univ. of Michigan, and Univ. of Toledo	Mich. Geol.Survey, Miscellany 1, 155 p.	Publications Room, Dept. of Natural Resources, Lansing, MI 48926
Seventh, 1971, Tampa, FL. Phosphate, dolomite, limestone, clay	Florida Bureau of Geology	Fla. Bur. Geology, Special Publication 17, 228 p.	Florida Bureau of Geology, Box 631, Tallahassee, FL 32302
Eighth, 1972, Iowa City, IA. Limestone, gypsum, shale.	Iowa Geol. Survey	Iowa Geol. Survey, Public Information Circular 5, 194 p.	Iowa Geological Survey, 16 West Jefferson St., Iowa City, IA 52240
Ninth, 1973, Paducah, KY. Fluorspar	Illinois Geol. Survey and Kentucky Geol. Survey	Kentucky Geol. Survey, Series X, Special Pub. 22	Kentucky Geol. Survey 307 Mineral Industries Bldg. Lexington, KY 40506
Tenth, 1974 Columbus, OH. Reclamation; carbonate rocks in environmental control.	Dept. of Geology, Ohio State Univ., and Ohio Geol. Survey	Ohio Geol. Survey, Miscellaneous Rept. No. 1	Ohio Geological Survey, Ohio Dept. of Natural Resources Fountain Square, Columbus, OH 43224
Eleventh, 1975, Kalispell, MT. Industrial minerals of Montana and contiguous states and provinces.	Flathead Valley Community College, and Montana Bur. Mines and Geology	Montana Bur. Mines and Geology, Special Pub. 74, 186 p.	Mont. Bur. Mines and Geology Room 203-B, Main Hall Montana College of Min. Sci. and Tech., Butte, MT 59701
Twelfth, 1976, Atlanta, GA Industrial minerals of Georgia and the southeastern states.	Geol. Survey of Georgia and Georgia State Univ.	Geol. Survey of Georgia (in preparation)	Geol. Survey of Georgia, Dept. of Natural Resources, 19 Hunter St., SW, Atlanta, GA 30334

CONTENTS

Gypsum (Session Chairman, Richard C. Runvick) *Page*

Silica-Rich Sediments (Session Chairman, Thomas E. Shufflebarger, Jr.)

Luncheon Talk

Natural Brines (Session Chairman, A. Gene Collins)

SOME FACTORS INVOLVED IN PROSPECTING FOR GYPSUM DEPOSITS, A BRIEF REVIEW

DUANE JORGENSEN[1]

Abstract—Two types of factors direct the search for gypsum deposits—geologic factors and economic factors. The prime control and major economic factor is the market for the possible products. The major geologic factor is the control of the depositional environment, which determines whether or not a deposit exists within a given market area. After discovery of a deposit, the distinction between economic and geologic factors is not as clear as before, and the geologic characteristics of the deposit become the economic factors in evaluating the deposit for production and processing. The geologic characteristics are concerned with 1) the gypsum rock, 2) the host or country rock, and 3) geologic fluids, such as gas and water.

Prospecting includes both original discovery and the continuing information-gathering period. During this time the above three characteristics of the deposit are determined, usually from core drilling, from phenomena observed during drilling, and from the core and hole. Important information and means of gathering it include sample analyses, sample volume, impurities and their distribution, water levels, aquifer tests, permeability measurements, rock strength tests, rock and overburden thicknesses, rock types, and direct observations of water and gas. Data gathered or inferred from all of these determine the mining or quarrying geometry and environment, which in turn determine the equipment, development, production, and processing costs.

Impurities in gypsum deposits are very important in manufacturing processes. The impurities and their effects vary widely from inert minerals with little effect to reactive minerals with strong and mostly detrimental effects.

INTRODUCTION

This paper is a review of the state of the art of prospecting for and evaluating gypsum deposits, as practiced by the United States Gypsum Co. Prospecting, as used here, includes both the original discovery of a deposit as well as the continuing information gathering in a preproduction time period. Two general types of factors control the search for deposits—geologic factors and economic factors. The primary consideration in measuring the utility of a deposit is its location relative to potential markets for gypsum products. This decides whether or not a search for a deposit will begin. The purely geologic factors of prospecting are depositional environment controls and subsequent geologic history, both of which determine whether or not a deposit now exists in a particular region (fig. 1). Recognition of favorable environments and geologic history is essential to prospecting regardless of the type material being searched for. After a deposit has been discovered, all the characteristics of the deposit become economic factors, whether or not they are geologic in nature or are cultural features of the human environment.

DEPOSITIONAL ENVIRONMENT MODELS

The calcium sulfate minerals, anhydrite ($CaSO_4$), bassanite ($CaSO_4 \cdot \frac{1}{2}H_2O$), and gypsum ($CaSO_4 \cdot 2H_2O$), occur in a wide variety of geologic environments. The basic principles of deposition of the calcium sulfate minerals are easily understood. The minerals are deposited by precipitation from aqueous solution when the concentration of the components exceeds the solubility of the

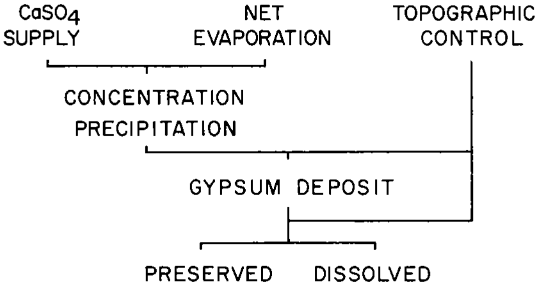


Figure 1.—Geologic requirements for formation and preservation of a gypsum deposit.

---

[1] United States Gypsum Company, Saltville, Virginia.

mineral. Exact definition of the chemical and physical environment at the time of deposition has been the subject of considerable and continuing study. The great majority of gypsum deposits now being worked are the result of precipitation of calcium sulfate minerals from concentrating marine brines in an arid climate, that is, evaporite conditions. A short discussion of the origin and occurrence of deposits with a selected bibliography can be found in LeFond (1975). Shaw (1977) presents a review of the chemistry and hydrology of deposition from marine brines and concludes all evaporite minerals were deposited under shallow-water conditions.

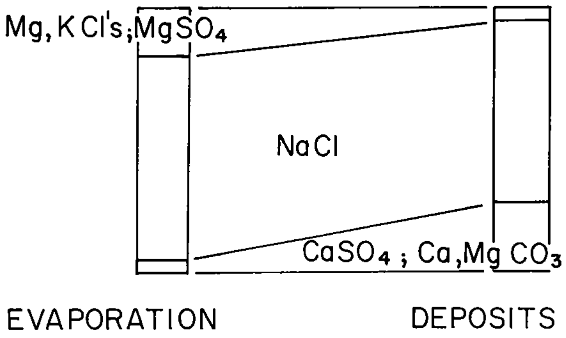


Figure 2.—Relative abundance of minerals formed from evaporated sea water (left) compared with relative abundance of minerals found in several evaporite deposits (right). Modified after Borchert and Muir (1964).

The prospectors' concept of the depositional model directs the placement of prospecting drill holes. Until recently, it was generally believed that the calcium sulfate minerals were deposited as gypsum in a subaqueous environment in a fully or partially enclosed basin. Examination of relative quantities of various evaporite minerals (fig. 2) and other criteria led to modification of simple "evaporating-dish" models (fig. 3). Although many calcium sulfate mineral deposits are unquestionably located in a former subaqueous basin, many others, including most of the deposits that are being worked in the eastern United States, appear to be the result of deposition in a sabkha environment (fig. 4). The sabkha is essentially a supratidal flat or lowland in an area with an arid climate. In this environment calcium sulfate precipitates inside a preexisting host sediment, and a part of the calcium sulfate is either deposited as, or undergoes an early conversion to, anhydrite under near-surface conditions. A well-defined basin is thus not an absolute essential for deposition nor is deep burial essential for the conversion of gypsum to anhydrite.

Regardless of the original depositional site of the calcium sulfate minerals, or of whether or not the major mineral was gypsum or anhydrite, most deposits undergo changes referred to as the gypsum-

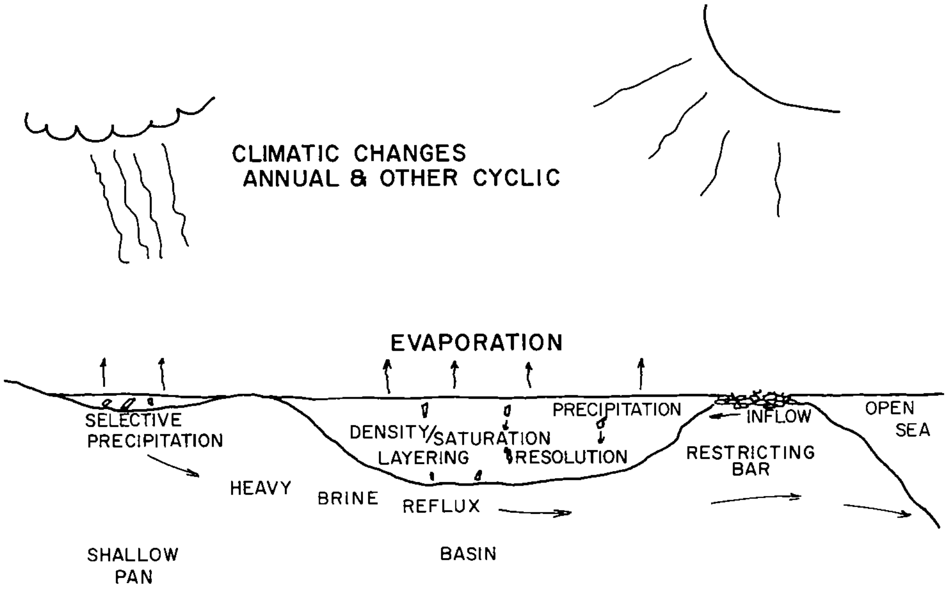


Figure 3.—Modified evaporating basin showing several mechanisms used to explain formation of evaporite deposits.

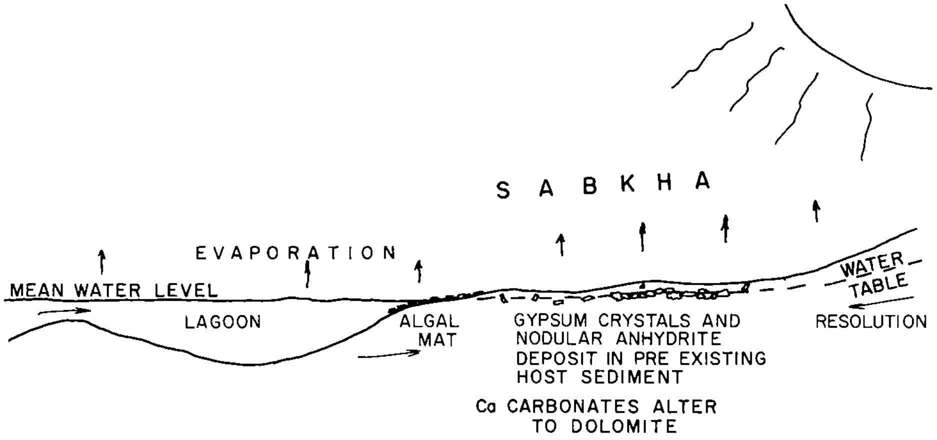


Figure 4.—Essential features of the sabkha environment as a site for deposition of calcium sulfate.

anhydrite cycle (fig. 5). In this cycle gypsum conversion to anhydrite accompanies deep burial; subsequent removal of overlying sediments is accompanied by hydration of anhydrite to gypsum in the presence of shallow ground water. However, at least one deposit, that at Shoals, Indiana, shows some evidence of anhydrite having been hydrated during Mississippian time and remaining as gypsum into the present (Jorgensen and Carr, 1973, p. 60).

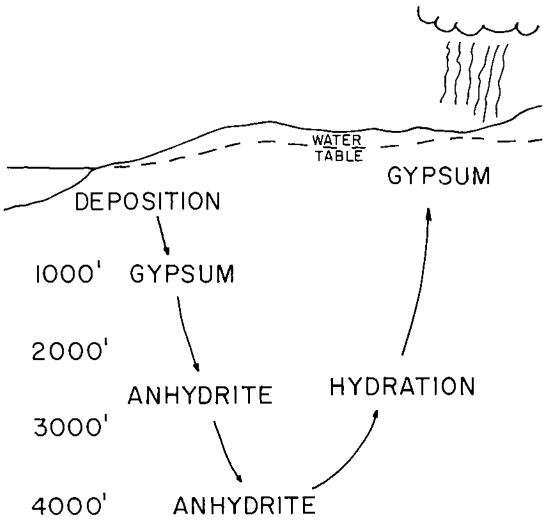


Figure 5.—Gypsum-anhydrite cycle showing changes that take place in calcium sulfate with depth. Modified after Murray (1964).

EVALUATION CONSIDERATIONS

Although distance from gypsum-product markets determines whether or not a region will be explored for gypsum deposits, the characteristics of the deposit itself determine whether or not the deposit is commercially valuable and can withstand competition from other producers. If an area is determined suitable for additional manufacturing capacity of gypsum products, prospecting begins with a gathering of as much usable information as can be collected from existing sources. This may include published and unpublished geologic reports on such things as existing operations, stratigraphy, depositional environments, geologic structure, mineral occurrences, and ground water. Analysis of preexisting information determines whether or not actual exploration will be done. Core drilling is the predominant prospecting method.

During the actual exploration, information about the gypsum rock (including impurities), the host rock and overburden, and geologic fluids, such as water and gases, is gathered. The information gathered determines the mine or quarry geometry and the mining or quarrying environment which, in turn, determine the equipment, development, and production costs. Each deposit is a unique entity, and the only firm rule that governs is whether the manufactured products can effectively compete in the marketplace. Proper interpretation of the initial information, as well as the information gathered from drilling, results in a successful operation or, alternatively, preventing the opening of a potentially unsuccessful operation.

A few of the geological-economical considerations are so important they can preclude operation. Gas, either hydrogen sulfide or methane and other natural gases, must be essentially absent for a successful

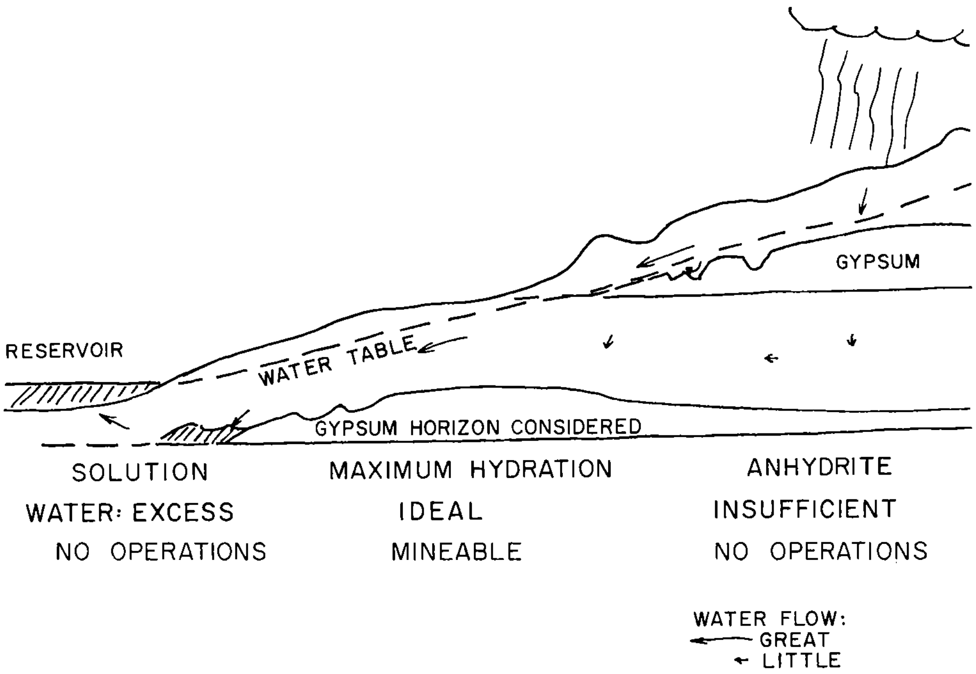


Figure 6.—Effects of ground water on gypsum and anhydrite in determining the minability of calcium sulfate deposits.

underground operation. One operation, an underground mine at Gypsum, Ohio, was closed recently in part because of problems of hydrogen sulfide encountered during mining. Hydrogen sulfide is dissolved in water associated with many gypsum deposits. Gas, especially hydrogen sulfide, is generally readily detected during drilling or later during core sampling. Gas of unknown composition is sometimes sampled as it issues from a drill hole. Quarries are rarely troubled with gases because of their openness to the air, and the operations are generally above hydrogen-sulfide-bearing ground water.

Water is more common than gas in gypsum deposits and is present in quarries and mines alike in widely varying quantities. Likewise, water control or pumping costs vary widely from essentially zero to a major production cost. Some of the cost of water control in existing operations can be postponed or completely avoided by applying hydrologic studies to mining or quarrying plans. Although water is required to make a gypsum deposit, excess water dissolves the deposit and precludes operation (fig. 6). Potential water problems can be recognized during prospecting by observing water levels during and after drilling of core holes. Positive correlation of water levels from strata affected by mining or quarrying with major aquifers or reservoirs usually precludes mining or quarrying. An example is given in Jorgensen and Carr (1973, p. 63–64). Further information about potential water problems is gathered by studying aquifer distribution, measuring permeability of core samples, using aquifer tests (such as pump and packer tests in drill holes), and by as simple a means as looking for water-worn surfaces on breaks in drill core and calculating recoveries. Water quantities and distribution can be estimated with fair accuracy, and pump locations and costs can then be planned efficiently.

Probably one of the best examples of nonutilization of gypsum deposits as a result of combined gas and water hazards is the gypsum that occurs as part of the caprock of several salt domes in the Gulf Coast region of the south-central United States.

Impurities in the gypsum are a major influence on the utility of the material. Figure 7 lists the common impurities and their general range of quantity in deposits currently being worked. Very briefly, the use of gypsum lies in its ability to be converted from gypsum (calcium dihydrate, $CaSO_4 \cdot 2H_2O$) to stucco (bassinite or calcium hemihydrate, $CaSO_4 \cdot \frac{1}{2}H_2O$) with the application of heat, and the stucco's great affinity for water and quick reversion to the stable mineral, gypsum.

Inert minerals are those that have no effect on the processes in manufacturing gypsum panels, the greatest single use for gypsum, other than replacing gypsum in the products. Reactive minerals are those that have serious or strong effects on the manufacturing processes. Strictly speaking, there are no totally inert minerals, for even chemically inert minerals such as quartz may be physically reactive by providing nuclei for crystal growth during stucco rehydration. The reactive minerals generally affect the rehydration characteristics of stucco because of their interaction with or affinity for water. The effects are diverse, varying from accelerating to retarding the stucco rehydration, from weakening to strengthening the bond between the stucco of the wallboard core and the enclosing paper cover, and from making the core more flexible to embrittling it.

The quantities of reactive minerals that can be tolerated in board manufacture are one or two orders of magnitude smaller than inert mineral quantities tolerable. As an example, several deposits being worked averaged about 10 percent dolomite, but no deposits known to this author being worked averaged as much as 1 percent thenardite (sodium sulfate), and only a few would contain as much as 0.1 percent. Local market conditions control the amounts of impurities tolerable, but a general maximum of total soluble-salt mineral contents is around 0.1 percent on a dry-weight basis. Soluble salts include all those evaporite minerals more soluble than gypsum that are found in gypsum deposits. Probably the most detrimental soluble salt minerals are the soluble magnesium compounds, which are known to migrate to the interface between the board core and the surface paper, weakening the bond between these two and causing what is known as humidified split.

If all the geologic characteristics of the deposit appear favorable, mine or quarry design is done by standard methods. Stripping ratios, and other parameters are determined, and favorable areas are chosen for initial production. In the case of an underground mine, overburden pressures are estimated, rock strengths are determined from core samples and mine dimensions determined by combining the rock parameters, equipment dimensions, and productivity factors such as tons per face, hypothesized mining cycle, and rock blending that may be required. Depth of a deposit below surface and the type overburden determine whether a deposit will be worked as a mine or quarry. Stripping ratios in quarries are usually low, rarely exceeding 3 or 4 to 1. Depth of deposits being mined is more commonly governed by anhydrite-gypsum hydration and development costs than by production costs. The reason for this is the production costs most affected by depth (water pumping and hoisting) are normally a small portion of the total production costs.

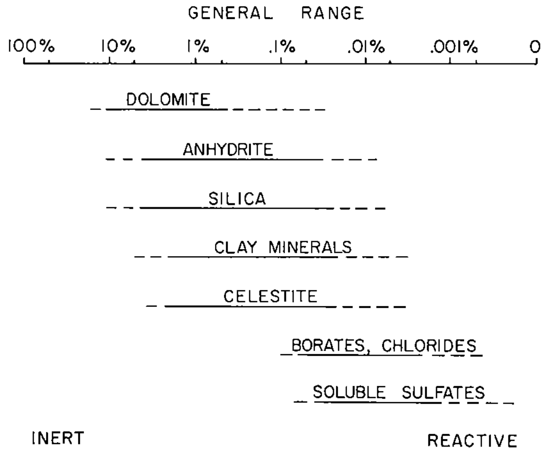


Figure 7.—Common impurities in gypsum deposits and their general range of quantity found.

REFERENCES CITED

Borchert, H., and **Muir, R. O.**, 1964, Salt deposits, the origin, metamorphism, and deformation of evaporites: D. Van Nostrand, London, 338 p.

Jorgensen, D. B., and **Carr, D. D.**, 1973, Influence of cyclic deposition, structural features, and hydrologic controls on evaporite deposits in the St. Louis Limestone in southwestern Indiana: Iowa Geological Survey Public Information Circular 5, p. 43-65.

Lefond, S. J., editor, 1975, Industrual minerals handbook, fourth edition: American Institute of Mining, Metallurgical, and Petroleum Engineers, p. 707-723.

Murray, R. C., 1964, Origin and diagenesis of gypsum and anhydrite: Journal of Sedimentary Petrology, vol. 34, p. 512-523.

Shaw, A. B., 1977, A review of some aspects of evaporite deposition: The Mountain Geologist, vol. 14, p. 1-16.

MAJOR GYPSUM DISTRICTS OF WESTERN OKLAHOMA

KENNETH S. JOHNSON[1]

Abstract—High-purity gypsum of Permian age crops out in three major gypsum districts of western Oklahoma. The northwest and southwest districts have important reserves in the Blaine Formation, whereas reserves of the west-central district are in the Cloud Chief Formation. Gypsum beds of the Blaine Formation typically are 10 to 30 feet thick, 95 to 99 percent pure, and interbedded with shales that are 2 to 30 feet thick. The base of the Cloud Chief Formation consists of a massive bed of gypsum that typically is 20 to 100 feet thick and is 92 to 97 percent pure. Anhydrite is present in the sulfate beds, beneath 20 to 100 feet of overburden, at a number of places in all three districts.

Total gypsum reserves in the three districts are estimated at 48 billion short tons. These reserves are well suited for open-pit mining or quarrying, because gypsum typically forms hills in the semiarid climate of western Oklahoma, and the gypsum layers are nearly flat lying, without folds or faults.

Seven companies currently mine a total of 1.0 to 1.4 million tons of Oklahoma gypsum each year for wallboard, for plaster, as a retarder in portland cement, and as a soil conditioner.

INTRODUCTION

The Permian basin was the site of a vast epicontinental sea in Permian time that extended across West Texas, western Oklahoma, eastern New Mexico, and northward into Kansas (fig. 1). During the Leonardian and Guadalupian Epochs, marine water entered the shallow sea from the area of the Delaware and Midland basins in the south and evaporated because of the warm, arid climate of the region. Thick sequences of marine carbonates (Yeso and San Andres Formations) were deposited in the southern end of the inland sea, whereas evaporites and red beds were being deposited farther north in Oklahoma and surrounding regions (fig. 1); fresh-water and land-derived clastic sediments entered the basin along its margins.

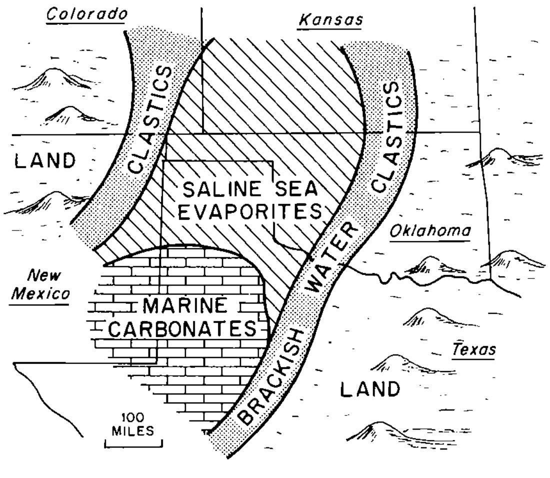


Figure 1. Principal facies and environments in Permian basin of southwest United States during evaporite deposition in Leonardian and Guadalupian time.

In the central part of the Permian basin, in western Oklahoma, four major evaporite units are known in a stratigraphic sequence 5,000 feet thick. Principal tectonic features that influenced evaporite deposition in Oklahoma were the Anadarko and Hollis basins. These basins are separated by the west-northwest-trending axis of the Wichita Mountain uplift (fig. 2). In ascending order, the units are the Wellington, Cimarron, Beckham, and Cloud Chief evaporites. Units are 100 to 1,300 feet thick and consist predominantly of sulfates (gypsum and anhydrite) or sulfates and rock salt. Reddish-brown shale and fine-grained sandstone separate each of the four evaporite units and are the principal nonevaporite rocks interbedded within each unit. Gypsum beds of the

---

[1] Oklahoma Geological Survey, The University of Oklahoma, Norman, Oklahoma.

Beckham and Cloud Chief units are the only evaporites to crop out, and they alone contain the minable gypsum resources.

GENERAL CHARACTERISTICS OF GYPSUM RESOURCES

Major gypsum deposits of western Oklahoma are geographically and geologically separated into three distinct regions: the northwest, southwest and west-central gypsum regions (fig. 3). The northwest and southwest regions consist of outcrops of the Blaine Formation (in the middle of the Beckham evaporites), where gypsum beds are generally 10 to 30 feet thick; whereas the west-central region includes outcrops of the Cloud Chief Gypsum, which is commonly 20 to 100 feet thick. To date, two general reports have been released on the State's gypsum resources (Snider, 1913; Johnson, 1972), and three detailed economic reports have been published (Scott and Ham, 1957; Ham and Curtis, 1958; Ham, 1962), one for a small portion of each of the three regions. In the present report I rely heavily on unpublished data from outcrops, quarries, cores, and boreholes that have been examined as part of an ongoing study of gypsum resources in each of the three regions.

Stone in all three regions is fine- to coarse-grained compact rock gypsum ($CaSO_4 \cdot 2H_2O$), which ranges in color from

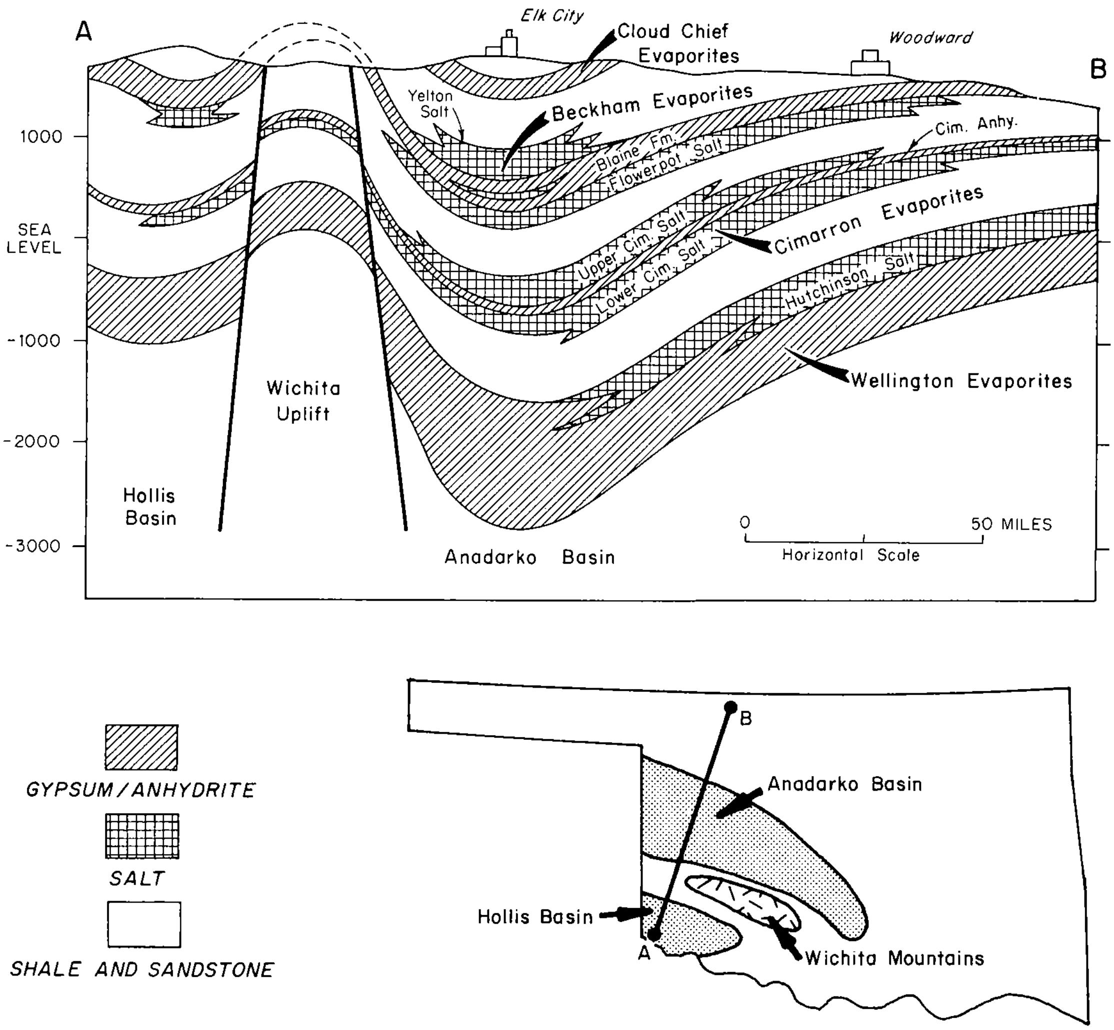


Figure 2. Schematic cross section showing evaporite units and predominant lithologies in Permian rocks of western Oklahoma.

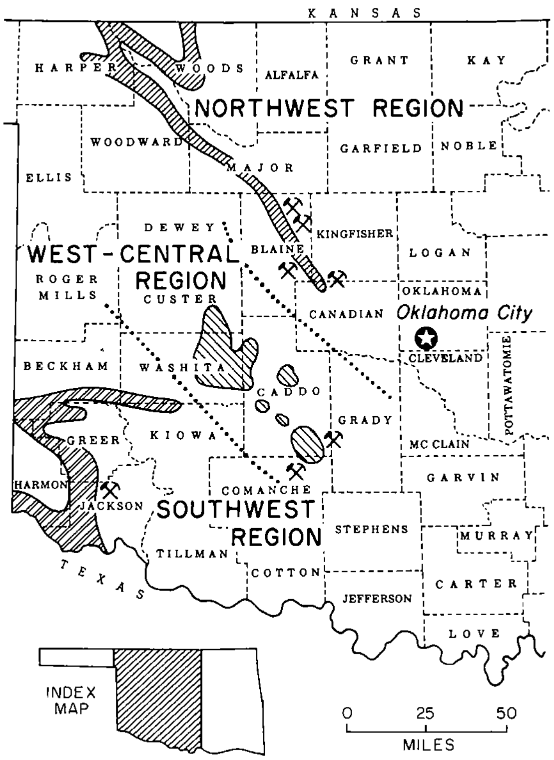


Figure 3. Map of western Oklahoma showing regions of major gypsum reserves and location of seven operating gypsum quarries. Modified from Johnson (1969).

white through light gray and pink. Finely crystalline alabaster gypsum makes up a substantial part of some deposits. In each region strata are essentially flat lying, with dips generally 10 to 40 feet per mile, and the beds are not disrupted by folding or faulting. Gypsum beds are resistant to erosion in the semiarid climate, and thus they generally cap broad benches or otherwise form topographic highs.

Minable deposits are 10 to 100 feet thick and consist of high-purity stone that can be worked by open-cut methods after removal of little or no overburden. Overburden is mostly moderately soft shale that is rippable, but some of the dolomite beds, 1 to 5 feet thick, need to be blasted. Seven open-cut mines currently produce gypsum in Oklahoma.

Gypsum reserves in all three regions are herein estimated to be 48.1 billion short tons (table 1). These reserves include only the surface and near-surface gypsum that can be mined by open-pit methods and exclude stone that in subsurface contains an objectionable amount of anhydrite ($CaSO_4$). Based on cores, borehole samples, and neutron logs, the depth at which anhydrite is present in objectionable

TABLE 1.—ESTIMATED GYPSUM RESERVES IN WESTERN OKLAHOMA[1]
(billion short tons)

Northwest Oklahoma Region	
(Blaine gypsum beds are 10 to 30 feet thick and 96 to 99 percent pure.)	
Blaine County[2]	0.282
Harper County	4.000
Major County	3.320
Woods County[3]	2.297
Woodward County	7.000
	16.899
Southwest Oklahoma Region	
(Blaine gypsum beds are 10 to 30 feet thick and 95 to 99 percent pure.)	
Beckham County	
southeast[4]	0.375
southwest	5.300
Greer County	2.820
Harmon County	5.160
Jackson County	3.570
	17.225
West-Central Oklahoma Region	
(Cloud Chief massive gypsum is 20 to 100 feet thick and 90 to 98 percent pure. Anhydrite reserves excluded.)	
Caddo County	2.500
Comanche County	0.180
Custer County[5]	1.296
Washita County	10.000
	13.976
Total reserves (all 3 regions)	48.100

---

[1] Only surface and near-surface gypsum is considered (maximum overburden, 30 feet).

[2] Ham, 1962.

[3] Fay, 1965.

[4] Scott and Ham, 1957.

[5] Ham and Curtis, 1958.

amounts (in layers or lenses more than 1 or 2 feet thick) commonly ranges from 30 to 100 feet in various parts of each region. For estimating gypsum reserves, a value of 140 pounds per cubic foot, or 3,000 tons per acre-foot, has been used.

NORTHWEST OKLAHOMA REGION

The northwest Oklahoma region consists of outcrops of the Blaine Formation on the north side of the Anadarko basin (figs. 2 and 3). The Blaine is 80 to 100 feet thick (Fay, 1964) and consists of three minable beds of white and light-gray gypsum, each 10 to 30 feet thick separated by shale layers 10 to 20 feet thick (fig. 4). A thin dolomite 0.5 to 2 feet thick commonly underlies each of the gypsum beds. Ham (1962) discusses the economic geology of gypsum and anhydrite in Blaine County, which has been historically the major producing area in the northwest region and, for that matter, in the entire State. Other important gypsum studies in the region include those of Blaine County (Fay, 1962), Harper County (Myers, 1959), and Woods County (Fay, 1965).

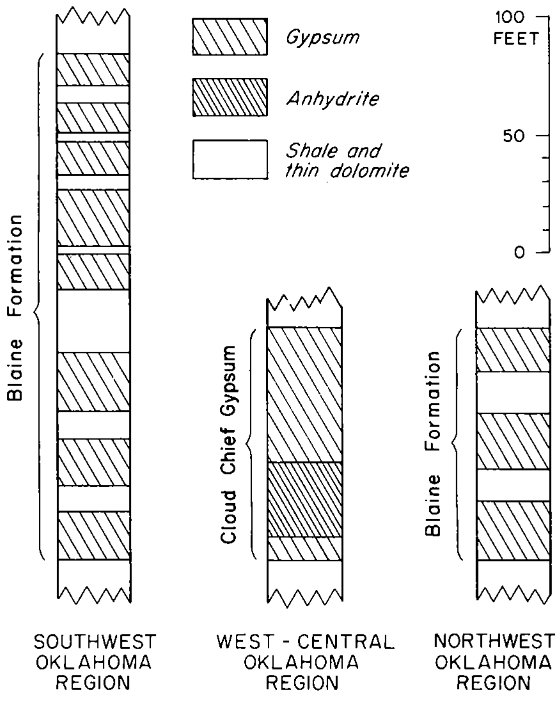


Figure 4. Columnar outcrop sections of Permian gypsum units in western Oklahoma.

Gypsum purity in the northwest region is slightly higher than in other regions. The stone in Blaine County is generally 96 to 99 percent pure gypsum, based upon 10 analyses reported by Ham (1962), and analyses of these same beds elsewhere in the region proved a similar high purity. Principal impurities are calcium and magnesium carbonates ($CaCO_3$ and $MgCO_3$), which together make up 0.3 to 2 percent of the rock, and silica (SiO_2) and alumina (Al_2O_3), which together make up 0.1 to 0.9 percent of the rock. The amount of anhydrite ($CaSO_4$) finely disseminated in gypsum ranges from 0.3 to 1 percent. Anhydrite is locally present as thin beds and lenses at the outcrop, but in most places it has been completely hydrated to gypsum except where more than 30 to 40 feet of strata overlie the sulfate bed.

Gypsum reserves in the region are estimated to be just under 17 billion short tons (table 1). Most of these reserves are in the western part of the region, in Harper and Woodward Counties, where the gypsum beds are thickest and crop out over vast areas.

Four companies are currently mining stone in the region and three operations are in Blaine County. U.S. Gypsum Company, the largest in the State, is located at Southard; Universal Atlas Cement Company is 5 miles northeast of Watonga; and Walton Gypsum Company is 1 mile northeast of Southard (fig. 5). The fourth operation, Schweitzer Gypsum Company, is located in northwest Canadian County.

Gypsum mining in Blaine County began early because these high-purity deposits are adjacent to railroads and are closer than others to market areas in central and eastern Oklahoma, as well as in much of Missouri, Arkansas, and Louisiana. The two beds being worked in the county are the Shimer and Nescatunga Gypsum Members, each of which is 10 to 15 feet thick (fig. 6). Mining is by conventional open-cut methods: shale overburden is scraped away, gypsum is then blasted by explosives set in both vertical and horizontal shot holes (horizontal holes are drilled near the base of the quarry, just above the underlying dolomite), and broken stone is then hauled to the nearby plant. The eroded edge of a gypsum bed is generally too weathered and contains too many clay-filled solution cavities for economic recovery of high-purity gypsum; thus, the thin outer margin is not quarried.

Thickness of shale overburden at any location is critical to the economics of mining these gypsum beds, because this determines the amount of scraping that must be done to expose the gypsum. Shale-overburden thickness also influences the distribution of anhydrite within the gypsum bed, and this is important because the presence of more than 5 to 10 percent anhydrite in gypsum makes the rock unusable for most purposes. Hydration of anhydrite to gypsum is generally incomplete in Blaine County where more than 30 to 40 feet of shale overlies and protects the bed. Thus, gypsum can generally be mined along a bench 100 to 700 feet wide before encountering residual anhydrite layers beneath thick overburden.

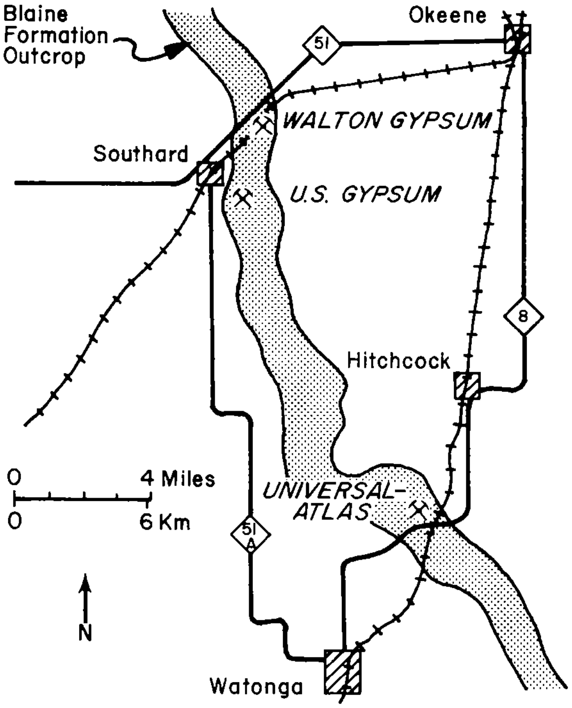


Figure 5. Map showing location of gypsum quarries and gypsum outcrops in Blaine County.

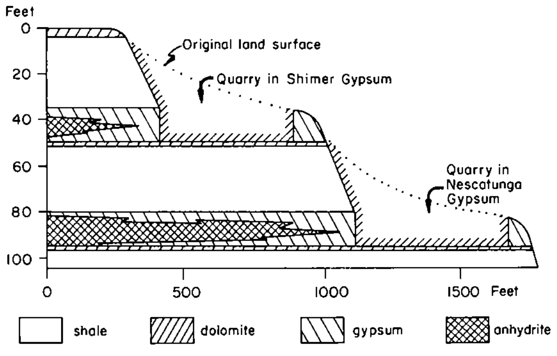


Figure 6. Schematic cross section showing relation between topography, lithology, and quarrying in Shimer and Nescatunga Gypsum Beds of Blaine Formation in Blaine County.

Gypsum mined in the county is used in the following ways: U.S. Gypsum uses most of its gypsum to make wallboard (sheetrock), although some is made into laths, sheathing, and various plasters (Westphal, 1978); Universal Atlas uses all its stone as a retarder in portland cement; and Walton Gypsum sells crushed gypsum as a retarder in portland cement and ground gypsum as a soil conditioner.

SOUTHWEST OKLAHOMA REGION

Gypsum deposits in southwest Oklahoma comprise outcrops of the Blaine Formation on the south side of the Anadarko basin and in the Hollis basin (figs. 2 and 3). The Blaine Formation in this region is 150 to 200 feet thick (Johnson, 1967) and consists of 5 to 8 beds of minable gypsum, each 10 to 30 feet thick (fig. 4) and white to light gray. Gypsum beds are interbedded with shales 2 to 30 feet thick, and each gypsum is directly underlain by 0.5 to 5 feet of dolomite. Scott and Ham (1957) published a report dealing with the economic geology of gypsum and anhydrite in southeast Beckham County, and Johnson (1964) described Republic Gypsum Company's operation at Duke in western Jackson County.

Gypsum beds are 95 to 99 percent pure, based on 7 published (Scott and Ham, 1957) and 102 unpublished analyses of all beds throughout the region. Calcium and magnesium carbonate commonly make up 0.5 to 2 percent of the rock, and silica and alumina, 0.3 to 0.8 percent. Disseminated anhydrite in most outcrops and quarries makes up 0.5 to 1.5 percent of the rock. Beds of anhydrite are rarely found at the outcrop, and in most core tests they are lacking at depths shallower than 75 to 100 feet below ground level.

Reserves in the region are estimated at slightly over 17 billion tons (table 1). Reserves are greatest in southwest Beckham County and Harmon County, where individual beds are thickest and where an aggregate thickness of 75 feet of gypsum can be bench stripped while removing 3 or 4 thin units of shale and dolomite.

Republic Gypsum is the only company to mine the large reserves of gypsum in southwest Oklahoma. Three gypsum beds being worked by Republic are in the upper part of the Blaine Formation, in the Van Vacter Member (fig. 7). Gypsum beds in the Van Vacter Member are numbered consecutively upward, and thus the mined units are beds 1, 2, and 4 (bed 3 is thin or absent in the Duke area). Bed 1, which is 9 feet thick, is overlain successively by 9 feet of shale, 18 feet of gypsum (Bed 2), 9 feet of shale, and 9 feet of gypsum (bed 4). Most of the mining is done in the thick bed 2, which is 17 to 21 feet thick in most of southwest Oklahoma.

Open-cut mining is carried out by Republic Gypsum. The quarry was opened in bed 2 after removing 3 to 10 feet of overburden with a scraper. As the pit was enlarged, a small amount of bed 4 was worked in a bench-stripping operation, and eventually the pit was dug deeper to develop bed 1 (fig. 7). Each of the gypsum beds locally contains irregular clay-filled solution cavities and sinkholes, and this presents problems in mining and in maintaining uniform purity in the feed for the company's wallboard plant. An average 1:1 ratio of gypsum to shale is anticipated for most of the 440 acres of company-owned land. Original reserves reported by the company were 12.5 million tons of gypsum (Johnson, 1964).

Republic Gypsum is Oklahoma's third-largest producer of gypsum and second-largest producer of wallboard. Since opening its plant in 1964, the company has steadily increased gypsum production and presently accounts for about 15 percent of the State's annual output. Its annual production has ranged from 120,000 to 166,000 tons of gypsum.

WEST-CENTRAL OKLAHOMA REGION

The west-central region consists of outcrops of the Cloud Chief Gypsum, which is present only in the central part of the Anadarko basin (figs. 2 and 3). The Cloud Chief is a single bed of massive sulfate rock with a full thickness of approximately 100 feet. The top part of the bed is commonly eroded, leaving some 20 to 75 feet of sulfate rock forming hills in most of the region. The lower part of the sulfate bed, up to 40 feet locally, is anhydrite, and the top 25 to 70 feet is massive gypsum (fig. 4). The Cloud Chief Gypsum is overlain and underlain by

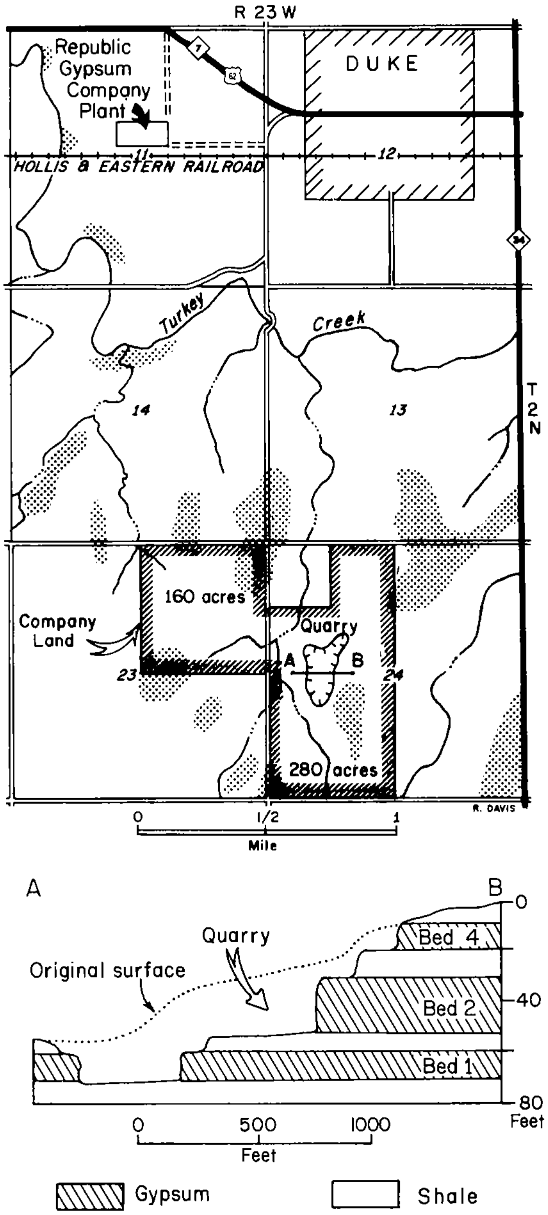


Figure 7. Map of Duke area (above) showing location of Republic Gypsum Company quarry and wallboard plant. Exposures of Blaine gypsum indicated by stipple. Below is schematic cross section through main quarry.

red-bed shales and sandstones, and the gypsum bed grades laterally into similar clastic units to the west and northwest. Gypsum and anhydrite resources at the north end of the region were evaluated by Ham and Curtis (1958), and outcrops of the Cloud Chief Gypsum in Custer County were mapped by Fay (in preparation). Gypsum is typically white or pink and is a medium-grained granular gypsum or finely crystalline alabaster.

Gypsum purity in the northern part of the region is generally 90 to 97 percent (Ham and Curtis, 1958), but in the central and southern part published (Johnson, 1965) and unpublished analyses show a gypsum purity of 95 to 98 percent. Calcium and magnesium carbonate are typically 1 to 7 percent of the rock, whereas silica and alumina range from 0.4 to 4 percent; gypsum with the highest impurities is restricted to the northern edge of the region. Anhydrite beds in the Cloud Chief generally are 86 to 92 percent calcium sulfate, with gypsum making up 2 to 6 percent of the rock.

Reserves are estimated to be just under 14 billion tons (table 1), with the greatest reserves being the purer stone in Washita County where the Cloud Chief Gypsum is at or just below the surface in some 200 square miles.

Two companies are currently mining gypsum in west-central Oklahoma: Temple Gypsum Company, the State's second-leading gypsum producer, located at Fletcher in Comanche County, and Harrison Gypsum Company, south of Cement in Caddo County. A single massive bed of rock gypsum 30 to 60 feet thick is mined at both sites by open-pit quarrying methods.

At Temple Gypsum (previously known as Texas Gypsum Company), the stone is mined in 2 benches: an upper bench 20 feet thick and a lower bench 35 feet thick, or down to the top of anhydrite where it is present (fig. 8). A system using conveyer belts, a screening station, and crushers was installed early in 1967 to expedite materials handling. The quarry superintendent manages all operations with the help of two men; one man operates the control tower, and the other works in the quarry and loads the trucks. Mechanization enabled this three-man crew to produce about 14.2 tons of gypsum per man-hour (t/mh) in 1968, compared to a State-wide average of 6.9 t/mh (Johnson, 1970).

Clays and soils that fill solution cavities and crevices are a problem at both quarries: the clays cannot be removed completely during the mining, crushing, and screening operations, and thus the purity of the product is reduced from about 97 percent for rock gypsum to 93–95 percent for the plant feed. Anhydrite is not present in the Harrison Gypsum quarry, but it is present as a residual lens 3 to 10 feet thick in the lower part of the Temple Gypsum deposit.

The top of the gypsum is eroded at the Temple and Harrison quarries and at all nearby outliers, so the original thickness of the sulfate bed in this area is unknown. Forty miles to the northwest, where the top of the bed is not eroded, the unit is 100 to 120 feet thick and crops out extensively (Ham and Curtis, 1958).

PRESENT AND POTENTIAL USES

Most of the gypsum presently mined in the United States is used in the construction industries. More than 65 percent of the annual production in 1974 went to the

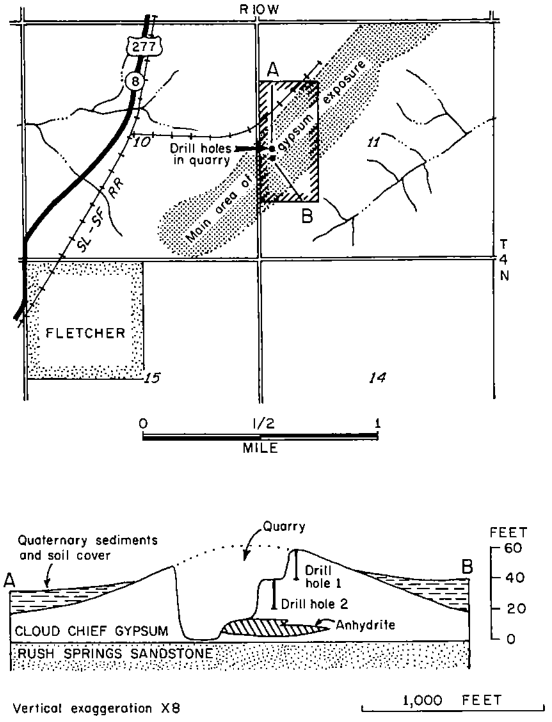


Figure 8. Map of Fletcher area (above) showing main gypsum exposures and limits (hachured lines) of Temple Gypsum Company property. Below is schematic cross section through main quarry.

manufacture of wallboard and plaster products, and most of the remainder was used as a retarder in cement (U.S. Bureau of Mines, 1976). The remaining prime use was as a soil conditioner for alkaline soils. The seven quarries in Oklahoma produced about 1.0 to 1.4 million tons of crude gypsum each year since 1971, making the State the 5th ranking producer behind California, Michigan, Iowa, and Texas.

Total United States needs for crude gypsum in 1974 were 19.4 million tons, of which 12.0 million tons were from domestic mines and 7.4 million tons were imported, primarily from Canada, Mexico, Jamaica, and Dominican Republic. The forecast for gypsum demand indicates that by the year 2000 the United States will require 26 to 56 million tons from domestic and imported sources (U.S. Bureau of Mines, 1975); this estimate is based solely on construction and agricultural needs and does not consider potential uses in the chemical industries.

Oklahoma gypsum is used primarily in the manufacture of wallboard, with U.S. Gypsum, Temple Gypsum, and Republic Gypsum being the principal producers. The two wallboard plants in the State are operated by U.S. Gypsum and Republic Gypsum, whereas Temple Gypsum supplies wallboard plants in Dallas, Texas, and Memphis, Tennessee. Other important uses for Oklahoma gypsum include retarder for portland cement and soil conditioner.

In addition to the standard uses in construction, gypsum from all three Oklahoma regions is valuable for use as a filler or extender. The high purity and good color of the stone make it useful in certain wood, paint, textile, paper, chemical, and food products.

Considerable research has been carried out in recent years on the use of gypsum and anhydrite as a source of sulfur, sulfuric acid, or ammonium sulfate, with coproduct production of lime and cement. Pure gypsum contains 44.6 percent SO_3, and pure anhydrite contains 58.8 percent SO_3. This research was spurred in the middle 1960's when sulfur supplies dropped well below demand and prices rose to more than $40 per long ton in 1968. But additional production from the west Texas bedded-sulfur deposits since 1969 and the subsequent surge of sulfur extracted from sour gas production in the Gulf Coast and in Canada have more than satisfied present market demands, and the price of sulfur has dropped below the cost of recovering sulfur from gypsum or anhydrite. With changes in market conditions, however, regions with large reserves of high-purity gypsum and anhydrite may once again be evaluated as a source for sulfur and sulfur products.

ECONOMIC DEVELOPMENT

Major gypsum resources of the United States are located in the western half of the country (fig. 9), and deposits on the east side of the Permian basin are among the closest of these major deposits to industrial and population centers of the East. Most deposits in the eastern half of the country are relatively small or are of only moderate purity. The Indiana and Illinois deposits are generally more than 500 feet underground, 5 to 15 feet thick, and typically 80 to 90 percent pure. New York deposits are only 4 to 6 feet thick and are being mined underground to a depth of 100 feet. Only the Michigan and central Iowa deposits are high-purity and thick (10 to 30 feet) units that constitute moderately large reserves.

Gypsum is produced in these eastern areas, however, because it is close to markets, and the higher mining and production costs are offset by lower transportation costs. The assigned value of crude gypsum, f.o.b. mine, in 1974 (U.S. Bureau of Mines, Minerals Yearbook) was $3.50 to $4.50 per ton in most western states and $4.50 to $6.00 per ton in most eastern states; assigned value in New York State was $8.08 per ton. The assigned value of crude gypsum in Oklahoma, f.o.b. mine, was $4.59 per ton in 1974.

Most of the gypsum now mined in Oklahoma is consumed or processed within the State for wallboard, plaster, cement retarder, or soil conditioner, and about 15 percent of the crude gypsum is shipped out of state for processing. Potential market areas for Oklahoma crude or processed gypsum include the large interior and central United States region, east and northeast of the Permian basin, in those places where gypsum is totally lacking or where high-purity stone is needed (fig. 9). Owing to the low cost of ocean transportation, gypsum used in East Coast and Gulf Coast regions will probably continue to be supplied by

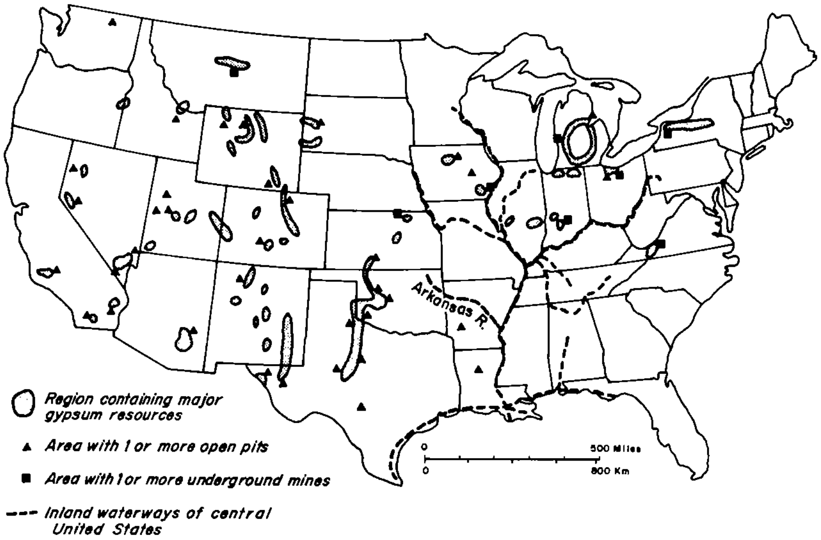


Figure 9. Gypsum resources and active mines and quarries in the United States during 1976. Modified from Withington (1962).

imports from Canada and Jamaica.

Factors favoring use of Oklahoma gypsum are its exceptional purity, vast reserves, and low mining costs. Current production capacity of existing mines is sufficient for construction needs in Oklahoma and immediately surrounding areas, but expansion of markets to the east or the development of new uses can cause the demand to increase sharply.

REFERENCES CITED

Fay, R. O., 1962, Stratigraphy and general geology of Blaine County, *part 1 of* Geology and mineral resources of Blaine County, Oklahoma: Oklahoma Geological Survey Bulletin 89, p. 8–99, 194–258.

______1964, The Blaine and related formations of northwestern Oklahoma and southern Kansas: Oklahoma Geological Survey Bulletin 98, 238 p.

______1965, Geology and mineral resources of Woods County, Oklahoma: Oklahoma Geological Survey Bulletin 106, 189 p.

______in preparation, Geology and mineral resources of Custer County, Oklahoma: Oklahoma Geological Survey Bulletin.

Ham, W. E., 1962, Economic geology and petrology of gypsum and anhydrite in Blaine County, *part 2 of* Geology and mineral resources of Blaine County, Oklahoma: Oklahoma Geological Survey Bulletin, 89, p. 100–151.

Ham, W. E., and **Curtis, N. M.**, 1958, Gypsum in the Weatherford-Clinton district, Oklahoma: Oklahoma Geological Survey Mineral Report 35, 32 p.

Johnson, K. S., 1964, New gypsum plant to open at Duke, Jackson County, Oklahoma: Oklahoma Geology Notes, vol. 24, p. 3–8.

______1965, Gypsum quarry operating at Fletcher, Comanche County, Oklahoma: Oklahoma Geology Notes, v. 25, p. 78–81.

______1967, Stratigraphy of the Permian Blaine Formation and associated strata in southwestern Oklahoma: Illinois University, unpublished Ph.D. dissertation, 247 p.

______1969, Mineral map of Oklahoma (exclusive of oil and gas fields): Oklahoma Geological Survey Map GM-15, scale 1:750,000.

______1970, Rock handled efficiently at Texas Gypsum Company quarry, Fletcher, Oklahoma: Oklahoma Geology Notes, vol. 30, p. 118–120.

______1972, Gypsum and salt resources of Oklahoma: Industrial Minerals, no. 62, November, p. 33–39.

Jordan, Louise, and **Vosburg, D. L.**, 1963, Permian salt and associated evaporites in the Anadarko basin of the western Oklahoma-Texas Panhandle region: Oklahoma Geological Survey Bulletin 102, 76 p.

Myers, A. J., 1959, Geology of Harper County, Oklahoma: Oklahoma Geological Survey Bulletin 80, 108 p.

Scott, G. L., Jr., and **Ham, W. E.**, 1957, Geology and gypsum resources of the Carter area, Oklahoma: Oklahoma Geological Survey Circular 42, 64 p.

Snider, L. C., 1913, The gypsum and salt of Oklahoma: Oklahoma Geological Survey Bulletin 11, 314 p.

U.S. Bureau of Mines, 1975, Mineral facts and problems: U.S. Bureau of Mines Bulletin 667, 1259 p.

______1976, Minerals yearbook 1974: U.S. Bureau of Mines, vols. I and II.

Westphal, E. B., 1978, Gypsum production and land reclamation by U.S. Gypsum Company at Southard, Oklahoma: Oklahoma Geological Survey Circular 79, p. 20-24.

Withington, C. F., 1962, Gypsum and anhydrite in the United States (exclusive of Alaska and Hawaii): U.S. Geological Survey Mineral Investigation Resources Map MR-33.

ENERGY USAGE IN THE GYPSUM INDUSTRY

E. Robert Kiehl[1]

Abstract—In the early days of the United States, gypsum was most commonly used for the manufacture of plasters with energy being used for quarrying, grinding, and calcining of gypsum rock. With the dramatic switch to gypsum-drywall construction after World War II, the energy usage per ton of rock processed increased more than threefold, and with the rapid growth of the construction industry, the total energy consumption in gypsum-board production alone increased eightfold during the period from 1940 to 1973. The gypsum industry was one of the first to recognize the need for energy conservation and has voluntarily reported its progress to the Federal Energy Administration for the past several years. Efficiencies in the use of energy have resulted in decreasing the unit consumption an estimated 10 percent during the past six years. Improved combustion efficiencies, optimum operating conditions, more liberal use of insulation, and heat recovery will all contribute to the gypsum industry's goal of using less energy. Gypsum products today are vital to over 85 percent of new housing construction in the United States.

BACKGROUND

Gypsum plaster (plaster of paris) has been used in the construction industry for centuries. The energy used in the early days of gypsum production was for calcining, which was crudely carried out. Rock gypsum was dug by hand, and the roughly broken pieces were calcined over an open bonfire. As the coarse stucco flaked off, it was then collected and transported to the construction site in bulk where it was then mixed with water and applied by hand. The finished plaster was slowly air dried. You can still see this process carried out today in such places as the outskirts of Tehran, Iran.

Plasters have been used for construction in the United States since the arrival of the first colonists. There are a number of calcining plants still standing that were constructed more than a century ago. One of these is at Celotex's Fort Dodge, Iowa plant.

Plasters continued in use with plaster lath eventually replacing wood and metal lath as the technology of controlling and retarding plaster set was developed. Plaster-lath production eventually led to the use of drywall for temporary military barracks during World War II, and, during this same period, the use of gypsum board for walls and roof sheathing spread through all sections of the United States and overseas.

The returning servicemen helped to establish an enormous market for new housing and set the stage for the surge in the use of drywall—a fire-resistant product that was unique because the process provided substantial construction time saving. Early gypsum drywall could be installed, finished, and ready for decoration in less than a week. Today there are systems which can be completely installed and finished in one day.

In the mid-1940's, gypsum drywall began a spectacular rise in use in the homebuilding industry in the United States. Without the development of the drywall industry, homebuilding could not have grown to its present size and importance to the American economy, where it is now used in over 85 percent of residential construction.

The processing of rock gypsum to gypsum board is based on calcination of the rock gypsum to stucco and its rehydration into the original rock form within a confined shape with some alterations to improve the basic characteristics.

Basic Reversable Reaction

$$\begin{array}{ccc} \mathrm{CaSO_4 \cdot 2H_2O} \longleftrightarrow & \mathrm{CaSO_4 \cdot \tfrac{1}{2}H_2O} & + \ 1\tfrac{1}{2}\mathrm{H_2O} \\ \downarrow & \downarrow & \downarrow \end{array}$$

Rock gypsum	Stucco	Water
Land plaster	Plaster of paris	
Gypsum-board core	Calcined gypsum	
	Molding plaster	
	Dental plaster	

Gypsum board is therefore a core sandwiched between two pieces of paper. The core is essentially stucco in which additives

---

[1] The Celotex Corporation, Tampa, Florida.

such as starch, paper pulp fiber, accelerator, foam, water, and dispersing agents are added. Each ingredient performs a definite function in the characteristics of the final product, and each has a relationship to the energy consumed in the process itself. Stucco and water alone account for approximately 95 percent of the gypsum-board core.

The average gypsum-board plant contains two major processing operations, namely, calcining (rock to produce stucco) and the board manufacturing.

In terms of energy required, the original production of plasters consumed only about 30 percent of the energy needed to produce the equivalent quantity of modern drywall today. Energy consumed in the major processing steps of gypsum-wallboard production are:

	Energy Consumed (in million Btu/thousand square feet of gypsum board)
Crushing & grinding	0.1
Calcining	1.0
Board drying	2.0
Total	3.1

CALCINING

The early calciners in the United States were usually batch kettles primarily using wood or coal as fuel. The mechanical energy needed for the process equipment was supplied by line shafts operated by steam from coal-fired boilers. Most stucco in the United States is still produced by batch calcining because it results in a quality product.

The batch-kettle process relies on heat transfer from the combustion chamber and from the flues as the gases pass through the kettles to the stacks. Since the heat transfer from the gases is through the walls of the kettle and the flues, the overall heat-transfer efficiency is low.

The fuels used in the calcining process gradually changed from wood and coal, to fuel oil, then to various forms of manufactured gas, and finally to natural gas, the most widely used fuel today.

Energy consumption today is being carefully controlled and reduced in the batch-kettle process by:

(1) improving the combustion efficiency with burner modification and controlling the excess oxygen in the flue gases;

(2) improved control of the calcining process with a slight lowering of the calcining temperature, and improved agitation of the stucco;

(3) use of additional insulation;

(4) heat recovery from the hot flue gases used for such items as preheating the air or preheating the rock.

Continuous calcining with its higher fuel efficiency has had some success for a number of years, but because of current fuel costs, a number of continuous calcining processes are coming into wider acceptance in the industry. Batch kettles can also be converted to continuous calcining but do not significantly contribute to higher fuel efficiencies. Most of the continuous calciners operate on a direct-fired basis with the ground gypsum intimately mixed with flue gases, providing for a significantly higher fuel efficiency. The major drawback with most continuous calciners has been the tendency to overheat or "burn" a portion of the ground gypsum, correspondingly reducing its usefulness in producing the final wallboard products. Because of the current economic impact of increasing fuel costs, continuous calciners are finding wider acceptance, and today there are a number of new ideas for continuous calcining that do not adversely affect the gypsum-board product quality.

Because of repetition in seasonal energy shortages during recent years, most calcining plants are now equipped to use two or more fuels. With today's rapidly increasing fuel costs, more frequent periods of fuel shortages, and the need to conserve energy, fuel consumption in calcining will of necessity be further reduced in the foreseeable future—probably by an estimated 20 percent during the next five years.

GYPSUM WALLBOARD

After completion of the calcining process, its product, stucco, is conveyed from the calciners to the gypsum-board plant for use in the core of the gypsum board. Stucco, the primary board core ingredient, is thoroughly mixed with the other ingredients such as starch, pulp, fiber, accelerator, dispersants, foam, and water (used for both the rehydration process and to facilitate the mixing operation). Each ingredient performs a definite functon in board quality and directly or indirectly is related to the fuel consumption.

All of the core components are fed simultaneously to a pin mixer and are thoroughly mixed and discharged as a wet slurry between a continuously moving web of face and back paper. The board is fed onto a continuous belt and allowed to set as it progresses to the knife in preparation for the board-drying process.

The board-drying operation is the largest single consumer of energy in the gypsum industry, using almost two thirds of the total. More than 90 percent of the energy used in board drying is for the removal of the excess water. The incentives for energy conservation at this point of the process are therefore obvious, and it should again be remembered that board drying as it is practiced today was virtually nonexistent before 1940.

Although the first gypsum-wallboard dryers were designed for continuous processing, they were indirectly heated, using steam generated from coal-fired boilers. The steam helped to limit the temperature in the dryer preventing excessive temperatures and recalcination, but overall fuel efficiency using this system was relatively low and, therefore, left a lot to be desired. Heat-efficiency losses occurred in the firebox, in the heat transfer from the firebox to the steam side of the boiler, from the steam lines to the dryer, from the steam tubes in the dryer, and from the air used for water evaporation. Overall energy consumption of more than 6,000,000 Btu per thousand square feet of board was common with the first board dryers.

With the surge in product demand during the last half of the 1950's, gypsum plants were hard pressed to produce enough gypsum board. In order to meet this demand quickly, and with the help of improved process technology, board-drying capacities were increased by the addition of directly fired supplementary heating units. These units generally increased dryer temperatures and, as a bonus, resulted in about 40-percent reduction in the total Btu energy consumption. After this initial dryer operation success, there was a quick conversion to direct-fired dryers, which are now almost universally used in the gypsum industry.

The first direct-fired units used no. 2 oil and later no. 6 oil. Some soon used local manufactured gas, and, as natural gas became increasingly available, there was a swift conversion to this clean fuel. Today, natural gas is the primary fuel used in most dryers.

Major considerations involved in wallboard drying are:

(1) total heat requirement (Btu);
(2) operating-temperature limitations, zone by zone;
(3) time available for the drying operation controlled by the dryer length and the speed of the forming line;
(4) the amount of water to be evaporated.

Other considerations are:

(5) air-feed temperature, velocity, and turbulence;
(6) the pressure within the dryer, and atmospheric pressure;
(7) the humidity of the combustion air and the humidity within the dryer.

Energy consumption is currently being reduced in the board-drying operation by a number of significant factors, including:

(1) reduction of combustion losses, by increasing combustion efficiency by operating with the lowest possible excess-air ratio (The fuel must be thoroughly mixed with the combustion air in the primary combustion zone where the temperatures are sufficient to ensure complete combustion.);
(2) control (reduction) of the amount of excess water used in the mix, consistent with maintaining a high quality board core;
(3) reductions in gypsum-board weights (using less stucco from the calcining operation and less water for the slurry formation);
(4) recovery of heat from the stack gases (This heat may be used to preheat the combustion air, used for space heating, or other areas where improved economics are possible.);
(5) more liberal use of insulation.

Today a typical energy-reduction program in the board-manufacturing section at a gypsum plant would include:

	Energy Reduction
Controlling excess water usage	8%
Improved combustion efficiency	2%
Controlling and lowering board weights	2%
Heat recovery	4%
Insulation and misc. improvements	2%
Total energy reduction	18%

With curtailments of varying fuel supplies, the energy system for today's typical gypsum-wallboard plant might contain:

(1) a board dryer normally burning natural gas as the primary fuel (supplied on an interruptable service basis and cut off during much of the winter);
(2) standby propane storage for quick conversion during interruptions (increased storage capacity year by year as the natural gas supplies continue to dwindle);
(3) board-dryer combustion chambers capable of burning fuel oil in addition to gas and propane;
(4) standby oil system for both the calcining and the board-drying process.

SUMMARY

With the dramatic switch to gypsum-drywall construction after World War II, the unit energy usage per ton of rock increased threefold. This was primarily the result of the addition of the board-drying process, which was not necessary with plasters. As construction increased, particularly housing using gypsum board, the energy consumption for gypsum-board production alone increased eightfold during the period from 1940 to 1973 as shown in the table:

Gypsum Industry Energy

Year	Gypsum production, million ft.	Trillion Btu (10^{12} Btu)
1973	15,159	31.7
1972	14,362	31.1
1971	11,939	26.6
1970	9,741	22.1
1960	7,982	18.1
1950	5,810	13.2
1940	2,039	4.1
1930	578	1.3

During 1974, when the first serious shortage developed in energy supplies, the gypsum industry was one of the first industrial groups, that agreed to voluntarily adopt formal energy-management programs and report their achievements to the U.S. Department of Commerce, Office of National Energy Conservation Program. The Gypsum Association and its members also participated and cooperated in a detailed energy study carried out by the Battelle Institute that is now being used as the basis of the FEA (Federal Energy Administration) energy-efficiency-reduction target.

The gypsum-products industry has been classified by the Department of Commerce as a family member of the stone, clay and glass products industry SIC 32 (Standard Industrial Classification). Gypsum products are one of the smaller segments of this industry group, accounting for only about 3.5 percent of the total energy used but more than 90 percent of the gypsum-board products are produced by five companies, and these five companies are listed among the 50 largest energy consumers in the stone, clay and glass group.

Gypsum Association members produce more than 90 percent of the gypsum products in the United States and today operate 73 gypsum plant facilities, 25 gypsum surface-mining operations, 13 underground mining operations.

The Energy Policy and Conservation Act of 1975 (EPCA) has directed the adminstration of FEA to exempt mandatory reporting of those who are already fully participating in a voluntary program. The gypsum industry, which is classified in this voluntary group, has shown the following progress during the 1970's:

Gypsum Industry—Unit Energy Consumption

Year	Total energy consumed in million Btu per thousand $ft.^2$ ½-inch board	Energy reduction using 1970 as base (%)
1970	3.24	—
1971	3.19	2.6
1972	3.09	4.5
1973	2.99	7.7
1974	2.99	7.7
1975	2.96	8.2
1976	2.90	10.6

Our future industry contribution to energy conservation may be less than others because of our high usage and the actions already taken which have resulted in substantial energy reduction.

Housekeeping items such as maintaining insulation, shutting down equipment not in use, elimination of all wasteful use, and just plain understanding the process are all important to continued energy reduction. Probably more important than energy use itself is improvement in the efficiency of energy production. The greatest promise for reducing industrial energy is increasing the usefulness of the Btu's available.

The overall efficiency of the work in industrial fuels is currently under 20 percent. Increasing the efficiency to 30 percent would do wonders in conservation of energy. The cheapest and most abundant new source of energy, therefore, lies in increasing its useful work. Higher energy prices will hasten the process.

GYPSUM PRODUCTION AND LAND RECLAMATION BY U.S. GYPSUM COMPANY AT SOUTHARD, OKLAHOMA

EDWARD B. WESTPHAL[1]

Abstract—One of the purest gypsum deposits in the United States is located in northwest Oklahoma about 90 miles northwest of Oklahoma City. Gypsum beds of the Blaine Formation (Permian) are each 10 to 15 feet thick and 97 to 99 percent pure; they are being quarried by four companies in the area. Most of the stone mined by U.S. Gypsum Company is calcined for the manufacturing of wallboard and special plasters, but some of the crude gypsum is marketed for cement manufacture and for use as soil conditioner. Reclamation of the mined lands at Southard, Oklahoma, has been carried out since 1968, and the company is now involved in a cooperative program of land revegetation to aid in erosion control, provide for wildlife, and for beautification.

INTRODUCTION

The Southard plant of the U. S. Gypsum Co. is probably the most diversified gypsum operation in the world. Located in the north end of Blaine County (fig. 1), the quarry is on the outcrop of the Blaine Formation (Permian) consisting of three principal gypsum beds that cap the Cimarron Gypsum Hills. These hills form a narrow band of escarpments and badlands between the Cimarron and North Canadian Rivers. Mining is done in the two upper beds, the Shimer and Nescatunga Gypsum beds, each of which is 10 to 15 feet thick and is 97 to 99 percent pure (fig. 2). Approximately 15 million short tons of rock have been extracted by various operations in the county, and reserves are conservatively estimated at 280 million tons (Ham, 1962).

The U. S. Gypsum Co. began operations about 1905 in Oklahoma near the south end of the Cimarron Gypsum Hills, west of Okarche. In 1912 the present operation was acquired from George Southard and Son with plans to manufacture white gypsum products from the abundant, exceptionally high-quality gypsum. Keeping pace with the changes in technology and market demands, the plant has developed into a compact and integrated manufacturing unit producing 175 finished materials for shipment to over 3,500 customers around the world.

The basic raw material is a rock consisting entirely of the mineral gypsum ($CaSO_4 \cdot 2H_2O$), in which approximately 20 percent of its weight is chemically combined water. A typical chemical analysis of gypsum in the Blaine Formation at Southard reveals the exceptional purity of this high-grade rock:

Chemical Analysis

Constituent	Percentage
Water, H_2O	20.10
Calcium oxide, CaO	32.40
Sulphur trioxide, SO_3	45.30
Magnesium oxide, MgO	0.32
Silica, SiO_2	0.56
Iron & aluminum oxides, R_2O_3	0.53
Carbon dioxide, CO_2	0.79
	100.00

Undesirable impurities are at minimum amounts. These include lead, which is present in concentrations of less than 5 ppm, and arsenic, present in concentrations of less than 0.025 ppm.

Gypsum is unique in that by calcination (removal of water by heating) it is converted to plaster of paris (partial water removal) or to an inert filler (total water removal). This simple process is the foundation of all the methods, formulations, and complicated developments that make up the Southard product line.

MINING AND PRODUCTION

The first part of Southard operations is the quarry, which involves 3,800 acres and is almost 7½ miles long. Overburden, up to 35 feet thick, consisting of sands, clays, and

---

[1] U.S. Gypsum Company, Southard, Oklahoma.

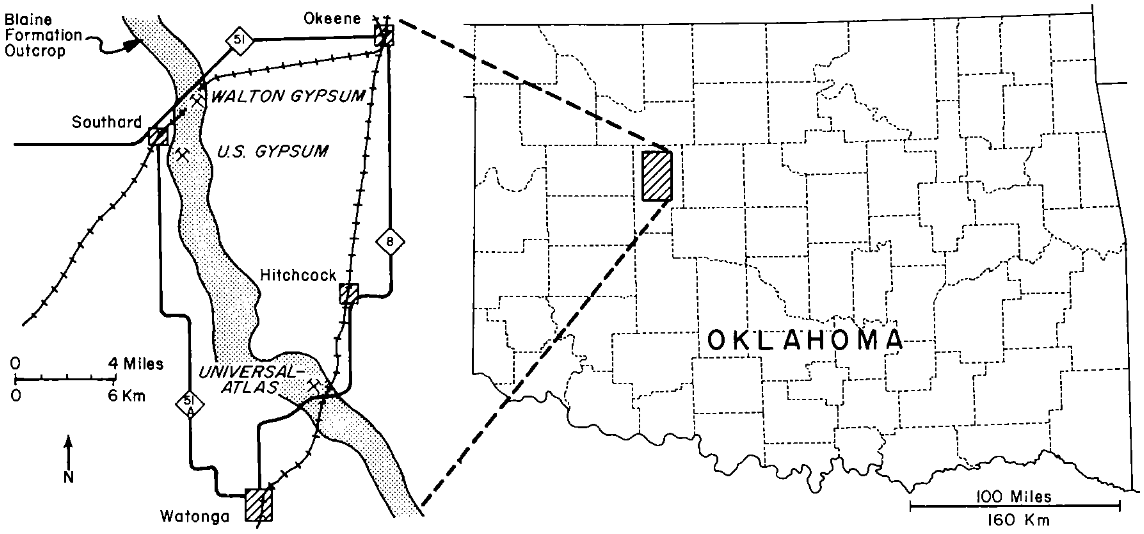


Figure 1. Map showing location of U.S. Gypsum Company and other gypsum producers in Blaine County, northwestern Oklahoma.

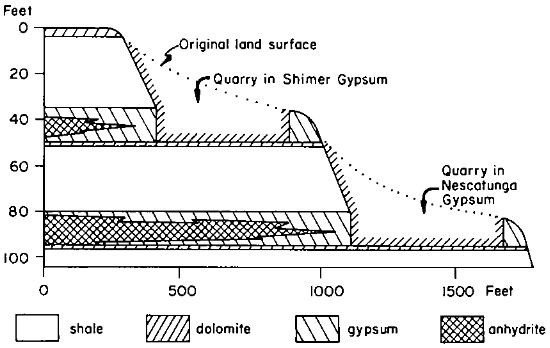


Figure 2. Schematic cross section showing relationship between topography, lithology, and quarrying in Shimer and Nescatunga Gypsum beds of Blaine County (after Johnson, 1972)

resistant shales, is removed from the horizontal gypsum beds by large mobile earthmoving equipment. The rock surface is further cleaned by scraping to expose the clean white gypsum. The rock is drilled, blasted, and loaded into 35-ton-capacity trucks for haulage to the plant where it is crushed and screened to a graded size either for shipment or for use in the plant.

In successive mill operations, the white rock (also called "terra alba") is finely ground using Raymond mills, calcined in large kettles, reground in Entoletors or tube mills, and sized by screens or air separation. Fineness varies from minus 100 mesh to low-micron range, dependent on use or product base.

Two types of kettles are used: a batch-type kettle, which holds approximately 18 tons of crude gypsum and takes 2½ hours per batch to cook, and a continuous kettle, which receives about 12 tons of gypsum and discharges about 10 tons of plaster per hour.

The kettle produces plaster of paris by the traditional "frying," or cooking method, and, when recombined with water, the plaster will reform as the "beta" or selenitic crystal. Under 500-power magnification, dark streaks and voids can be seen in the light fluffy particle indicating the escape route of the chemically combined water. Normal consistency of this plaster is achieved by adding 65 parts by weight of water per 100 parts of plaster.

A second method of calcination in the mill is by steam calcination, which includes both bulk and slurry processes. In the bulk process, sized gypsum is pressure cooked in autoclaves under controlled conditions, ground in impact mills, reground in ceramic ball mills and Entoletors, and then is screened for proper size distribution.

In the slurry Hydrocal process, ground crude gypsum is cooked in an acid-water solution that modifies the crystal much the same as the bulk Hydrocal process. The finished material is then filtered, dried, ground, and screened.

The Hydrocal processes produce "alpha" gypsum that, when recombined with 35 to 42 parts of water per 100 parts of gypsum, gives a very dense, high-strength product.

Crystals are short and stubby cylinders, totally different than the long needle or micaceous varieties of gypsum.

A third area of process in the mill consists of manufacturing inert fillers, both raw and dead burned. Crude gypsum is dried, ground (Raymond mill), and screened (air separators) to a 325-mesh size for use as raw filler. Dead-burned fillers are manufactured in a flash calciner where the ground gypsum is conveyed by air through a 2,200-degree atmosphere, and collected for further grinding. This material becomes an ultra white, very fine powder, with no chemically bonded water.

Huge storage bins throughout the mill accumulate various manufactured plasters, Hydrocals, and fillers for later distribution to either the board plant or the packing plant.

The board plant uses, basically, the continuous-kettle or "beta" stucco to manufacture sheetrock gypsum panels. The dry plaster is fed into a mixer in which water, fiber, and foaming agents are combined mechanically. The resultant slurry then flows onto a bottom sheet of paper. A top sheet of paper is applied at a master roll to gauge thickness, form edges, and complete the sandwich. The paper sandwich is carried along on a continuous belt machine. Near the end of the belt machine, the gypsum core has set sufficiently so it can be cut in lengths and fed into a kiln for final drying to rock-like hardness. The wallboard is then packaged and stored or loaded directly on rail cars or trucks for shipment. Sheetrock gypsum panels are manufactured in thicknesses of ⅜ inch, ½ inch, and ⅝ inch, in a standard width of 48 inches, and in lengths varying from 96 inches to 192 inches. Other features of the total product line include special edges, paper, and water resistance.

The second and most important area for distribution of milled plasters, Hydrocals, and filler products is the packing plant. Here the various materials are combined with additives in mechanical mixers and either shipped by bulk rail cars and trucks or packaged in paper bags for shipment. Here more than 220 gypsum products are readied for both industrial, commercial, and retail markets; these include moulding plasters, tooling and die cements, oil-field cements, art plasters, dental plasters, fillers for chalk, wine making, beer processing, paint additives, toothpaste, pill fillers, food fillers, orthopedic-cast plasters, and high-strength, fast-setting, highway-patching material. Plasters are made that are stronger than cement, and others so weak they can be dug out by hand. Bagged plasters are stacked on pallets and packaged in 2-ton units using a shrink-film plaster cover to protect the material in shipment from exterior damages or unusual climatic conditions.

Among other products shipped from the plant are approximatly 100,000 tons per year of chemical-grade rock used by cement-manufacturing plants for controlling the performance of portland cement. Also, many thousands of tons of fine-size gypsum are sold through a contractor and agricultural supply stores for use as soil conditioner in the peanut and wheat industries and for lawns and gardens.

LAND RECLAMATION

The Southard plant is among the largest employers in western Oklahoma. The gypsum plant makes a substantial contribution at a remarkably low cost to ecology. There is no emission of harmful gases or dusts. In fact the dusts from the mill are highly beneficial to all plant life. There is no adverse effect on water from gypsum waste since the gypsum is already in use as a cleanser and flocculating agent in water systems. Ponds below the plant and throughout the quarry abound in fish, plant, and bird species.

The most outstanding detriment to the ecology is the remnants of open-pit mining, such as spoil piles, empty pits, and waste dumps. U.S. Gypsum Co. has been reclaiming land disturbed by mining operations for over 20 years, long before laws requiring such action existed in most states. However, the overall progress was not too organized or dramatic.

Social pressure in the early 1960's prompted the Southern Conference of State Governments to take action by convening an interstate conference on surface mining. The direct result of the mining conference, held in Roanoke, Virginia, in April 1964, was the enactment of the first state environmental protection laws. A further result was that the stage was set for the formation of the Interstate Mining Compact (IMC).

At that time, with all the pending federal bills to abolish or greatly restrict surface mining, the main purpose of the compact was to save the mining industry. The compact was also a needed vehicle for interstate cooperation in surface mining and accomplished two primary aims: to enact environmental legislation in member states, and to protect the environment while balancing the interest between economic growth and conservation. At present there are 12 states in the IMC—Pennsylvania, Texas, Oklahoma, Maryland, North Carolina, South Carolina, West Virginia, Kentucky, Tennessee, Illinois, Indiana, and Alabama.

Oklahoma adopted its first reclamation act in 1968 and then upgraded the statute with its Mining Lands Reclamation Act of 1972. Enforcement of Oklahoma's mining and reclamation activities is carried out by the Chief Mine Inspector of the Oklahoma Department of Mines (1973). Basically, the 1972 law requires an application for a permit to mine, an operator's plan of reclamation, location drawings, plant property description maps, and a surety bond or collateral of $350 to $650 for each acre to be mined. The Department of Mines makes inspections, approves plans, and issues permits upon reports of the inspectors. During 1977 more than 300 mining permits existed in the state.

The Southard plant began land reclamation under the first State legislation of 1968, but no great progress was made until 1971, when the company entered into a cooperative program with the Blaine County Soil Conservation District and the Soil Conservation Service of the U.S. Department of

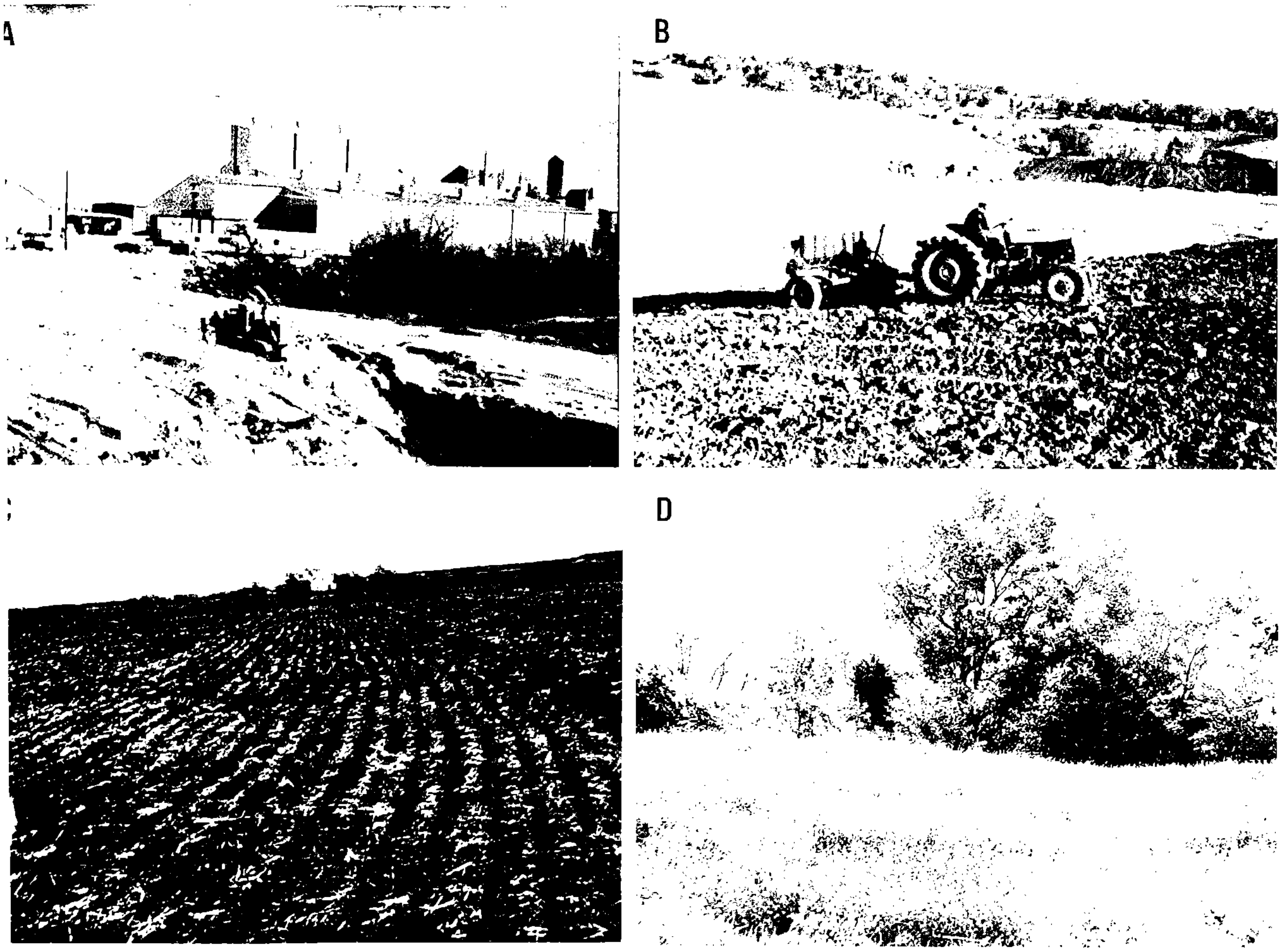


Figure 3. Reclamation of mined land at U.S. Gypsum Company's plant near Southard is shown: (A) backfilling of pit; (B) grading and soil conditioning; (C) planting of crops; and (D) planting of native grasses.

Agriculture. As a result of this agreement, a group of specialists and company officials met to discuss the project. A plan of action was developed for revegetation to aid in erosion control, provide for wildlife, and for beautification. Much was learned from the early tests about revegetating an area that lacks top soil and has a semi-arid climate. Land-surface slopes of no more than 3 to 1 must be achieved by stripping or subsequent grading to control erosion and to sustain plant life. Areas lacking suitable surface material, such as shale piles, plant dumps, and rocks floors, had to be graded and covered with soil or crushed shale applied by scrapers or trucks (fig. 3). The areas had to be further prepared by discing the surface material and removing large blocks of gypsum or other rock.

Several methods of seed application were attempted; drilling was the most successful, but broadcasting and sprigging of roots were also used. Seeding in this area must be accompanied by mulching. This serves as a heat barrier to preserve moisture and shelter the tiny seedling.

Native grasses and shrubs are the safest choices in these reclaimed areas. It is also of benefit to make the area appear more compatible with the surroundings. A plant that has had good growth in the semi-arid alkali soil is the new crown-vetch plant. The fastest growing plants for revegetation, which are not entirely endorsed by conservationists and others, are the yellow clover and the cottonwoods.

There is still a long way to go at Southard along the lines of reclamation, but we have developed a new attitude that spoil piles are no longer a necessary evil of mining.

REFERENCES CITED

Ham, W. E., 1962, Economic geology and petrology of gypsum and anhydrite in Blaine County, *pt. 2 of* Geology and mineral resources of Blaine County, Oklahoma: Oklahoma Geological Survey Bulletin 89, p. 10-11, 100-151.

Johnson, K. S., 1972, Northwest Oklahoma, *Book II of* Guidebook for geologic field trips in Oklahoma: Oklahoma Geological Survey Educational Publication 3, 42 p.

Oklahoma Department of Mines, 1973, Mining Laws of the State of Oklahoma: Chief Mine Inspector, Oklahoma Department of Mines, 162 p.

ECONOMICS OF GLASS-SAND PROSPECTS

THOMAS E. SHUFFLEBARGER, JR.[1]

Abstract—Glass sand is a virtually pure, fine- to medium-grained, quartz sand. It is produced in 25 states from a variety of chemically different source rocks. Deriving their raw material largely from either friable sandstones or loosely consolidated sands, 59 operations produced 14.9 million tons of melting sand in 1976. About one-third of this tonnage was obtained from the Oriskany and St. Peter Sandstones. Glass-sand prospects are discussed in this paper with regard to chemistry, environment, transportation, and costs. Demand for a quality product will range from 36 million to 46 million short tons in 1995.

BACKGROUND

Glass must surely be considered one of man's most useful products. The oldest pure glass is a molded amulet reported to have been made about 7000 B.C. (Encyclopaedia Britannica, 1953). The earliest glass from Egypt dates some time after 2500 B.C., and glass of Babylonian origin may have been made about 2600 B.C. (Encyclopaedia Britannica, 1975).

As early as 1535, the Spanish established glassmaking plants in Puebla, Mexico, possibly the first such enterprise in the Americas (Encyclopaedia Britannica, 1975). In 1608, Captain John Smith, with the help of skilled workmen from Poland and Prussia, erected a building for making glass in Jamestown, Virginia Colony; by December of that year, he provided Captain Newport with small samples of glass for his return to England (Wust, 1969).

Glassmaking in Colonial America, however, became firmly established in New England, New Jersey and eastern Pennsylvania. By 1808 operations were established as far west as Pittsburgh. Beginning in the 1860's, in response to increased demand for fuel, the industry moved toward the Ohio Valley. This move resulted in the use of the glass sands for which the Oriskany (Devonian) and St. Peter (Ordovician) Sandstones have become singularly well known (Keroher and others, 1966; Fettke, 1918, p. 19; Willman and Payne, 1942).

Beginning about 1902, again pressed by the demand for natural gas as fuel, many glass plants moved to southeastern Kansas. These plants depended primarily upon the St. Peter Sandstone in eastern Missouri for their melting sand and later depended on the sand from the Oil Creek and McLish Formations (Simpson Group) in Oklahoma as well as the St. Peter in Arkansas (Giles, 1930; Ham, 1945, p. 15-16).

Currently, there are 190 glass plants (Bentzen, 1977) in the contiguous United States. Upon inspection it is apparent that competitive advantage in marketing rather than proximity of raw materials (other than fuel) is the decisive factor in considering locations for plants.

DEFINITION AND SOURCES OF GLASS SAND

Glass sand is a virtually pure, fine- to medium-grained, quartz sand (Fettke, 1918, p. 19; Gary, McAfee and Wolf, 1972; Tooley, 1974), which may constitute as much as 75 percent of the glassmaking raw materials. Although produced in comparatively small tonnages, germanium, phosphate, and borate glass are examples of the non-silicate glasses.

Definitions of glass sand are apparently subject to opinion; this is particularly the case where chemical composition is concerned. Tooley (1974) and Murphy (1975) provide definitions which are useful in the industry and approximate the following: 95 percent of the grains passing 30 mesh and essentially 100 percent retained on 140 mesh; the composition of "No. 1" glass sand approximates 99.6 to 99.8 percent SiO_2. Alumina Al_2O_3 seldom exceeds 0.3 percent and iron (Fe_2O_3) will range consistently from 0.02 to 0.03 percent. Other grades of

---

[1] Pennsylvania Glass Sand Corporation, Berkeley Springs, West Virginia.

sand may contain 0.05 to 0.15 percent iron. However, acceptable glass sands are those which most nearly fit the glassmaker's economic needs, and any method used to evaluate a raw material's potential must finally prove compatible with such needs (Shufflebarger, 1974).

Sources of glass sand include sandstones, unconsolidated silica sands, quartzites, pegmatites, and vein-quartz. Admixtures of silica sand and either feldspar or kaolin have proven useful. These admixtures may prove readily separable and result in a two-product operation (such as silica sand and kaolin produced from the Wilcox Group in east Texas). Unconsolidated feldspathic sands, as well as feldspar and quartz "fines" which result from granite-quarrying operations, are beneficiated and marketed successfully.

GLASS-SAND PRODUCERS

The St. Peter and Oriskany Sandstones deserve special attention because of their long-established value to the glass industry, and the fact that nearly one-third of the glass-sand producers in the contiguous United States derive their raw materials from these sandstones.

Grimsley (1916, p. 332) considered the Ottawa, Illinois, glass sand the standard sand of the West and mentioned that the Berkeley Springs (Oriskany) sand was of similar quality. Lower Paleozoic sandstones, those below and including the Oriskany, supply nearly 30 percent of the nation's melting-sand requirements.

Where it is a source of glass sand in Pennsylvania, Virginia, and West Virginia, the Oriskany (more precisely, the Ridgeley Sandstone, Keoher, 1966) is an indurated, friable to tightly cemented rock. Attitude of beds and outcrop patterns favor modern materials-handling methods, and conventional methods of reduction and beneficiation result in a consistently high-quality product (Fettke, 1919, p. 149-261; Butts and Edmundson, 1966; Grimsely, 1916, p. 321-345).

The St. Peter, as well as the Galesville, Jordan, Oil Creek, McLish, and Sylvania sandstones, account for practically the total melting-sand production in the central re-

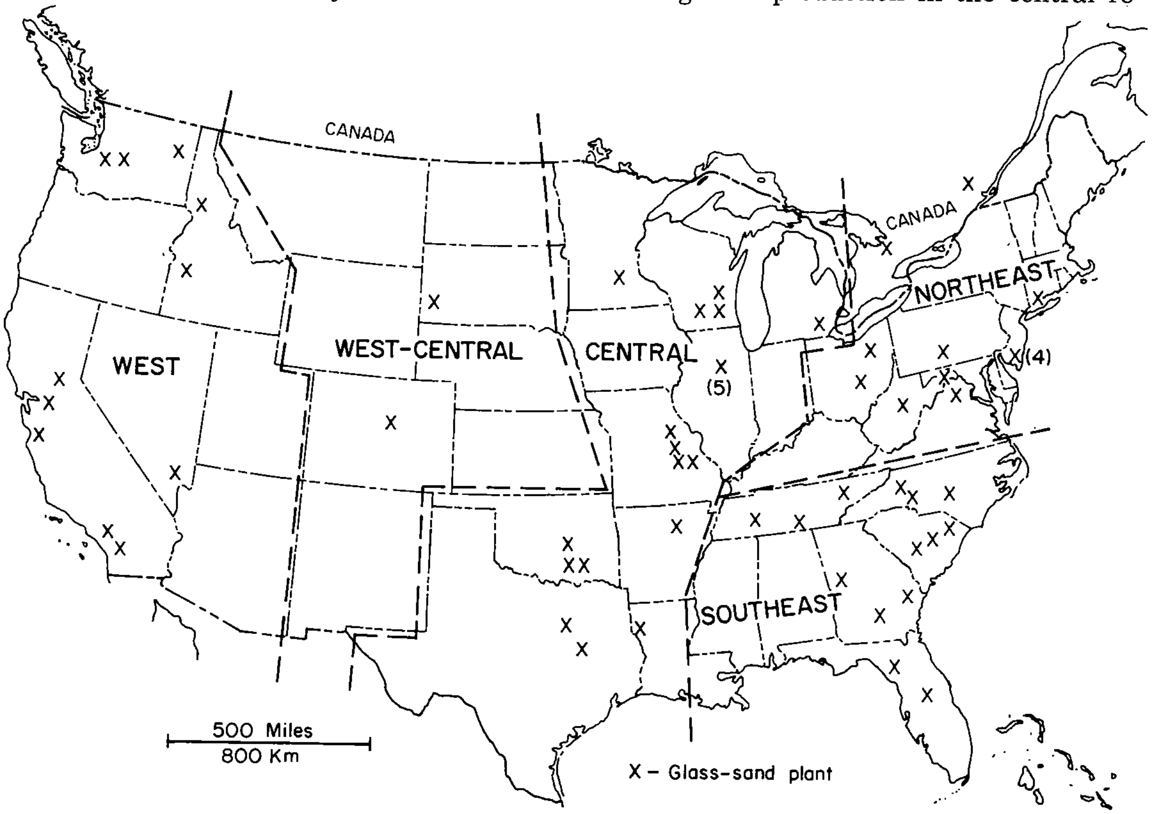


Figure 1. Distribution of the 59 glass-sand producers in the United States.

gion (fig. 1; Keroher, 1966; Willman and Payne, 1942; Giles, 1930, p. 1-112; Ham, 1945, p. 15-16; Grabau and Sherzer, 1910, p. 40-86; Landes, 1951; Dake, 1918, p. 105-169).

Glass sand is produced in 25 states from a variety of chemically different source rocks that constitute an apparently adequate reserve base (table 1). Clearly, melting-sand resources are a select portion of quartz-bearing rocks in general, and standards of acceptance, affected either by economics or by rock properties, act to further restrict possible uses. Hence, the various land-use regulations (Ketner, 1973) and punitive tax legislation (Engineering and Mining Journal, 1977) could prove particularly detrimental to future prospects.

Because of the proprietary nature of the information, the tonnage of melting sand produced annually is difficult to determine. However, two independently derived estimates indicate that the production from 59 plants ranged from 14.6 million (Bentzen, 1977) to 14.9 million short tons in 1976 (fig. 2). The median output of all producers approximated 210,000 tons of melting sand in 1976 (fig. 2). A more realistic tonnage, about 250,000 tons/year, is indicated for the principal producers if the distribution is adjusted by eliminating the relatively small-tonnage operations. Melting sand constitutes about 80 percent of the total silica output of glass-sand producers.

TABLE 1.—LIST OF GLASS-SAND PRODUCERS
(Does not include all producers of quartz-bearing, melting materials)

ARKANSAS		
		1. Silica Products Co. Guion, Ark. St. Peter Sandstone (-40 mesh)
CALIFORNIA		
	F[1]	2. OIG Ione, Calif. Ione formation, clay-sand
	F	3. Wedron Byron, Calif. Domengine Sandstone, feldspathic
	F	4. OIG Pacific Grove, Calif. Beach (Recent) sand, feldspathic
	F	5. OIG Mission Viejo, Calif. Silverado Formation, feldspathic
	F?	6. Ottawa Silica Co. Oceanside, Calif. Tejon Formation, feldspathic
CANADA		
		7. Indusmin Midland, Ont. Lorrain quartzite
		8. Indusmin St. Canut, Que. Quartzite, Grenville Age
COLORADO		
		9. Columbine Sand Co. Morrison, Colo. Source?
CONNECTICUT		
		10. Ottawa Silica Co. Lantern Hill, Conn. Pegmatite
FLORIDA		
		11. Standard Silica Co. Davenport, Fla. Citronelle Formation (40 mesh)
		12. NL Industries (Edgar Plastic Kaolin) Edgar, Fla. Citronelle(?), kaolin byproduct
GEORGIA		
	F	13. Dawes Silica Mining Co. Thomasville, Ga. Recent(?) sand
	F	14. Georgia Marble Co. Junction City, Ga. Tuscaloosa Formation(?)
	F	15. Dawes Silica Mining Co. Eden, Ga. Terrace (Recent) sands
IDAHO		
	F?	16. Simplot Silica Co. Bovill, Id. Source(?), clay-sand(?)
	F	17. Wedron (Gem Silica) Emmett, Id. Payette Formation

---

[1] F = Flotation

ILLINOIS

Ottawa District

18. (A) Arrowhead (Manley Bros.)
(B) Bellrose Silica Co.
(C) Manley Sand Division, Martin Marietta
(D) Ottawa Silica Co.
(E) Wedron Silica Division

St. Peter Sandstone ("reconstituted" and naturally occurring 40 mesh)

LOUISIANA

F 19. Dresser Industries
Minden, La.
Recent sands(?), Sparta sands(?)

MICHIGAN

20. Ottawa Silica Co.
Rockwood, Mich.
Sylvania Sandstone (40 mesh)

MINNESOTA

21. Unisil (Gopher State)
Le Suer, Minn.
St. Peter Sandstone (40 mesh)

MISSOURI

22. PGS Corp.
Pacific, Mo.
St. Peter Sandstone (-40 mesh)

23. PGS Corp.
Augusta, Mo.
St. Peter Sandstone (-40 mesh)

24. Manley Sand Division
Festus, Mo.
St. Peter Sandstone (-40 mesh)

25. Unisil
Crystal City, Mo.
St. Peter Sandstone (-40 mesh)

NEVADA

26. Simplot Silica Co.—Johns Manville?
Overton, Nev.
Baseline Sandstone

NEW JERSEY

F 27. PGS Corp.
Newport, N.J.
Cohansey Sand

28. J. Morie
Millville, N.J.
Cohansey Sand

F 29. Unisil
Millville, N.J.
Cohansey Sand

30. Whitehead Bros.
Millville, N.J.
Cohansey Sand

NORTH CAROLINA

F 31. Carolina Silica, Inc.
Cognac, N.C.
Tuscaloosa Formation

F 32. Kings Mountain Mica Co.
Kings Mountain, N.C.
Pegmatite (40-50 mesh)

F 33. IMC (Sobin)
Spruce Pine, N.C. (Kona)
Pegmatite

OHIO

F 34. The Central Silica Co.
Zanesville, Ohio
Sharon Sandstone(?)

35. Walter Best
Chardon, Ohio
Sharon Sandstone

OKLAHOMA

36. PGS Corp. (2 plants)
Mill Creek, Okla.
Oil Creek Sandstone (-40 mesh)

F 37. Mid-Continent Glass Sand Co.
Roff, Okla.
McLish Sandstone (40 mesh)

PENNSYLVANIA

38. PGS Corporation
Mapleton Depot, Pa.
Oriskany Sandstone

SOUTH CAROLINA

F 39. PGS Corporation
Columbia, S.C.
Tuscaloosa Formation

F 40. Wedron Silica Division
Lugoff, S.C.
Tuscaloosa Formation

41. E. R. Pitts Sand Corp. (Locher)
Nichols, S.C.
Recent sand

SOUTH DAKOTA

42. Pacer Corporation
Custer, S.D.
Pegmatite

TENNESSEE

F 43. Wedron Silica Division
Sewanee, Tenn.
Sewanee Conglomerate

F 44. Hardy Sand Co.
Camden, Tenn.
McNairy Sand

F 45. ASG Industries, Inc.
(Hunt's Gap Mine)
Kingsport, Tenn.
Bays Formation

TEXAS

F 46. Dresser Minerals
Kosse, Tex.
Wilcox (-30 mesh)

F? 47. Wedron Silica Division
Cleburne, Tex.
Paluxy Sand (-40 mesh)

VIRGINIA

F 48. Unisil
Gore, Va.
Oriskany Sandstone (40 mesh)

WASHINGTON

49. Lane Mountain Silica Co., Inc. (Del Monte)
Valley, Wash.
Addy Quartzite?

50. Smith Bros. Silica Co., Inc.(?)
Plant—Ravensdale,
King County, Wash.
or P.O. Box 236, Auburn, Wash.
Raw material?

51. Alberg Associates, Inc.(?)
Plant—Cedar Mountain area, Wash.
Raw material?

WEST VIRGINIA

52. PGS Corporation
Berkeley Springs, W. Va.
Oriskany Sandstone

53. Greer (Deckers Creek Sand Co.) (?)
Morgantown, W. Va. (near)
Pottsville Formation(?)

WISCONSIN

54. Manley Bros.
Hanover, Wisc.
St. Peter Sandstone (40 mesh)

55. Manley Sand Division
Portage, Wisc.
Galesville/St. Peter Sandstone (40 mesh)

56. Chier Ste. Marie Sand Co.
(C. A. Chier Sand Co.)
Fairwater, Wisc.
Jordan/St. Peter Sandstone (40 mesh)

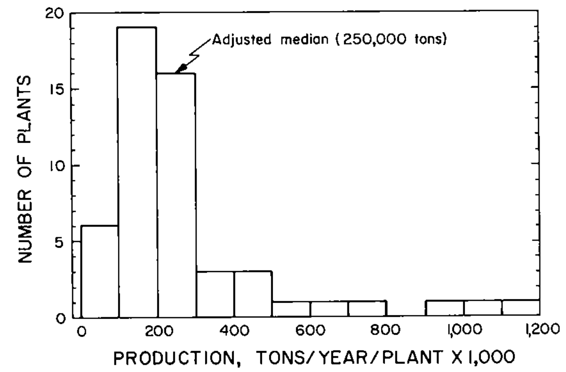


Figure 2. Graph showing number of glass-sand plants in various levels of estimated production.

BASIC CONSIDERATIONS IN DEVELOPING GLASS-SAND PROSPECTS

Market

One company's measure of an adequate return on investment may differ radically from another's. Moreover, the cost of design as well as operation is the result of local experience and time. Hence, it is relatively easy to analyze the industry's hardware and opportunity for expansion but practically impossible to derive standards from the results of their use.

Either a significant expansion of existing plants or the establishment of new operations is largely the result of an increased demand for melting sand. However, a market that includes industrial sands, chemical sand, fillers and abrasives, as well as melting sand, is the desirable goal, and all these uses are important in evaluating a prospective market.

During a period of about five years, three glassmakers have built new plants in the southeastern United States (fig. 3). Coincident in time and area, three new glass-sand plants began operations. It is estimated that the combined melting-sand capacity (not actual sales) of the three new sand producers ranges at least from 600,000 to 750,000 short tons per year (tpy). The new

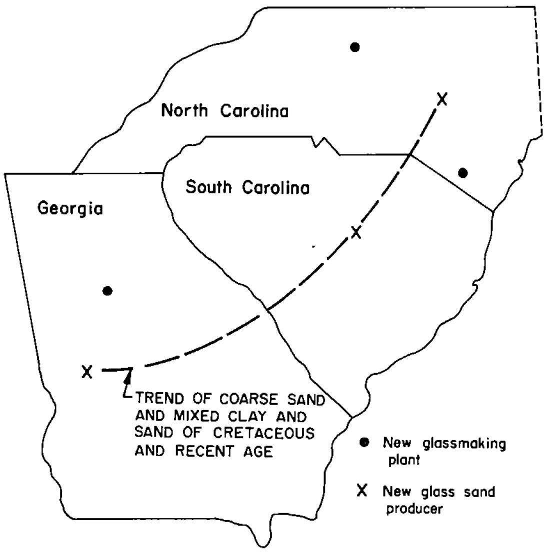


Figure 3. New glassmaking plants and glass-sand producers in southeastern United States.

sand producers derive their raw materials from coarse-grained, Cretaceous (or Recent) sands. These sands require scrubbing and flotation, and their grain-size distribution results in about 50 percent recovery in the glass-sand-size range. Initially, the total, new demand created by these glassmakers approximated 230,000 tpy. Moreover, for a period of nearly two years, one glassmaker responded to the increase in regional sand-producing capacity by obtaining melting sand from Guion, Arkansas. Unless markets other than melting sand are developed, idle capacity could result in an economically indefensible situation.

Development Potential

The location and geology of broadly defined prospect areas, such as the strike belts of the St. Peter Sandstone, are generally well known. Hence the investigator is concerned with reappraisal in light of his particular set of economics rather than the evaluation of an untried prospect.

Unlike most metals, glass-sand prospects may not be judged solely by the adequacy of reserves. A combination of characteristics that favor the development of a prospect rather than one redeeming virtue is necessary to assure the success of an operation. Hence, proximity to markets or "place value" (Murphy, 1975), though certainly important, may be overridden by impractical operation and established competitive practice. The growth of the glassmaking industry in the 48 contiguous states has fixed the distribution of glass-sand producers; few possible markets are beyond reach of an existing supplier. These existing producers tend to augment capacity by additions to existing facilities rather than by the development of new operations.

Investment

I. F. Stone (*The Daily Princetonian*) said in part—"It's very easy to create plausible patterns from the little we know, put them together, make them look very interesting, very meaningful, and feel like a very bright and very good *engineer* and say to yourself, 'Well, it sounds good, but is it true'?"

(1) The cost of construction as well as the return on investment may be estimated with reasonable accuracy.

(2) Melting sand required by a major glassmaking operation will range from 50,000 to 200,000 tpy but less often the larger tonnage.

(3) The development of prospects is solely the result of a significant increase in the demand for melting sand. It does not follow, however, that a given tonnage, area by area, will prove sufficient to warrant the investment.

(4) For example, a modern glass-sand plant built to produce 300,000 tpy melting sand might have a basic capacity in the range of 500,000 to 1,000,000 tpy. Depending upon the nature of the raw material as well as the diversity of products, the cost of such an operation will range from $7.00 to $15.00 per ton of annual capacity.

(5) The silica prospect, if considered competent, will include a minimum of 20 years of reserves. However, few, if any operations are considered where reserves are so narrowly limited; Murphy (1975) considers 50 million tons in salable reserves necessary to insure the success of the operation.

Fettke (1919, p. 211-212) reports that in 1869 "first class" glass sand sold for $12.00 per ton f.o.b. Pennsylvania origin. In 1914 glass sand was marketed in Pennsylvania for an average price of nearly $1.20 per ton. Ham (1945, p. 15-16) estimates that the value of glass sand produced in Oklahoma in 1944 was about $1.80 per ton.

It is probably true that a modern glass-sand operation requires a sophistication of equipment as well as management which is beyond the product's commensurate value. Since 1968 the average price of melting sand (fig. 4) has not kept pace with the rate of inflation (6.5 percent for 1969-1976); the inflated (6.5 percent) curve is probably near current values.

Growth in tonnage output, about 5.5 percent, is entirely a function of the glass industry's fortune. The 5.5 percent projected growth rate (fig. 5), when used with information derived locally, results in a demand of 41 million tons (melting sand) in 1995. If the locally obtained data is adjusted by a tonnage equal to two standard deviations, the demand in 1995 will range from 36.6 million to 46.3 million tons.

EVALUATION OF PROSPECT

By far the major tonnage of glass sand produced in the United States is taken from friable sandstones and unconsolidated sands. The widespread nature of such prospects, a region of nearly 300,000 square miles for the St. Peter and equivalent sands alone, renders dependence on the more indurated rocks to a secondary importance.

Of principal concern to the investigator are those properties of the orebody which include (1) total chemistry of the silica-bearing body, (2) the nature and diversity of the component grains, and (3) the grain-size distribution.

Chemistry

Iron-bearing contaminants are particularly objectionable to the glassmaker. Iron oxides usually form either crusts or stains on quartz grains and, ideally, should be so weakly bonded as to permit their removal by simple washing methods. Attrition (scrubbing) is used to remove stubbornly held crusts and films; in some cases, flotation (Bentzen, 1977) may be used to remove iron-stained quartz. Also, clays and other minerals in the clay-size range will have been reduced to an acceptably uniform amount by use of conventional washing equipment. Except when used in the production of special-purpose silica, flotation is seldom a necessary adjunct to the beneficiation of lower and middle Paleozoic sandstones.

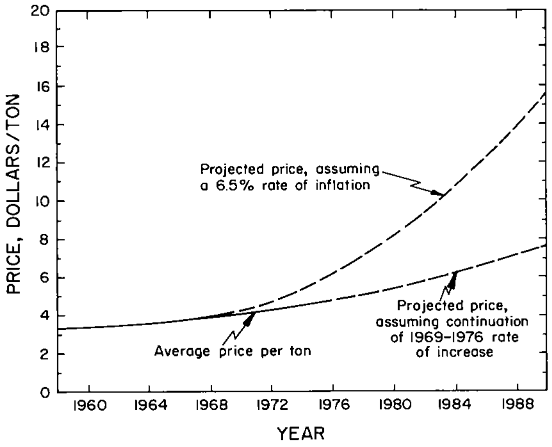


Figure 4. Projected average price through 1990 of melting sand.

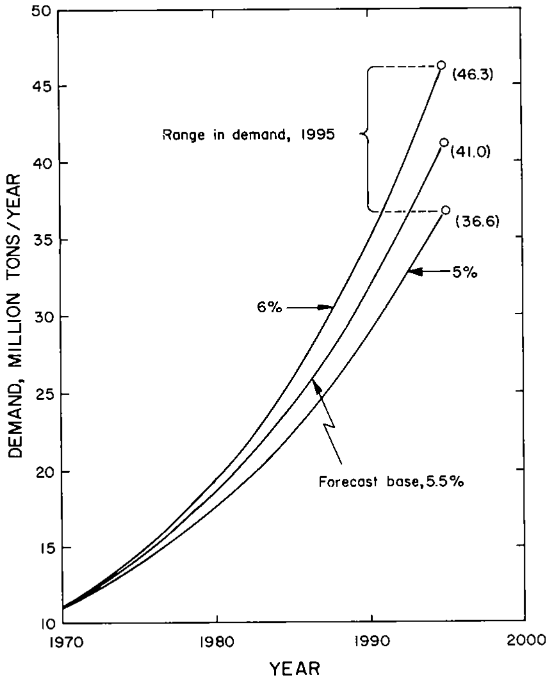


Figure 5. Chart showing projected growth in demand through 1990 for melting sand.

Heavy Minerals

The wide variety of heavy minerals commonly found in glass sands (table 2) are typically the durable mineral grains that have withstood long periods of abrasion prior to deposition. The lower and middle Paleozoic rocks contain a restricted suite of heavy minerals, and they are present in small proportions (Stow, 1938; Martens, 1939; Willman and Payne, 1942, p. 71-72). This assemblage is consistent in its composition and is rarely objectionable to glassmakers.

TABLE 2.—HEAVY MINERALS THAT COMMONLY OCCUR IN SILICA-SAND SOURCE ROCKS

Opaque Minerals--Excessive proportions may discolor or leave unmelted residual in glass melts.

- Chromite
- Hematite, limonite magnetite[1]
- Ilmenite, leucoxene[1]
- Iron sulphides
- Rock fragments

Transparent Minerals--Refractory minerals with melting points generally higher than glass-melting temperatures.

- Beryl
- Corundum
- Kyanite
- Sillimanite
- Spinel
- Staurolite
- Topaz
- Zircon[1]

Transparent Minerals--Nonrefracotry.

- Andalusite
- Apatite
- Epidote
- Garnet
- Hornblende
- Monazite
- Rutile
- Titanite
- Tourmaline[1]

[1] Components of heavy-minerals assemblages in lower and middle Paleozoic source rocks.

Coastal plain sediments, and practically all post-Paleozoic sources of silica sand, contain a varied and commonly distinctive, detrital-mineral suite. This suite includes refractory minerals, particularly beryl, corundum, kyanite, sillimanite, spinel, and topaz, that can prove detrimental in glass melting. Those refractories, generally larger than 80 mesh, may remain unmelted and become particularly damaging in the glass batch; ordinarily, flotation is the remedy for separating these refractories from glass sand (Bentzen, 1977).

Byproducts

In special instances, naturally occurring mixtures of clay-silica and feldspar-silica are used in the production of glass-making materials. Examples include sandy clays of the Wilcox belt in Texas and of the Ione and Tejon Formations in California. The clay and feldspar may, in some areas, prove to be a valuable byproduct, whereas the heavy minerals are seldom economically recoverable.

Grain Size

Glass sand is defined by its particle-size range, as well as its chemical characteristics, and a source whose component grains nearly approximate the appropriate screen limits is indeed desirable.

Local techniques of sand melting, as well as the glass product, may dictate size specifications. Generally top sizes are given as minus 20 mesh, but may commonly include minus 30 and minus 40 mesh limits and in each instance with practically all sand retained on the 140 mesh screen. Typically, about 80 percent of the sand is confined between the 30 and 80 mesh screens. Pre-batching and pelletizing techniques, providing they prove acceptable to the glass industry, could result in an increased demand for finer grained silica sand.

Mining and Production

Open-pit quarrying is the dominant method employed in mining glass sand, although there are exceptions, such as the operations near Guion, Arkansas. Tunnel—or coyote blasting methods as practiced in the Oriskany Sandstone may be combined with high-capacity haulage and conventional crushing. Hydraulic mining is used effectively in poorly cemented sands of the St. Peter, Oil Creek, and McLish Formations. Where near-surface water and geologic conditions permit, unconsolidated sands are removed by dredging. Either hydraulic mining or dredging and subsequent removal by pumps offer a relative optimum in economy; fluid mechanics, applicable to flow in pipelines, may also provide a measure of attrition scrubbing and prove an aid to beneficiation (Shufflebarger, 1974).

Environmental Factors

In addition to state laws, there are at least 20 federal acts that are designed to either regulate mining or protect the environment. Ad hoc groups as well as nationally established organizations have pursued the cause of environmental protection—in some instances with dramatic effect.

Except that these laws may effectively bar mineral development in wetlands, wilderness areas, national parks, and certain public lands, the prospector's most immediate concern is zoning. Zoning is the principal method by which land-use plans are either policed or administered. The aesthetic, economic, ethical, political, and environmental considerations of land-use planning must be weighed in every land-use situation (Knight and Duhaime, 1977).

Essentially, land-use regulations may be considered as (1) either use- or area-restrictive, (2) as landscape-cosmetic, and (3) as air/water protective.

While the areas now affected by zoning practices, public land controls, and local landowner associations may be apparent, neither the future extent of these areas nor the intentions of policy makers are so readily predictable. Until a degree of predictability becomes possible, it will be prudent to assume that future controls will not necessarily respect mineral development.

The terms sand, silica sand, and glass sand are relatively commonplace; they tend to connote abundance—something less than elegant. Indeed, melting sand (in dollars per ton) is the least expensive of the glassmaker's raw materials. Glass-sand operations are long term ventures; the visibility of the operation increases as a function of time. Hence, efforts to lessen the impact of mining on the countryside in general are a matter of common sense and well-considered public relations as well as law.

Any prospect for the development of a glass-sand operation must include a readily accessible source of water. Long established in some areas, regulations that concern the withdrawal of ground water, diversion of surface water, and the possible contamination of either ground or surface water have nationwide effects.

Air-pollution controls, used in the abatement of dust and either airborne or air-mixed matter, may be considered indispensable.

Finally, all of these regulations combine to become a significant factor in the cost of production and a vital element in the prospector's appraisal of a mineral venture (Shufflebarger, 1974).

Energy Requirements

Practically all melting sand is sold on a near-moisture-free basis, and modern plants are equipped with either oil- or gas-fired rotary or fluid-bed dryers. Coal-fired, steam-tube dryers are used locally.

Exclusive of mining, initial electric power requirements range from 0.75 to 1.75 connected horsepower per ton of product per day. The figures for installed horsepower are approximate; the minimum being more nearly applicable to operations involving hydraulic mining and a single-product, melting-sand milling circuit. By comparison, the addition of crushing, grinding, and scrubbing circuits will substantially increase power requirements. Nearly one half of the glass-sand plants in the conterminous United States include flotation.

TABLE 3.—SAND SCALE (CLASS) RATES
(from PGS Corp.—Traffic Division; subject to revision)

Official or Eastern Territory

Miles	Truck	Rail
100	$ 7.00 pnt	$ 8.11 pnt
200	13.00	9.64
300	19.20	10.99
400	25.40	12.23
500	30.80	13.76
600	35.40	15.36
700	39.80	16.44
800	45.40	17.18

Southern Territory

Miles	Truck	Rail
100	$ 6.92 pnt	$ 3.78 pnt
200	11.18	5.14
300	14.83	6.10
400	20.12	7.16
500	25.44	8.14
600	29.66	8.95
700	33.94	9.87
800	39.57	10.48

Southwest Territory

Miles	Truck	Rail
100	$ 4.83 pnt	$ 6.79 pnt
200	7.67	8.93
300	11.50	10.35
400	15.32	11.48
500	19.15	12.86
600	22.98	14.26
700	26.81	15.10
800	30.64	15.77

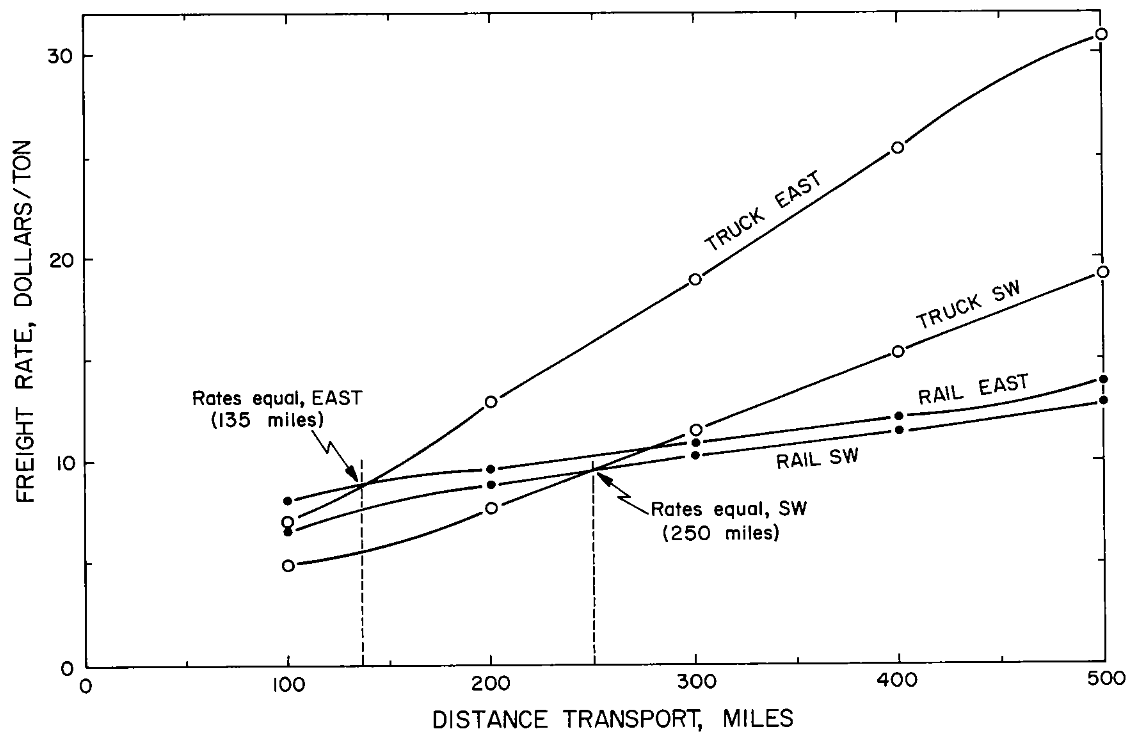


Figure 6. Comparison of freight rates for shipment of glass sand by truck and rail in eastern and southwestern territories.

Transportation

The cost of transportation is a standard by which the market must be tested. Few, if any, producers of glass sand in the United States are waterway-oriented; highway and railway systems are practically the sole carriers of this commodity.

Immediate access to truck and rail transportation is as essential to the supply of the glass-sand plant as it is to the most economical distribution of its product. An examination of the final sale price (per ton) of glass sand shows that the cost of transportation may exceed the f.o.b. value threefold. Either redistribution from off-plant storage facilities or multiple handling in shipment becomes prohibitively expensive as well as undesirable because this treatment provides possible inlets for contaminants.

Truck transportation, with the advantage of schedule and route flexibility, is at least competitive with rail shipments within a range of about 150 miles. Truck transportation accounts for a maximum of about 15 percent of the total glass-sand traffic. Traffic beyond the 150-mile range is almost entirely rail directed. Bulk rail shipments customarily require covered hopper cars. The average load per hopper car is about 80 tons whereas a truck, depending upon state laws, may be loaded to a maximum gross weight of 36.5 tons.

Freight rates which have been given herein concern official (eastern), southern, and southwestern (western) territories (fig. 6). The numbers used represent class (scale) rates. Rail carriers as well as truckers have established, in all areas, commodity rates between points of major usage. Commodity rates reflect competitive practices and are generally less than the class rate (table 3).

During 1976, Southern Railway System (J. A. Johnson, personal communication, 1977), for example, handled more than 7,000 carloads (about 613,000 tons) of industrial sand. The average loading per car was 87.5 tons while the charge for transportation was less than 1.75 cents per ton-mile. This charge is probably less than that for any other mode; it is largely the result of increase in car capacity, the efficiency of a four-man train crew and a consist which includes 8,000 horsepower coupled to a net lading of about 4,000 tons. (Southern Railway System's routes span a wide variety of topography.)

FUTURE PROSPECTS

The current pace of glassmaking technology, the manufacturer's demand for high-volume output, the significance of fuel economy, and faster schedules for melting of sands indicate more stringent demands for quality control.

As a result of the glassmaker's efforts to fit efficiency to product quality, the glass-sand producer must respond with a melting sand that is (1) virtually free of refractory minerals (these are particularly objectionable in thin-wall containers and plate glass), (2) screened to specifications (oversize quartz-grains may remain unmelted) and (3) so beneficiated as to remove practically all components other than the mineral, quartz.

Future prospects will, then, be concerned with raw materials of the best quality—a concern which will possibly prove more difficult and surely more expensive to dispatch as markets and product lines are expanded.

SUMMARY

The competency of silica-sand prospects may be measured by three fundamental factors—(1) a new market of a significant volume either by value of tonnage or by a single product, (2) a raw material suitably located with respect to transportation, and (3) a single prospect from which would result in minimum costs of production.

A number of questions must be asked in evaluating a particular silica-sand prospect. Is the overall chemistry of the raw material suitable? To what extent is beneficiation necessary? How will the raw material be mined? Does grain-size distribution fit glassmakers' specifications? Finally, have land-use laws been properly evaluated?

REFERENCES CITED

Bentzen, E. H., III, 1977, Producing sand for the glass industry: Atlanta Annual Meeting, American Institute of Mining, Metallurgical and Petroleum Engineers, Society of Mining Engineers Preprint 77H37, 22 p.

Butts, C., and **Edmundson, R. S.,** 1966, Geology and mineral resources of Frederick County: Virginia Division of Mineral Resources Bulletin 80, 142 p.

Dake, C. L., 1918, The sand and gravel resources of Missouri: Missouri Bureau of Geology and Mines Reports, v. 15, second series, 274 p.

Encyclopaedia Britannica, 1953: v. 10, p. 398-401.

Encyclopaedia Britannica, 1975: Macropaedia, v. 8, p. 181-211.

Engineering and Mining Journal, 1977, This month in mining: Development of Wisconsin's mineral potential is stymied by the state: Engineering and Mining Journal, v. 178, p. 23-27.

Fettke, C. R., 1918, Glass manufacture and the glass sand industry of Pennsylvania: Topographic and Geologic Survey of Pennsylvania Report Number XII, 278 p.

Gary, M., McAfee, R., Jr., and **Wolf, C. L.,** 1972, Glossary of Geology: American Geological Institute, Washington, D.C., p. 581, 626-627, 659.

Giles, A. W., 1930, St. Peter and older Ordovician sandstones of Arkansas: Arkansas Geological Survey Bulletin 4, 187 p.

Grimsley, G. P., 1916, Jefferson, Berkeley, and Morgan Counties: West Virginia Geological Survey County Reports, 644 p.

Grabau, A. W. and **Sherzer, W. H.,** 1910, The Monroe Formation of southern Michigan and adjoining regions: Michigan Geological and Biological Survey for 1909, Publication 2, Geological Series 1, 248 p.

Ham, W. E., 1945, Geology and glass sand resources, central Arbuckle Mountains, Oklahoma: Oklahoma Geological Survey Bulletin Number 65, 103 p.

Keroher, G. C., and others, 1966, Lexicon of geologic names of the United States, for 1936-1960: U.S. Geological Survey Bulletin 1200, 3 parts, 4341 p.

Ketner, K. B., 1973, Silica sand, in United States Mineral Resources: U.S. Geological Survey Professional Paper 820, p. 577-580.

Knight, C. G., and **Duhaime, P. G.,** 1977, Land use considerations in the premining plan: Atlanta Annual Meeting, American Institute of Mining, Metallurgical and Petroleum Engineers, Society of Mining Engineers Preprint 77F7, 24 p.

Landes, K. K., 1951, Detroit River Group in the Michigan Basin: U.S. Geological Survey Circular 133, 23 p.

Martens, J. H. C., 1939, Petrography and correlation of deep-well sections in West Virginia and adjacent states: West Virginia Geological Survey Reports, v. 11, 255 p.

Murphy, T. D., 1975, Silica and silicon, *in* Lefond, S. J., editor, Industrial minerals and rocks, 4th edition, American Institute of Mining, Metallurgical and Petroleum Engineers, New York, p. 1043-1060.

Shufflebarger, T. E., Jr., 1974, The evaluation of silica deposits: Dallas Annual Meeting, American Institute of Mining, Metallurgical and Petroleum Engineers, Society of Mining Engineers Preprint 74H76, 17 p.

Stow, M. H., 1938, Conditions of sedimentation and sources of the Oriskany Sandstone as indicated by petrology: American Association of Petroleum Geologist Bulletin, v. 22, p. 541-564.

Tooley, Fay V., 1974, The handbook of glass manufacture: Books for Industry, Inc., New York, v. 1, p.30.

Willman, H. B., and **Payne, J. N.,** 1942, Geology and mineral resources of the Marseilles, Ottawa, and Streator quadrangles, (Illinois) State Geological Survey Bulletin 66, 388 p.

Wust, Klaus, 1969, The Virginia Germans: Charlottesville, The University Press of Virginia, p. 3-4.

STUDIES OF THE VARIABILITY OF FELDSPATHIC SANDS REFINED FROM THE ARKANSAS RIVER

FRANK W. BOWDISH[1]

Abstract—During the early 1960's, a method was developed for refining sand from the Arkansas River to produce a feldspathic product that was proposed for use in making colorless glass. Because of the need for chemical uniformity, a cooperating glass manufacturer specified certain ranges of percentages for each chemical constituent of the sand. These specifications were met by fulfilling the single requirement that alumina vary by no more than ±0.1 percent from the specified value. This translated to a total variation of only about 1 percent in the feldspar content of the mixed quartz-feldspar products.

Because the feldspar was lighter than the quartz, the average density of refined sand varied depending on composition. Densities, determined to five significant figures, of several samples were correlated with their chemical analyses, and the correlation could then be used with density determinations to more reliably indicate compositions than by chemical analyses only.

The effects of several variables on the composition of refined sands were studied. There was a regular variation in the proportion of feldspar with screen size. A series of samples with their natural size distributions were more nearly uniform in composition than the same sands after screening and recombination. The screening and recombination process was done so that the sands had identical size distributions. Variations in the refining showed little effect on composition.

A pile of flow-back sand from a construction sand washer was found to be severely segregated. However, samples taken from many points in the river near the sand plant and from the flow-back discharge pipe over several weeks very nearly met the uniformity specification.

If care was taken to avoid segregation either before or during processing, it should be possible to meet the uniformity specifications for a feldspathic glass sand.

INTRODUCTION

Among the materials required in the manufacture of glass for food and beverage containers are the minerals quartz and feldspar. Quartz or glass sand provides most of the silica needed, while feldspar is used for its alumina content to make the glass corrosion resistant. Ordinarily, supplies of these minerals in rather pure form are obtained separately and mixed together in exact proportions along with the other ingredients required in the glass. Since the color of glass depends upon certain minor constituents, it is customary to select materials that are as low as possible in these coloring agents, notably iron. Good supplies of glass sand are rather widespread, but deposits of suitable feldspar are more limited and are often located far from the glass plant.

Quartz and feldspar occur together in rocks such as granites, but unfortunately they are generally so contaminated that they are unsuitable for glass making. In certain places, sands containing both quartz and feldspar are processed to yield pure mineral concentrates or unseparated mixtures of the two (Bowdish, 1967). About 25 years ago, I began research on methods of making glass products from sands of the Kansas and Arkansas Rivers. These sands are essentially ground up granite eroded from the Rocky Mountains of Colorado having been deposited first as the Late Tertiary Ogallala Formation and then reworked by the tributaries of the Kansas and Arkansas Rivers or carried downstream directly from the mountains by the Arkansas River (fig. 1). The sands contain quartz, feldspar, iron-bearing accessory minerals, and a small amount of calcite. In addition to being mixed with a host of unwanted minerals, the quartz and feldspar particles are stained and impregnated with iron oxides.

At first research followed the procedure of grinding the sand, treating it by wet magnetic separation, desliming it, and making concentrates of the feldspar and quartz by flotation (Bowdish and Runnels, 1952). This was followed by development, in cooperation with Owens-Corning Fiberglas Corp., of a procedure to remove enough of

---

[1] Nevada Mining Analytical Laboratory, Mackay School of Mines, Reno, Nevada.

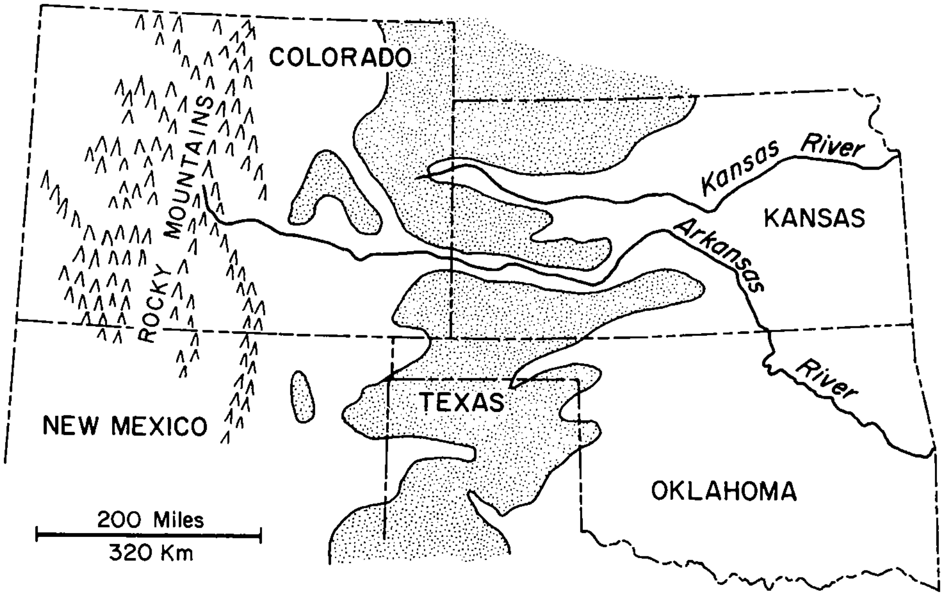


Figure 1. Map showing location of Kansas and Arkansas Rivers crossing the Late Tertiary Ogallala Formation (stippled).

the iron minerals by magnetic separation to permit the non-magnetic sand to be used in making glass wool, as has been done at Kansas City since 1953 (Bowdish, 1955, p. 55). Research a few years later resulted in magnetically separated and acid-leached products from the Arkansas River sufficiently low in iron for use in making colorless container glass. I was then joined by Arkhola Sand and Gravel Co. and Brockway Glass Co. in a cooperative project to commercialize such refined feldspathic sands. At this point, however, questions were raised by the glass manufacturer regarding the uniformity to be expected in a mixed product derived from the river sand. This paper deals with studies made to answer these questions.

DESCRIPTION OF REFINED SAND

For this research, samples of crude sand were sent to me in Reno, Nevada, and refined by procedures intended to produce products suitable for glass making. The sands were scalped by screening through either 20 or more usually 28 mesh (Tyler Standard Screen Scale), and the undersize was washed to remove slimes if this had not already been done. Then the dried undersize sand was treated once or twice on an induced-roll magnetic separator having three rolls to remove about 30 percent of its weight which was rejected. After being separated, the non-magnetic sand was leached in a hot acid solution to remove iron stains and filling. Washing and drying resulted in refined sands that were light colored in comparison to the brownish red of the crude sand, yet a pinkish gray in comparison to white quartz sand.

Samples of refined sand were analyzed by a commercial laboratory, and the averages for five samples of unsegregated sand are shown in table 1. Also shown are the variations in these analyses and those indicated by the glass manufacturer as being permissible. The data indicate that these sands met or nearly met the requirements for uniformity.

The refined sand appeared to consist of quartz and feldspar with a trace of white mica, and since the treatment should have removed or dissolved all other minerals, all of the K_2O, Na_2O, and CaO were assumed to occur as feldspar. Table 2 shows chemical

TABLE 1.—COMPOSITION AND VARIABILITY OF REFINED SANDS

Five samples	SiO_2	Al_2O_3	K_2O	Na_2O	CaO
Average	91.32	4.59	3.04	0.78	0.08
Variation	0.5	0.23	0.35	0.01	0.05
Allowable variation	0.6	0.2	0.4		0.15

In addition: 0.035% Fe_2O_3 and 0.013% TiO_2

formulas and theoretical compositions for these minerals, and table 3 gives calculations for the mineralogical composition of the average sand tested. The sand is about 25 percent feldspar of which about 72 percent is potassium feldspar (K-spar).

Data in table 1 suggest that most of the variations in the analyses may be caused by variations in the content of K-spar and corresponding variations in the quartz content; the other feldspars having rather little variation. The specification of an allowable variation ± 0.1 percent Al_2O_3 from the average sand composition would correspond to a variation of about 1.09 percent in the K-spar content. Since the allowable variation for each of the other analyses would require an even greater variation in feldspar content, they could all be replaced by a single requirement for uniformity of alumina.

DENSITY DETERMINATIONS OF REFINED SAND

Answers to questions about sand uniformity were required before commercial development could proceed, and a program of sampling and testing of sands was planned. My chief problem was the determination of the composition of numerous samples of refined sand. Not only were commercial analyses expensive, but there was doubt about their reliability. Some alternative methods including x-ray fluorescence were considered and abandoned. Finally it was suggested by John Butler of the Mackay School of Mines that because quartz and K-spar have different densities, it might be possible to correlate the compositon of the refined sands with their average densities. This idea was developed into a usable method that proved to be more dependable than individual chemical analyses. The effect of sand composition upon average density is shown by the calculations in table 4. A variation of ± 0.5 percent in the proportions of K-spar and quartz should cause a total variation of only 0.0011 g/ml in the average density. Thus the density values should be determined with five significant figures.

TABLE 2.—FELDSPARS AND THEIR COMPOSITION

Name	Formula	Composition, weight percent		
		K_2O, Na_2O or CaO	Al_2O_3	SiO_2
K-spar (Orthoclase or microcline)	$K_2O{\cdot}Al_2O_3{\cdot}6SiO_2$	16.9	18.4	64.7
Albite	$Na_2O{\cdot}Al_2O_3{\cdot}6SiO_2$	11.8	19.5	68.7
Plagioclase – Mixtures of albite and anorthite				
Anorthite	$CaO{\cdot}Al_2O_3{\cdot}2SiO_2$	20.1	36.7	43.2

TABLE 3.—CALCULATION OF MINERALOGICAL COMPOSITION OF AVERAGE SAND

Mineral	Calculation	Weight percent of mineral in sand
K-spar	$\frac{3.04}{0.169}$	18.0
Albite	$\frac{0.78}{0.118}$	6.6
Anorthite	$\frac{0.08}{0.201}$	0.4
Quartz	—	75.0 By difference

In the technique that was developed for determining average sand densities, all weights were determined to the nearest tenth of a milligram. This was preferably done with a modern single-pan balance on which the pycnometer could be weighed quickly before evaporation of water changed its weight. About 50 grams of dry sand were weighed and placed in a 50-ml pycnometer fitted with a thermometer through a ground glass joint and a side arm for final filling. The sand was covered with distilled water and the air in it was removed by gentle stirring while the mixture was heated to the bubble point of water. It is believed that steam bubbles nucleated on the tiny bits of air which otherwise could not be removed from the sand, and then the air diffused into

TABLE 4.—CHANGE IN DENSITY CAUSED BY 1 PERCENT CHANGE IN K-SPAR

Mineral	Handbook density g/ml	High spar sand		Low spar sand	
		Weight percent in sand	Contribution to density	Weight percent in sand	Contribution to density
K-spar	2.54	18.5	0.4699	17.5	0.4445
Albite	2.62	6.6	0.1729	6.6	0.1729
Anorthite	2.75	0.4	0.0110	0.4	0.0110
Quartz	2.65	74.5	1.9742	75.5	2.0008
		Density of sand	2.6281		2.6292
		Change in density		0.0011	

the steam to be carried away with it. Only in this way could consistent results be obtained. At first this was done by heating the pycnometer vessel in a small oven until bubbles appeared and then stirring the sand before it boiled over, but the care required and frequent mishaps made the method unsatisfactory. Figure 2 is a diagram of a deairing oven that facilitated this operation. The pycnometer body was held at an angle and slowly rotated on its axis by a small gear motor while a lamp at the end of the enclosing tube provided heat. The heat was adjusted by a Variac to give gentle boiling while a glass rod was inserted into the pycnometer through a hole in the enclosing wall to stir the sand.

After deairing, the pycnometer body and its contents were allowed to cool, and then it was filled with distilled water and the thermometer installed. Consistent results were obtained only by placing the assembly in a small wooden box for half an hour to allow it to come to a uniform temperature. Just before the final weighing the temperature was read to 0.05°C, and the side arm was filled and wiped off at the very top with water from a hypodermic needle.

Calculation of density from data on the weights of the sand, the dry pycnometer, and the total assembly involves the volumes of the pycnometer and the water in order to obtain the volume of sand by difference. To obtain the accuracy desired, a calibration curve was prepared showing temperature versus the volume of the pycnometer to 0.00001 ml. Water volume was calculated by multiplying its weight by the specific volume, to seven significant figures, for the temperature mentioned earlier.

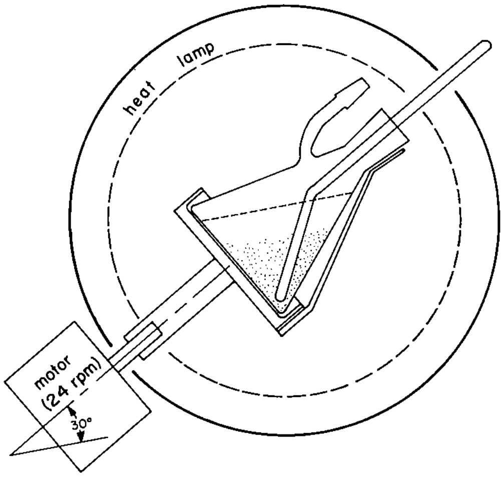


Figure 2. Cross-sectional view of apparatus for deairing sand in a pycnometer.

Density values obtained by dividing the weight of sand by its volume were recorded to five or six figures. While the sixth figure probably had little significance, the fifth one was generally reproducible within two units, and thus was significant. Tables 5 and 6 show that repeated determinations on the same sample either with the same pycnometer or with different pycnometers gave maximum variations of less than 0.0004 g/ml. Since it was determined later that the permissible variation corresponded to a density range of 0.0014 g/ml, it is clear that such density determinations might be used to indicate sand compositions.

One interesting observation was that the density determined for a sample shortly after it had been deaired was about 0.0002 g/ml lower than if determined several hours or more after deairing. This must be caused by dissolution in the water of a tiny volume of air remaining in the sand.

TABLE 5.—REPRODUCIBILITY OF DENSITY DETERMINATION ON SAME SAMPLE USING SAME PYCNOMETER

Date of determination	Density, g/ml
January 10, 1965	2.62875
February 23, 1965	2.62887
February 24, 1965	2.62872
February 25, 1965	2.62903
Maximum variation	0.00031

TABLE 6.—REPRODUCIBILITY OF DENSITY DETERMINATIONS ON SAME SAMPLE USING DIFFERENT PYCNOMETERS

Pycnometer number	Density, g/ml
1	2.6268
2	2.62715
3	2.6270
Maximum variation	0.00035

CORRELATION OF DENSITY WITH COMPOSITION

Complete chemical analyses of 17 samples of refined sand were used in correlating density with composition. Of these, nine analyses were available at first, and attempts at correlation were encouraging but not entirely convincing. Alumina analyses on two samples failed to fit a pattern established by the other seven, but when reanalysed later they fitted. Silica values determined by difference, mirrored the correlation of alumina values. The sum of the alkalies did not correlate well with density.

Table 2 shows that all of the feldspars contain alumina and alkali or alkaline earth oxides in equal molecular quantities. Thus values for alumina analyses and those for K_2O, Na_2O, and CaO could be used in a single correlation with density by calculating and plotting the moles of alumina in a given quantity of sand as well as the sum of the moles of alkali and lime. This has been done in figure 3 for analyses from all 17 samples. Certain analyses have been omitted from the plot because they were corrected by reanalysis, or because the samples are believed to have been contaminated during preparation. The values plotted in figure 3, all of which are based on analyses that appear to have been done correctly, vary considerably from the correlation. This is based on the assumption that the straight line on the figure is the correct correlation of composition with density and that the density determinations of the samples were correct. On the other hand, the variation in composition indicated by the correlating line and the densities reported in either table 5 or table 6 are small in comparison. Thus single density determinations should indicate the composition of sand samples more reliably than single chemical analyses, especially since more than a dozen points were eliminated from figure 3 because of questionable analyses.

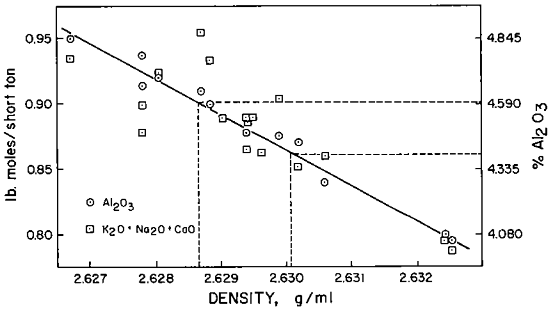


Figure 3. Correlation of average sand densities with chemical analyses. (Dashed lines show density spread corresponding to a variation of 0.2 percent alumina.)

SIZE DISTRIBUTION AND VARIATIONS IN DENSITY AND COMPOSITION

Several series of samples were prepared by refining the sands as described, then the density of each sample was determined. These series were designed to show the effects of different factors on sand densities and their variations.

The effect on the density of the refined sand of the fraction of crude sand removed by magnetic separation was studied by four tests made on identical portions of crude sand. Table 7 shows that this had no effect on the density or composition of the sand.

A sample of refined sand was screened and the density of each size fraction is reported in table 8. From these limited data, there are apparently at least two factors that work together to determine the quartz-feldspar proportions in the different sizes. Feldspar is softer and more easily broken than quartz. Thus feldspar would be expected to break down and enter finer sizes proportionately more rapidly than the quartz and will therefore become enriched

TABLE 7.—EFFECT OF PERCENTAGE REMOVED BY MAGNETIC SEPARATION ON DENSITY AND COMPOSITION

Percent removed as magnetic	Density, g/ml	Indicated Percent Al_2O_3
12.4	2.6290	4.54
22.2	2.6292	4.52
32.3	2.6290	4.54
42.0	2.6293	4.50

TABLE 8.—VARIATION OF DENSITY AND COMPOSITION WITH SIZE FRACTION

Size, mesh	Weight, percent	Density, g/ml	Indicated Percent Al_2O_3
Plus 28	1.0	—	—
28–35	16.5	2.6278	4.71
35–48	47.4	2.6269	4.83
48–65	26.0	2.6296	4.45
Minus 65	9.1	2.6318	4.16

as the size becomes smaller. This is the pattern when the 28-35 and 35-48 mesh fractions are compared, but it is not true for finer adjacent fractions. There must be another factor that helps remove feldspar from these finer fractions more rapidly than it is added through breakage of coarser particles. This is probably because of chemical weathering which would be more rapid on the feldspar than on the quartz. The increasingly greater specific surface area as the particles become finer permits weathering to remove feldspar at even higher rates resulting in the decreased alumina contents shown in table 8.

Sand in the river was carried in a leap frog sort of fashion for hundreds of miles, being swept up and redeposited repeatedly. This has resulted in wide variations in the general size of the sand in different places with some parts being quite coarse and others much finer. Natural classification is not perfect, however, so that even coarse deposits of sand carry much material of the size required for glass making. Two samples, one from a sand bar consisting of coarse-grained sand and the other consisting of a fine-grained sand, were studied to determine the effects that the depositional setting has on composition of the glass-sand sizes.

The hand-screened minus 28 mesh portions of these sands had different size distributions as shown by the curves in figure 4. The graph of the sample from the coarse-grained sand bar shows the truncated finer end of its size distribution, modified perhaps by imperfect screening of particles near the 28-mesh size. Nearly three quarters of this sample was coarser than 48 mesh and over half of it was between 35 and 48 mesh. Sand from the fine-grained sand bar on the other hand had almost no plus 28 mesh material to be removed, and the sample for study contained less than 15 percent of plus 48 mesh. Its most abundant size, with well over half of the sand contained in it, was the 48- to 65-mesh fraction, and there were substantial amounts of still finer sand.

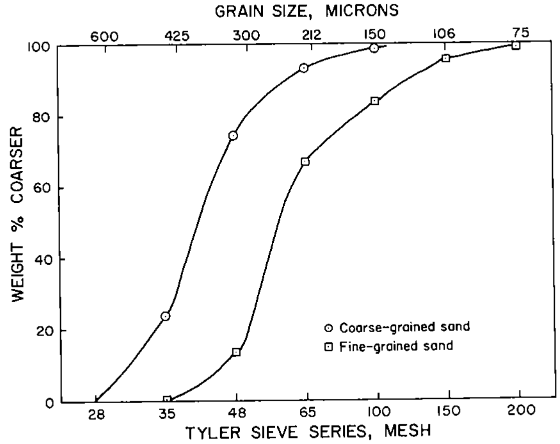


Figure 4. Plots of percent oversize versus screen size for minus 28 mesh samples screened from coarse and fine sand bars.

Since there was a whole screen size difference in the average size of the two samples, a difference in composition was expected. Thus in the hope of lowering this discrepancy, samples were prepared from each sand by screening and recombining weighed portions of the size fractions to yield identical size distributions. Then these prepared samples, and naturally occurring ones, were refined and their densities determined as shown in table 9. It was surprising and gratifying to find that the natural size distributions yielded identical densities, and that the adjustment to identical size distributions had caused a wide difference. Other experiments also indicated that sands with their natural size distributions were generally more nearly uniform in composition than those with size distributions adjusted to be identical.

In the commercial operation that was contemplated, the crude sand for refining would consist of the fines rejected by a sand-production unit as well as sand pumped from fine deposits in the river. In order to simulate sand that might be available for refining over a long period of time, 15 samples were refined with their natural size distributions. Several of these were taken directly from widely separated places from sand bars in the river at times

TABLE 9.—DENSITY OF REFINED SAND FROM COARSE AND FINE DEPOSITS

Parent sand	Density, g/ml	Indicated Percent Al_2O_3
Samples with natural size distributions		
Coarse	2.62875	4.58
Fine	2.62875	4.58
Samples with identical size distributions		
Coarse	2.6302	4.37
Fine	2.6278	4.71

more than a year apart, and others were taken at weekly intervals from the fines-discharge pipe of the operating sand plant.

Statistics on the distribution of the densities of these samples are shown in table 10. If the requirement for uniformity is for sample densities to be within a range of 0.0014 g/ml centered on the average density of 2.6291, then only three samples fall outside the range and one of these is just barely outside. These samples came from points in a very large amount of material, yet they very nearly meet the uniformity requirement. Mixing occurring during processing should help keep the products uniform, if care were taken to avoid segregation.

Even though feldspar and quartz are only slightly different in density and their particles have generally similar shapes, under some circumstances it is possible that they might become segregated while being deposited from flowing water. Such segregation may occur in the river, but an analysis there appeared too complicated to be attempted. However, there was a low pile of fine sand several hundred feet across that had been built up by discharging the water and fine sand overflow from construction-sand classifiers onto the pile and letting the water flow back to the river. Since the water flowing in shallow streams had carried the sand away from the discharge point in all directions and built up sort of a flat cone-shaped pile, the sand would likely have been segregated as to size and perhaps also as to composition. Because this pile of sand would be used first in any commercial sand-refining operation, it became essential to study it.

Thirty-two samples of sand were taken by augering a hole through the full depth of sand. Sand depths ranged from about 9 feet near the center to about 2 feet near the edges. The minus 28-mesh material from each sample was refined and its density determined. These values were plotted in their proper positions on a map of the pile, and lines were drawn to represent contours of equal density as shown in figure 5. It may be seen that the sand was severely segregated with the central portion near the discharge pipe having higher densities than the edges which were enriched in the lighter feldspar. When this pile was subsequently mined for feed to the refinery, it was necessary to mix material from the edges with that from the center in order to maintain a reasonably uniform product. Failure to do this one time resulted in difficulty at the glass plant because the alumina content of the glass became too high.

CONCLUSIONS

A study was made of the variability of quartz-feldspar sands from the Arkansas River prior to commercialization of the sands as material for making colorless

TABLE 10.—DISTRIBUTION OF DENSITIES OF NON-SEGREGATED SANDS FROM RIVER AND PLANT

Number of samples	Density, g/ml Within specification	 Outside specification
1		2.6300
1	2.6298	
6		
Average	2.6291	
5		
	2.6284	
1		2.6283
1		2.6280

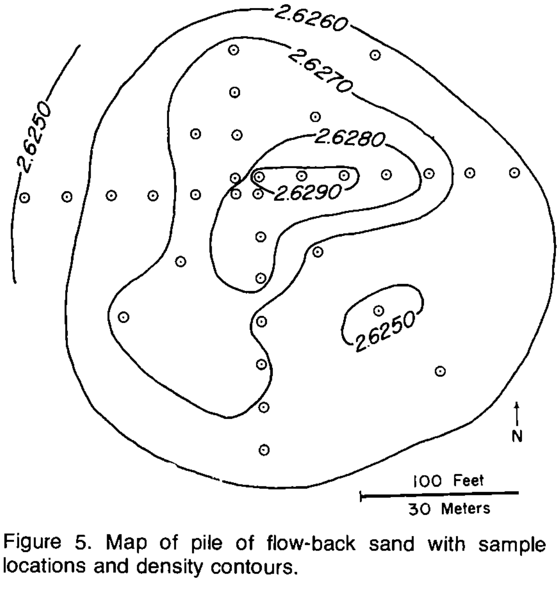


Figure 5. Map of pile of flow-back sand with sample locations and density contours.

container glass. A method was developed for use in this study to estimate the composition of refined sand by determining its average density to five significant figures. This method proved to be more dependable than chemical analyses of the samples.

The study showed that the fraction of material removed during refining did not cause the composition to vary. Variations in composition of different size fractions of sand were explained by the opposite effects of the softness of feldspar and its lower resistance to weathering. Fine feldspar with a high surface area weathers away faster than it is created by the breaking of coarser particles. When fine sand is washed down a gentle slope and deposited there, the quartz and feldspar can become segregated with the feldspar being enriched down slope. It was concluded that the requirement for chemical uniformity of refined sand specified by a glass manufacturer could be maintained if care were taken to avoid segregation of the sand.

REFERENCES CITED

Bowdish, F. W., 1955, Investigations into the beneficiation of river sands from Kansas and application of the resulting processes: Thesis for Professional Degree, Montana School of Mines, 64 pages.

______1967, Opportunities in the beneficiation of feldspathic sands *in* Angino, E. E., and Hardy, R. G., editors, A symposium on industrial mineral exploration and development: Kansas Geological Survey Special Distribution Publication 34, p. 126-131.

Bowdish, F. W., and **Runnels, R. T.**, 1952, Experimental production of feldspar and silica from several river sands in Kansas: Kansas Geological Survey Bulletin 96, pt. 6, p. 279-300.

IMPACT OF ENVIRONMENTAL CONSIDERATIONS ON THE INDUSTRIAL-SAND INDUSTRY

RICHARD A. HUNNISETT[1] and GEORGE H. DIDAWICK[1]

Abstract—Silica sand is one of the world's most plentiful resources and is a basic necessity in our way of life. The end uses of silica sand are an integral part of our homes, transportation, and places of work.

The environmental legislation enacted in the early 1970's, coupled with the oil embargo and higher than normal inflation, have had a very real impact on the industry and its primary consumers, the foundries and glass producers. The present environmental laws directed at air and water pollution and the working environment can, in most cases, be met, but not without large capital expenditures for equipment. These expenditures must reduce the funds available for expansion and modernization of existing processes which are necessary if the costs to produce industrial sand are to remain at acceptable levels. The concern for the future is the enactment of more stringent laws, and the available technology and equipment to economically comply with them.

INTRODUCTION

The term industrial-sand industry, as used here, covers those plants producing foundry sand, oil-well "frac" sand, and high-purity silica sand (used primarily as a melting sand by the glass industry). The processes used in operating these plants include quarrying, crushing, washing, drying, grinding, and shipping both bulk and bagged material.

In common with all industry, industrial-sand plants are affected by the federal and state legislation concerning plant effluents, air pollution, and the working environment. In attempting to meet this legislation, the expenditures have been substantial. Over the past six years it is estimated that 11 percent of total capital expenditures, or $23.0 million, have been spent on equipment directly related to pollution control. An additional $7.5 million will be required in the next four years to bring the plants, presently operating under a variance from the law, into compliance.

This level of capital spending that is required just to remain in operation must limit, at least in the short term, the finances for more efficiently producing the industrial sand. In the meantime, operating costs, particularly those for fuel and power, go up. Indeed, apart from using capital at zero return, the environmental installations add to the already increasing operating costs.

ENVIRONMENTAL CONSIDERATIONS

If we consider that investment opportunities giving returns of 12 percent after taxes were lost because of the environmental expenditures, a truer cost to the industrial-sand industry between 1972 and 1981 would be closer to $60.0 million or $0.20 per ton produced during those years.

What do we get for these expenditures? How well do they allow compliance with the legislation? How clean will the water and air be, and how acceptable the working environment? What problems, if any, remain unsolved, and what is the practicality of meeting them? Some of these questions can best be answered by briefly reviewing what is presently being done.

Water Pollution

As of July 1, 1977, or until presently held permits expire, Environmental Protection Agency (EPA) effluent guidelines that will apply for industrial-sand plants are:

No discharge will be allowed of process water or any pollutants they carry. Mine

---

[1] Pennsylvania Glass Sand Corporation, Berkeley Springs, West Virginia.

dewatering discharge will be limited to a maximum daily concentration of suspended solids of 30 mg/liter (approximately 30 ppm) and a pH range of 6.0 to 9.0, although, under certain natural circumstances, a discharge may have a pH as low as 5.0. However, the overflow from settling-pond dams caused by excessive storms will be allowed, and area runoff is not regulated, unless the runoff enters the process or mine dewatering impoundments. Obviously, meeting these requirements will all but eliminate pollution of the country's streams and rivers by the industrial-sand industry.

Industrial-sand plants use large quantities of water in their washing processes to remove clay and the fine sand with as much as 100 gallons/minute per ton used. In many cases, thickeners and settling ponds have always been part of the plant process circuit so that most process water could be reclaimed. However, the finer sand and clay that settled during washing were discharged into the natural waterways. Additional settling ponds are now required to contain the fine sediments, and pumping installations to return the clarified water from these ponds. Putting all plant process water in closed circuit are mandatory. Approximately 15-20 percent of mined material consist of unsalable fine sand and clay. For the industry this amounts to over 5 million tons per year that must be impounded.

The cost to provide and operate the ponds can vary a great deal, depending on the availability of land close to the plant and the topography of the terrain. A recent investigation of a 1-million-ton-a-year silica-sand plant in Pennsylvania showed that over the next six years the capital and operating cost of providing settling ponds and pumping to and from them will add at least $0.10 a ton to the operating cost.

A flocculating agent is often, but not always, required to achieve adequate settling of the suspended particles, and this can affect flotation circuits. Closing the water circuit at one plant increased chemical costs for flocculation and flotation by $0.04 per ton. These costs are significant and increasing.

Air Pollution

The areas of the plant that require controls for preventing air pollution are stack gases from the combustion of fuel in indirect–heat exchangers, such as coal–and oil–fired boilers, pollution from process operations, and fugitive dust. The pollutants from these sources are emissions of particulates and sulfur dioxide which cause opacity.

The regulations covering stack emissions from the combustion of fuel are normally related to the amount of btu's generated per hour. The permitted emissions per hour from process operations are based on process through weight per hour. The allowable concentrations are often again modified depending on locality and size of operation.

In general a plant in a populated area will have tighter restrictions than a plant in a rural area. Most industrial-sand plants will be considered small polluters and as such will have the less stringent requirements.

Industrial–sand plants have for many years used dust collection in their crushing, dry screening, pulverizing, and material handling situations. Many of these installations met the particulate emission standard; others required the installation of a more efficient collector.

Cleaning the stack gases from fuel-burning units, very few of which had collectors on them in the past, is the greatest additional capital expenditure. These collectors, although often the same design as those used for dust collection (namely wet scrubbers) have a 30 percent higher capital cost because of the extensive use that must be made of stainless steel to overcome the corrosive action of the sulfur dioxide. Operating costs of dust and stack collectors in the industrial-sand industry will add anywhere from $0.07 to $0.14 per ton to operating costs.

Table 1 shows how effective a wet impingent-type scrubber is on the particulate matter in the stack gases from an oil-fired fluid-bed sand dryer.

The cost to the industrial-sand industry, high as it is, to meet the air-pollution requirements would be much greater if the more stringent sulfur dioxide emission standards, such as are required of power plants, were required of them. It is hoped that such standards will not be applied to all industry until the newer developments to solve the sulfur dioxide problem are more thoroughly tested and have become more economic. Such developments involve improved coal preparation to reduce the coal's

TABLE 1. FLUID-BED DRYER STACK TEST
(location, Pennsylvania; collector,
impingent-type scrubber)

	Test 1	Test 2	Test 3
Stack gas flow rate SCF at 70° F	26,800	29,000	30,000
Particulate concentration Grains/SCF	0.003	0.005	0.004
Allowable concentration Grains/SCF	0.04	0.04	0.04
Pollutant mass rate lb./hr.	0.746	1.34	0.923
Allowable mass rate lb./hr.	9.8	9.8	9.8

TABLE 2. DUST-SURVEY RESULTS
(location, inside primary-crusher control room)

Date	Threshold Limit Value mg/M^3	Air Sample mg/M^3
October 1971	0.20	0.6255
"		1.2284
"		0.7023
January 1972 Installed Electrostatic Air Cleaner		
February 1972		0.0190
"		0.0086
"		0.0155
"		0.0051

sulfur content, improved lime-based systems for stack-gas scrubbing, and the development of synthetic fuels.

Working Environment

Federal regulations for the condition of the working environment are issued and enforced by the Mining Enforcement and Safety Administration. Apart from safety regulations, which are not considered here, maximum allowable noise levels and respirable free-silica-dust levels have been established.

The maximum allowable noise level of 90 decibels is being successfully met by isolation of equipment, isolation of the worker in a control booth, and (or) silencers on the equipment.

For the respirable free silica dust, the maximum time weighted allowable level for a daily 8- to 10-hour exposure, or the threshold limit value, calculates to approximately 0.20 mg/m^3 for industrial-sand plants. This is assuming a 50 percent silica level in the dust.

Careful attention to the maintenance of dust collecting equipment, limiting exposure in areas of known dust hazard, improving housekeeping with the use of large vacuum cleaners, and the use of electrostatic air cleaners in control rooms has allowed the threshold limit value to be reached for most workmen without the use of respirators. Table 2 shows the effect of an electrostatic air cleaner used in a crusher control room.

In the areas such as bagging ground and unground sand and bulk loading, however, it is more difficult, certainly in the short term, to reduce the airborne concentration of dust to safe levels by dust control alone, and there is the problem of the maintenance worker who must at times enter the dust collector itself. In these circumstances we do what we can by dust control and then protect our work people with respirators. An interesting alternative to the face mask respirator is the airstream anti-dust helmet which provides head, eye, face, and lung protection, togther with a high degree of user comfort.

CONCLUSION

In conclusion, we can say that the cost to meet the present environmental legislation concerning plant effluent, air pollution, and the working environment has been and will continue to be high. Some plants have closed because of it, other plants must accept smaller profit margins or increase the product price and thus add to the inflationary trend.

The effect would have been more crippling if water conservation and dust collection had not been a major consideration in the industrial-sand industry since the 1930's, and much of the basic equipment to meet the legislation had already been installed.

However, existing practical technology is already being applied and further tightening of the constraints, particularly in the area of air pollution, could be difficult, costly, and unnecessary. Compliance with the existing environmental codes virtually eliminates water pollution, cleans the air dramatically, and provides an acceptable working environment. Of course in the future the evaluation of potential industrial-sand deposits must take more fully into account the aspects of environmental control.

TRIPOLI DEPOSITS OF SOUTHWEST MISSOURI AND NORTHEAST OKLAHOMA

W. F. QUIRK[1] and A. K. BATES[2]

Abstract—The Missouri-Oklahoma tripoli district was discovered and first mined in 1869 near Seneca, Missouri. Tripoli is a microcrystalline form of high-purity silica that is porous, lightweight, and friable and is derived from a parent siliceous sedimentary rock from which soluble minerals have been leached. Tripoli deposits, 2 to 20 feet thick, occur in cherty limestones of Mississippian age beneath 2 to 10 feet of overburden. They are mined in open pits up to 9 acres in size. The color of tripoli is white, but it also commonly is light pink or red where stained by red iron oxides and clays. Ground tripoli is used commercially as an abrasive or in buffing and polishing compounds and is prized for such physical characteristics as its abrasiveness, porosity, permeability, absorption, and specific gravity.

INTRODUCTION

The name tripoli was originally applied to siliceous material found near Tripoli in North Africa. In the late 1800's, it was also applied to material found near Seneca, Missouri, that appeared similar to North African tripoli. Subsequent studies showed that the two materials are quite different; the North African material, which consists of siliceous skeletons of diatoms, is now called tripolite. The Seneca deposits, which are still referred to as tripoli, consist of a microcrystalline form of high-purity silica (SiO_2) that is porous, lightweight, and friable and that apparently is derived from a parent siliceous sedimentary rock from which soluble minerals have been leached. The term tripoli is also now applied in a general way to most silica deposits similar in physical characteristics and geologic origin to the Seneca deposits (Bradbury and Ehrlinger, 1975).

The Missouri-Oklahoma tripoli district, with Seneca near the center, includes several small to medium deposits scattered in Newton County, Missouri, and Ottawa County, Oklahoma (fig. 1). Major mining areas in the district are near Peoria, Oklahoma, and Seneca, Racine, and Spring City, Missouri; although additional deposits are found in the area from Spring River on the west to Neosho on the east.

GEOLOGIC SETTING

Tripoli occurs as flat-lying deposits that are 2 to 20 feet thick. The deposits typically are located beneath a thin overburden of topsoil and residuum on broad, flat-topped hills. Overburden is commonly 2 to 10 feet thick and consists of a poor grade of "rotten" tripoli that grades up into red-brown cherty clay at the surface. Individual deposits are lenses or pockets that range in size from a few tens of feet across to several acres, and the largest known deposit, located 0.8 mile south of Peoria, is about 9 acres.

Tripoli in the Missouri-Oklahoma district occurs in cherty limestones of Mississippian age that previously were assigned to the "Boone Formation." According to current stratigraphic nomenclature, most of the tripoli occurs in the Warsaw Formation, with the remainder in the underlying Keokuk Formation (Fellows, 1967).

Chert occurs in many of the deposits, and in some places it negates the commercial value of the deposit. Primary chert occurs as interbedded layers and nodules, whereas secondary chert results from later deposition in near-vertical cracks and fissures (Dobbs, 1960).

---

[1] Electro Minerals Division, The Carborundum Company, Niagara Falls, New York.

[2] American Tripoli Division, The Carborundum Company, Seneca, Missouri.

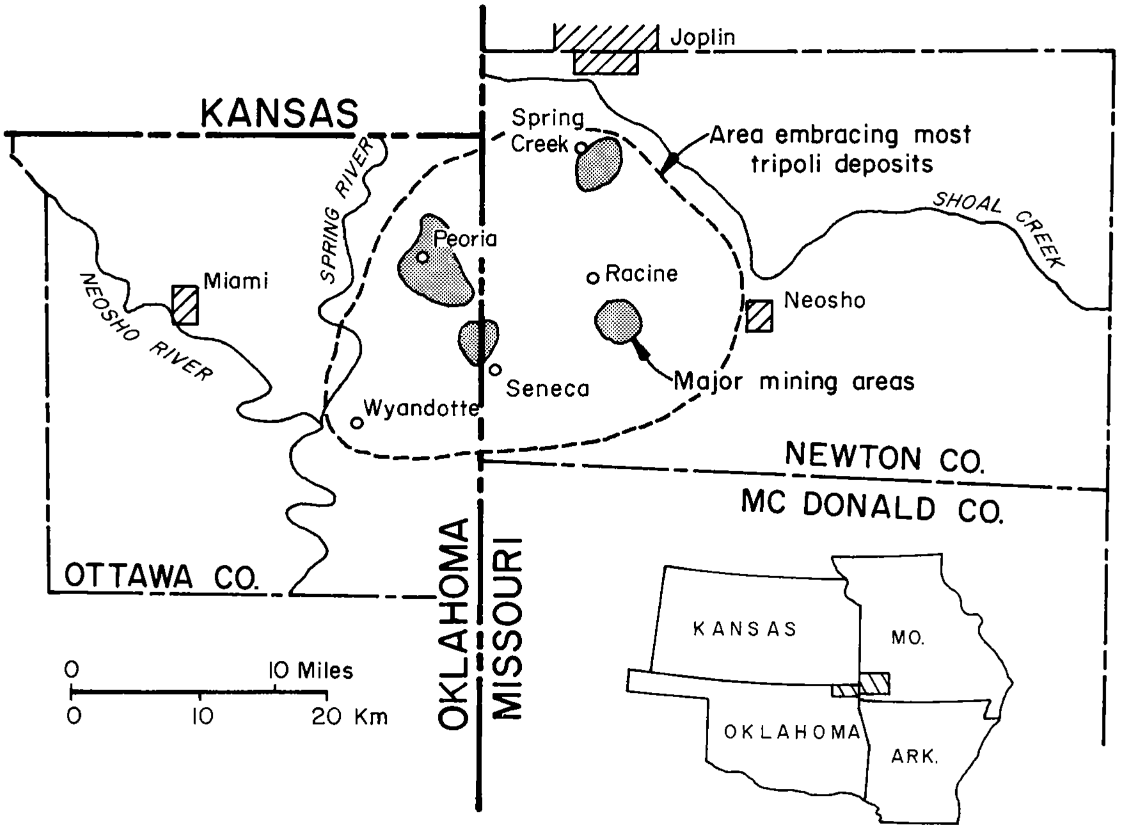


Figure 1. Map showing area of Missouri-Oklahoma tripoli district and major mining areas within the district.

PHYSICAL AND CHEMICAL CHARACTERISTICS

Tripoli consists almost entirely of double-refracting chalcedony and has a purity of 90 to 98 percent silica (SiO_2). It typically is soft, porous, and fibrous, and the average grain size is less than 0.01 millimeter. When ground, the individual grains lack sharp edges or corners and have a grain size ranging from 100 microns to 0.02 micron.

The bulk weight of crude tripoli from the quarry averages 35 pounds per cubic foot, and this led early residents to refer to the material as "cottonrock." Although the bulk weight is low, the specific gravity of the mineral grains is high, ranging from 2.15 to 2.6. The porosity of the crude tripoli is 45 percent, whereas the powdered or ground tripoli ranges from 63 to 68 percent, depending upon fineness (Dobbs, 1960). Absorption of water is 35 percent by weight for crude tripoli and 52 percent for the ground variety. Oil absorption ranges from 48 to 52 percent (by weight), depending upon how fine it is ground.

For commercial purposes, the tripoli is classified as *cream* for the white deposits and *rose* for the light-pink to red deposits. Both types are found in the same areas and, in fact, are intermixed in some of the quarries. The rose tripoli is colored by red iron oxides and clay that have percolated down through the red clay overlying the deposit. A flint-like cap overlying the cream-colored deposits is sufficiently impermeable so that iron oxide and clays do not penetrate and thereby color the tripoli.

Aside from color, the principal differences between the rose and cream tripoli are in their chemical composition (table 1). The rose tripoli contains more iron oxide, alumina, and titania than the cream variety, and these elements contribute to the color of the product. Variation in the concentration of these three oxides from deposit

TABLE 1.—AVERAGES OF CHEMICAL ANALYSES FOR ROSE AND CREAM VARIETIES OF TRIPOLI FROM MISSOURI-OKLAHOMA DISTRICT

Constituent	Percentage	
	Rose	Cream
SiO_2	92.08	97.81
Fe_2O_3	1.29	0.29
Al_2O_3	3.63	0.64
TiO_2	0.11	0.01
Other	1.02	0.74
LOI (not including moisture)	1.87	0.51
pH	4.6	6.5

to deposit accounts for the color gradation from light pink to dark red. Because of the chemical constituents, the fusion point of the rose tripoli is 2985°F whereas that of the cream is 3105°F.

The following is the summary of a company report provided to American Tripoli Division in 1948 by A. E. Austin and C. M. Schwartz:

> "Physical properties of Rose and Cream Tripoli have been determined by optical and electron microscopy, X-ray diffraction, air classification and specific surface area measurements. The particle size distribution ranges from 100 micron down to 0.02 micron in diameter. There is a larger amount of very fine particles in the Rose variety than in the Cream variety. Specific surface area as determined by nitrogen-adsorbtion measurements range from 11.9 square meters per gram for the Rose variety down to 4.7 square meters per gram for the Cream variety. X-ray diffraction shows that Tripoli has the crystal structure of alpha quartz. Optical examination shows it to be of the chalcedony form of silica which does have the quartz structure."

ORIGIN

Several hypotheses have been advanced over the years on the origin of the Missouri-Oklahoma tripoli deposits, but no fully acceptable explanation has been made as to why these deposits are concentrated in this relatively small district.

One of the early theories held that the beds of tripoli are the result of weathering and alteration of thick beds of chert (Perry, 1917). It was also suggested that the tripoli is the residual concentration of porous silica after leaching of siliceous limestone or calcareous chert (Fellows, 1976; Bradbury and Ehrlinger, 1975). However, it is our belief that these tripoli deposits are due to deposition of colloidal silica and alkaline salts, and that subsequent dissolution of the soluble alkalies has left the silica little changed from its original condition. This view is well summarized in a company report prepared in 1931 by G. V. B. Levings, who was manager of American Tripoli Division from 1919 to 1937:

> "The deposits are of sedimentary origin found in the Boone formation of the lower Mississippian. They have not been subjected to any appreciable faulting and no folding or crushing; they remain in their original condition except for the removal of the soluble alkalies by percolating surface waters where the conditions have been favorable. It is in no sense an altered chert, as was at one time assumed from the fact that primary chert occurs in the deposits. These chert occurrences are identical with those in the neighboring siliceous limes . . . . The present Tripoli is not a product of alteration, decomposition or disintergration, it is simply the original silica remaining after the soluble alkalies, which constituted a considerable portion of the original mass had been removed; it has very evidently experienced little change from its original condition other than an evident hardening and increased density."

PRODUCTION TECHNIQUES

Mining has been carried on in the Missouri-Oklahoma tripoli district since 1869. All mining now is by open-pit methods following removal of overburden in a ratio that rarely exceeds 1:1. After the surface of the tripoli is cleaned, to prevent contamination by clay, the material is blasted into large chunks that can be sorted by hand according to color and grade. At this time nodules or other masses of chert are hand cobbed and discarded.

Crude tripoli is highly absorbent and quarry-run material contains 20 to 35 percent moisture, depending upon the weather conditions. Therefore, the crude tripoli is stored in drying sheds for several months before it is processed in the mill at Seneca. Tripoli is then crushed, dried in a rotary dryer, and then ground in a hammermill and a tube mill. The powder then passes through screens and air separators and is packed in 100-pound bags for shipment to domestic and foreign users.

INDUSTRIAL USES

Industrial use of tripoli is not based mainly upon its chemical purity, but upon such physical characteristics as abrasiveness, porosity, permeability, absorption, and specific gravity. Early uses included cut blocks for filtering water and for use in scouring and polishing. Currently, however, most tripoli is crushed and used as an abrasive or in buffing and polishing compounds. As an abrasive, it is used in soaps, cleansers, powders, and teeth-cleansing preparations, whereas the buffing and polishing compounds are used mainly in lacquer finishing and the automobile industry. Ground tripoli is also used as fillers and extenders in paints and plastics. Other uses include foundry parting, wood finish, insecticides (fillers and carriers), and cosmetics.

REFERENCES CITED

Bradbury, J. C., and **Ehrlinger, H. P., III,** 1975, Tripoli, *in* Lefond, S. J., editor, Industrial minerals and rocks, 4th ed.: New York, American Institute of Mining, Metallurgical, and Petroleum Engineers, Inc., p. 1209-1218.

Dobbs, E.H., 1960, Missouri-Oklahoma type tripoli: Annual Meeting of American Institute of Mining, Metallurgical, and Petroleum Engineers, New York, February 14-18, 1960, Preprint no. 60H41, 5 p.

Fellows, L. D., 1967, Tripoli, *in* Mineral and water resources of Missouri: Missouri Division of Geology Survey and Water Resources, v. 43, Second Series, p. 220-223.

Perry, E. S., 1917, Tripoli deposits of Oklahoma: Oklahoma Geological Survey Bulletin 28, 32 p.

ARKANSAS NOVACULITE—A SILICA RESOURCE

DREW F. HOLBROOK[1] and CHARLES G. STONE[1]

Abstract—Most of the siliceous rocks of the Arkansas Novaculite are novaculite, but they also include some chert, siliceous shale and, rarely, sandstone. Novaculite is defined as a homogeneous mostly white or light-colored rock, translucent on thin edges, with a dull to waxy luster, and comprised almost entirely of microcrystalline quartz. The most plausible theory of origin for novaculite is that primary silica from submarine volcanism was picked up by organisms and deposited as amorphous silica, which was subsequently converted to microcrystalline quartz (novaculite) through diagenesis. The Arkansas Novaculite crops out over an east-west distance of 200 miles in the Ouachita Mountains of Arkansas and Oklahoma. Three divisions of the formation have been defined: a Lower Division, almost entirely massive light-colored novaculite; a Middle Division of interbedded dark chert and shale; and an Upper Division of massive calcareous novaculite. The Lower Division and most of the Middle Division are Devonian in age, and the remainder of the Middle Division and all of the Upper Division are Mississippian. The massive novaculites of the Upper and Lower Division attain their maximum development along the southern and central outcrop belts of the formation in Arkansas, and it is these rocks that are the source of current silica production. The calcareous novaculite of the Upper Division weathers readily to a light-colored, porous, less brittle rock, and in places to tripoli deposits. Currently tripoli is mined from a single deposit near Hot Springs, Arkansas, and the rock is processed for highly specialized filler and abrasive applications. In the vicinity of Hot Springs, Arkansas, certain novaculite layers from the Lower Division with unique textural characteristics are quarried and processed into whetstones. Several small quarries produce this rock for two local and one out-of-state whetstone-fabricating plants. Chemical analyses of composite samples of novaculite from both the Upper and Lower Divisions taken at widely separated localities average 99 percent SiO_2 indicating a substantial resource of high-silica rock.

INTRODUCTION

For many years siliceous rock in the vicinity of Hot Springs, Arkansas, has been used as whetstones. In his book on the geology of Missouri and Arkansas, Schoolcraft (1819, p. 183) named the rock novaculite, a term that had been in use for sometime to describe a fine quality of whetstone. In 1892 Griswold published a comprehensive report on the very fine grained siliceous rocks of the Ouachita Mountain region in Arkansas entitled, *Whetstones and the Novaculites of Arkansas*. He mapped these rocks and called them the Arkansas Novaculite, but he included what is now known as the Bigfork Chert in the mapped unit. It was Purdue in 1909 that named the group of siliceous rocks lying between the Stanley Shale and the Missouri Mountain Shale as the Arkansas Novaculite. Other workers identified the Arkansas Novaculite in the Black Knob Ridge and Potato Hills in McCurtain County, southeast Oklahoma. The Arkansas Novaculite is comprised largely of novaculite, lesser amounts of shale, and a few thin sandstone beds. This report is concerned particularly with those deposits of novaculite that are the source of current tripoli and whetstone production and that are a potential source of these and other industrial mineral products.

DEFINITION OF NOVACULITE

When the term novaculite was first applied to the rock found in the vicinity of Hot Springs, Arkansas, it referred to a white siliceous rock whose textural characteristics and hardness made it particularly suitable for whetstones. Griswold (1892, p. 89) in fact described the fine-grained whetstone known as Arkansas Stone as a "true novaculite satisfying all the necessary conditions regarding homogeneity, grittiness, finely granular structure and siliceous composition, it is translucent on the edges and has a marked conchoidal fracture." As mapping of these remarkable rocks was extended throughout the Ouachita Mountains, the

---

[1] Arkansas Geological Commission, Little Rock, Arkansas.

term novaculite was retained to describe them despite the fact that they showed some variation in both physical and chemical characteristics from place to place. To accommodate these variations, novaculite is here defined as a homogeneous, mostly white or light-colored rock, translucent on thin edges, with a waxy to dull luster, and almost entirely comprised of microcrystalline quartz.

ORIGIN OF NOVACULITE

The subject of the origin of the novaculite in the Arkansas Novaculite has intrigued geologists ever since the rock was first identified, not only because of its unusual texture, but also because it is essentially pure silica that occurs in massive layers over a very broad area. At the time that Park and Croneis (1969) published their version of the origin, 13 alternatives had already been proposed. They grouped those theories into three categories: direct precipitation of silica by chemical or organic means; replacement of non-siliceous deposits; recrystallization and silicification of volcanic material. As a result of their studies of both the Arkansas Novaculite and the Caballos Novaculite of Texas, they proposed that novaculite was formed from organically precipitated silica particles in the 1 to 10 micron range, and that the ultimate texture was the result of diagenetic processes. More recently Lowe (1975) has agreed that siliceous organisms were the local source of the silica in the novaculite, but proposed further that volcanism away from the immediate sites of accumulation may have provided much of the primary silica.

DESCRIPTION OF ARKANSAS NOVACULITE

The Arkansas Novaculite crops out along the borders of the Benton-Broken Bow Uplift in Arkansas and southeastern Oklahoma and at Potato Hills and Black Knob Ridge in southeastern Oklahoma, a distance of some 200 miles (fig. 1). The formation varies in thickness throughout its outcrop area. It attains its maximum thickness, 950 feet, near West Hannah Mountain in Polk County, Arkansas. It thins rather gradually both eastward and westward from this point, but it thins very rapidly northward. Miser (1917) subdivided the formation into three lithologic divisions based on the exposures at Caddo Gap, Arkansas; a Lower Division of almost entirely massive white novaculite, a Middle Division of interbedded dark chert and shale, and an Upper Division of massive mostly calcareous novaculite (fig. 2).

Very few fossils have been found in the Arkansas Novaculite. Findings thus far have been limited mostly to conodonts, sponge spicules, radiolarians, and spores. Hass (1951), on the basis of conodont studies at Caddo Gap, placed the Lower Division of the formation and all except the upper 28 feet of the Middle Division in the Early or Middle Devonian. The remainder of the Middle Division and all of the Upper Division were defined as Early Mississippian in

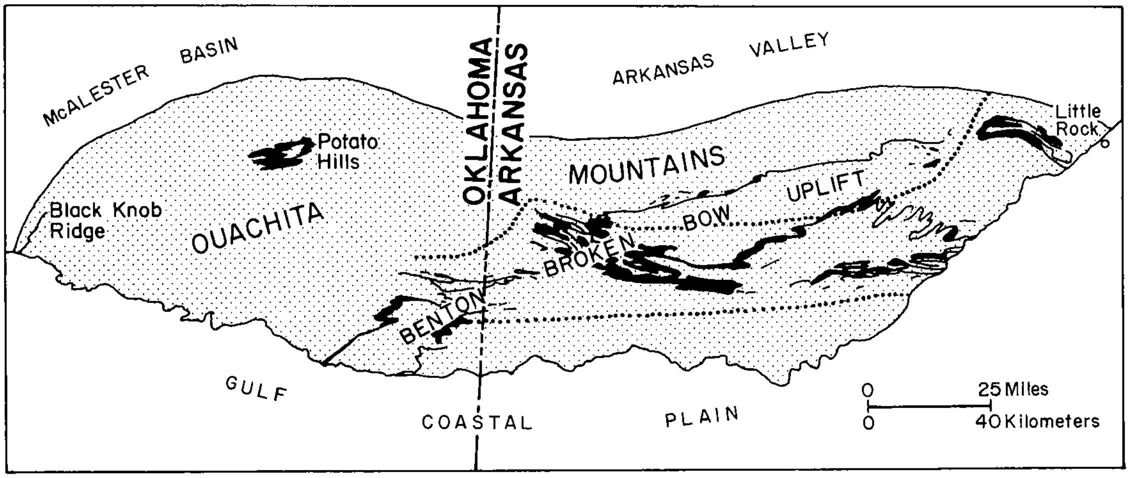


Figure 1. Map of Ouachita Mountains (stippled area) region showing outcrop of the Arkansas Novaculite (black lines) in Arkansas and Oklahoma. Thick, shale-free portions of novaculite unit are within area outlined by dots.

age. The contact between the Arkansas Novaculite and both the underlying Missouri Mountain Shale and the overlying Stanley Shale are conformable.

The Ouachita Mountains are a product of extensive folding and thrust faulting followed by erosion. This intense deformation resulted in the folding and fracturing of the novaculite beds as well as the variation in the attitude of these beds at different places. Along the southern belt of exposures of the formation, particularly, the massive novaculite of the Lower Division forms the steep-sided ridges of the region. The Middle Division cherts and shales underlie very narrow adjacent valleys, and the thinner bedded less resistant novaculites of the Upper Division are frequently expressed as a series of low knobs paralleling the main ridges.

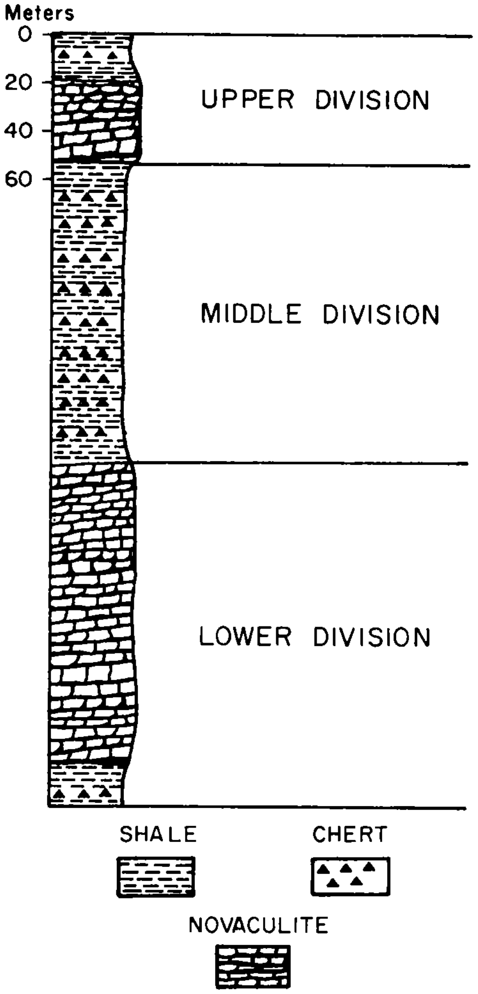


Figure 2. Diagrammatic columnar section of the Arkansas Novaculite (after Sholes and McBride, 1975).

The relative proportions of each constituent (novaculite, chert, and shale) of the Arkansas Novaculite vary throughout the outcrop area. The thicker shale-free sections of novaculite, which are the particular concern of this report, are restricted to the Upper and Lower Divisions along the southern and central outcrop belt, specifically that segment of the outcrop belt within the area outlined by the row of dots on figure 1.

Lower Division

The Lower Division of the formation contains the thicker sections of novaculite that form the most prominent ridges and outcrops. This division in the southern outcrop belt is comprised of massive novaculite in beds 4 to 30 feet thick with the thicker beds being near the top. The novaculite is white, gray, or light brown, with black and reddish-brown beds in a few places. Near the base of the division the massive novaculite is slightly calcareous, and it is the leaching of the calcite rhombohedra that has developed the whetstone texture found in the novaculite near Hot Springs. Laminations are present throughout the Lower Division novaculite but they are particularly prominent near the base. Jointing is common, the most prevalent set being normal to the bedding and the joints are frequently filled with quartz. A few very widely spaced thin shale beds are present, and in places thin quartzitic sandstone beds occur near the base of the Lower Division.

Upper Division

The Upper Division of the novaculite is generally thinner than the Lower Division, attaining a maximum thickness of 120 feet at Hot Springs and thinning abruptly to the north and south and gradually to the west. This division is entirely absent from the northern outcrop belt except near Little Rock. Beds are even to irregular and up to four feet thick. It consists chiefly of massive novaculite that when fresh is light gray to bluish black and generally resembles the novaculite of the Lower Division. In much of the area, however, the Upper Division novaculite is calcareous, and it has weathered to a light-brown or buff-colored punky rock with a gritty texture giving it the appearance of a porous siltstone. Weathered novaculite varies from a firm, slightly porous rock to tripoli depending on the percentage of carbonate present in the original rock. The carbonate in the fresh novaculite, which can constitute up to 30 percent of the rock, may be rhodochrosite, calcite, manganiferous calcite, or ankerite. In fact, it is the manganese-bearing carbonates that are the primary source of the manganese in the ores found in both the Upper and Lower Divisions of the Arkansas Novaculite in the southern outcrop belt.

TRIPOLI

The term tripoli is used in this report in the geologic sense rather than as a trade term, and it refers to a microcrystalline, finely particulate, more or less friable form of silica. In the Ouachita Mountain region of Arkansas and Oklahoma, the tripoli deposits have been formed by the leaching of calcium carbonate from the Upper Division of the Arkansas Novaculite. Tripoli deposits and prospects occur in three general areas of novaculite outcrop (fig. 3). East-northeast of Hot Springs, tripoli float and outcrops occur on the flanks of the novaculite ridges in T. 2 S., R. 18–19 W., Garland County, Arkansas, and the only currently active tripoli mine, Malvern Minerals Company operation, is located in this area. Further west at Blocker Creek are two quarries in sec. 1, T. 5 S., R. 27 W., Pike County, Arkansas, that mark the eastern end of a tripoli trend that continues practically uninterrupted for 7½ miles to the west. The two Blocker Creek quarries have produced tripoli used in buffing compounds in the recent past. In this same general area just west of the Blocker Creek trend is a mile long trend from which a small tonnage of tripoli was produced at a quarry near Shady Lake in the NE¼SW¼ sec 26, T. 4 S., R. 29 W., Polk County, Arkansas.

The third area is near Bog Springs, Arkansas in the NW¼NW¼ sec. 16, T. 5 S., R. 32 W., Polk County, near the Arkansas-Oklahoma border. This locality is the beginning of a tripoli trend that extends westward a distance of 5 miles of which 3 miles are in Oklahoma. Also in Oklahoma, tripoli float has been found along the upper outcrop of the novaculite in secs. 19, 20, and 21, T. 2 S., R. 25 E., just west of Broken Bow Reservoir and southeast of the reservoir in secs. 4, 5, 6, and 7, T. 4 S., R. 27 E.

Exploration and Mining

The tripoli beds are confined to a specific stratigraphic horizon, the Upper Division of the Arkansas Novaculite, that frequently has a characteristic topographic expression, a series of low knobs or ridges that parallel the higher main novaculite ridges. Exposures in stream beds and float blocks are relatively common, and all these factors combine to simplify exploration. The procedure generally used is to bulldoze off the shallow soil and vegetation cover to determine the width and quality of the material, and, if justified, drill to ascertain the depth of the deposit. Open-pit mining methods are used. Both the overburden and the tripoli must be drilled and blasted, and scrapers or front-end loaders are used to remove the overburden and mine the tripoli.

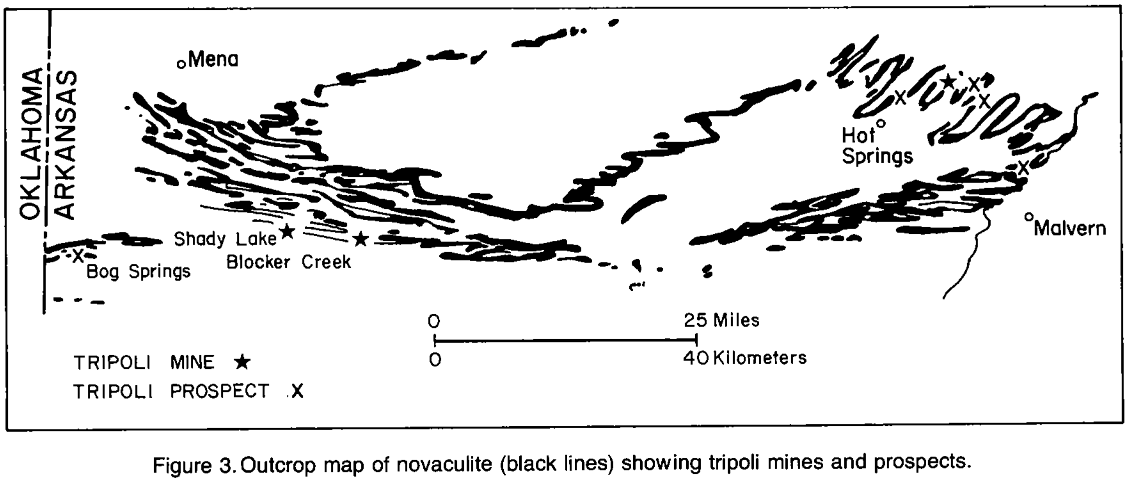


Figure 3. Outcrop map of novaculite (black lines) showing tripoli mines and prospects.

Character of the Tripoli

The tripoli deposits range from inches to over 100 feet in true thickness. There is a wide range of hardness in the individual beds that constitute the tripolitic zone reflecting the variation in carbonate content of the unweathered novaculite. The beds vary from material that can be crumbled by hand to hard unweathered non-calcareous novaculite layers. The tripoli consists of cryptocrystalline quartz grains or aggregates of grains more or less firmly bonded together. The range of particle size of individual quartz grains is from 1 to 10 microns, and the quartz particles are essentially equidimensional. The color of the tripoli varies considerably even within the same deposit. Original colors are frequently contaminated by surface wash or seepage along joints and fractures. Original colors are white, cream, tan, and brown, with white being the least prevalent.

Malvern Minerals Company Tripoli Deposit

As noted, the only tripoli producer at this time is the Malvern Minerals Company whose quarry is located 5 miles northeast of Hot Springs in the NE¼NW¼ sec. 21, T. 2 S., R. 18 W., Garland County. The deposit is situated on an overturned fold so that the tripoli (Upper Division) is overlain by shale of the Middle Division and massive novaculite of the Lower Division of the Arkansas Novaculite. The tripoli bed is 40 feet thick and dips 35 degrees to the northwest. Both the overburden and ore are drilled, shot, and moved by scrapers, and the stripping and mining is done by contract. The ore is shipped by truck to the mill at Hot Springs. Beneficiation consists of drying, grinding, and classification by air separation. Several fine-grained silica products are derived from the tripoli, some with a maximum particle size of 10 microns, and others ranging up to 200 mesh maximum particle size. These products are shipped for use in highly specialized filler and abrasive applications. Production in 1976 was approximately 10,000 short tons.

WHETSTONE ROCK

Novaculite has been mined for whetstones in the Hot Springs, Arkansas, area since 1832. For many years novaculite blocks were shipped to out-of-state plants for processing into whetstones. In 1962 a local processing plant was built, and there has been at least one such processing plant in Arkansas since that time. At this writing there are two plants in the state and one out-of-state processor.

Location of Deposits

The area of active whetstone mining is located just northeast of Hot Springs (fig. 4). All of the mining and most of the exploration has been confined to two areas; T. 2 S., R. 18 W. and T. 2 S., R. 19 W., Garland County. Recently a small tonnage has been produced from a deposit in Pike County some 50 miles west of Hot Springs. All of the commercial whetstone rock deposits are confined to the massive novaculite in the lower part of the Lower Division of the Arkansas Novaculite.

Exploration and Mining

The area where whetstone rock is mined is one of steep, densely-wooded hills. Good outcrops are scarce, because the hillslopes where the whetstone rock layers occur are usually covered with novaculite debris. Furthermore, these whetstone layers are somewhat less resistant to erosion than the adjacent novaculite. From experience the miners know the approximate elevation on a particular hillside where the whetstone rock layers are likely to occur. They first clear the selected site with a bulldozer, and, if the rock looks promising, the exposure is drilled and shot. Quarrying follows if the quality of the rock persists. Quarrying consists simply of drilling and blasting using a very light explosive charge. A follow-the-ore concept is used in quarrying the whetstone rock; following along the strike and dip of the bed until the quality of the rock deteriorates, or quarrying becomes too expensive.

The quality of a particular whetstone rock layer (lead) may vary both along the strike and the dip of that layer. Individual leads are narrow varying from 6 to 35 feet, but they may persist up to 900 feet along strike. After the rock is broken up it is hand mined with bar and pick. Blocks are trimmed

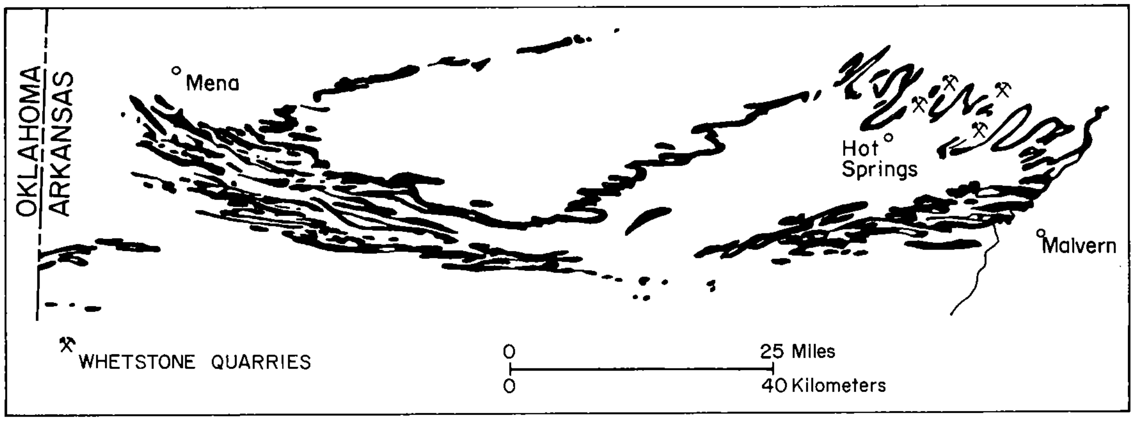


Figure 4. Outcrop map of novaculite (black lines) showing whetstone quarries.

to a roughly equidimensional shape weighing 10 to 20 pounds and are hand sorted for quality before shipment to the plant for processing. Quartz veins, cavities, cracks or fractures, laminations, stylolites, and lack of uniform texture are all a basis for rejection.

Characteristics of the Whetstone Rock

Whetstone-grade novaculite or whetstone rock, as it is called here, is found in the lower part of the Lower Division of the Arkansas Novaculite. These particular layers of novaculite are especially suited for whetstones because of their porosity, uniformity of texture, and the sharp edges of the minute quartz grains making up the rock. The porosity is due to rhombic cavities from which carbonate has been leached during weathering. Uniformity of texture implies not only uniformity in the size of the individual quartz grains but more especially a uniform distribution of the cavities throughout the rock. Individual quartz grains present sharp edges because the grains are not rounded but rather are closely packed in a mosaic texture, the individual grains exhibiting polygonal shapes in cross section (fig. 5).

In the sharpening process small micro-quartz particles bounding the pore spaces break off preventing the pores from being filled with steel particles which would cause the stone to glaze over. Several varieties of whetstones are manufactured under different trade names, and the essential difference between them is a difference in porosity. Thus, the Arkansas Stone has a porosity of 0.07 percent, while the more rapid-sharpening Washita Stone has a porosity of 16 percent. The increased porosity in the Washita Stone is due not only to a greater frequency of rhombic cavities but also to an increase in the size of the individual cavities. This variation in porosity is reflected in a difference in luster in the two stones. Thus, the denser Arkansas Stone is characterized by a waxy luster while the more porous Washita Stone has the dead appearance of unglazed porcelain.

Whetstone Processing

Quarry blocks are sawed into desired shapes with a diamond saw using cutting oil as a lubricant. These shapes are then finished on a lap with carborundum powder, given a final visual quality-control check, then packaged and shipped. Only about 5

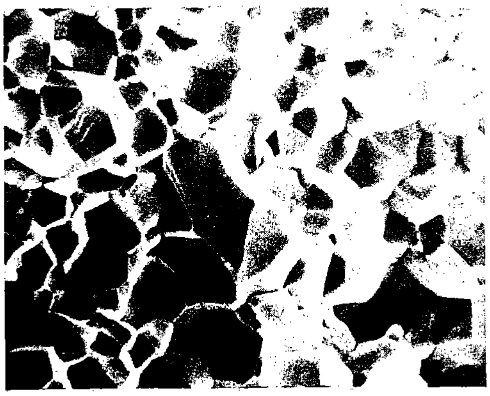


Figure 5. Scanning electron micrograph of whetstone novaculite showing sharp edges of quartz grains (SEM courtesy of W. D. Keller and George W. Viele, University of Missouri-Columbia).

percent of the blocks quarried end up as finished whetstones.

The four types of stones produced for market are listed in order of decreasing porosity:

Trade Names	Use
Washita Stone	for rapid sharpening
Soft Arkansas	for general all round sharpening
Hard Arkansas	for polishing a blade to a very fine edge
Black Hard Arkansas	for polishing to the most perfect possible edge

Arkansas whetstones are marketed worldwide, but the bulk of the sales are in the United States. Approximately 1,700,000 pounds of novaculite were quarried for making whetstones in 1976.

OTHER USE OF NOVACULITE

For several years novaculite has been used in making silica-brick refractories, and small tonnages have been shipped for test purposes as lightweight aggregate, nonpolishing asphalt aggregate, and for grinding media. Chemical analyses of quarry and outcrop samples (fig. 6) reveal that it has potential as a high-silica rock resource (table 1).

REFERENCES CITED

Goldstein, A., Jr., and **Hendricks, T. A.**, 1953, Siliceous sediments of Ouachita facies in Oklahoma: Geological Society of America Bulletin, v. 64, p. 421-442.

Griswold, L. S., 1892, Whetstones and the novaculites of Arkansas: Arkansas Geological Survey, Annual Report for 1890, v. 3, 443 p.

Hass, W. H., 1951, Age of Arkansas Novaculite: American Association Petroleum Geologists Bulletin, v. 35, p. 2526-2541.

Lowe, D. R., 1975, Regional controls on silica sedimentation in the Ouachita System: Geological Society of America Bulletin, v. 86, p. 1123-1127.

Miser, H. D., 1917, Manganese deposits of the Caddo Gap and DeQueen quadrangles, Arkansas: U.S. Geological Survey Bulletin 660-C, p. 59–122.

Miser, H. D., and **Purdue, A. H.**, 1929, Geology of the DeQueen and Caddo Gap quadrangles: U.S. Geological Survey Bulletin 808, 195 p.

Park, D. E., and **Croneis, C.**, 1969, Origin of Caballos and Arkansas Novaculite Formations: American Association Petroleum Geologists Bulletin, v. 53, p. 94-111.

Purdue, A. H., 1909, Structure and stratigraphy of the Ouachita Ordovician area (abs.); Geological Societv of America Bulletin 19, January 30, 1909, p. 556-557.

Schoolcraft, H. R., 1819, A view of the lead mines of Missouri, including some observations on the mineralogy, geology, geography, antiquities, soil, climate, population and production of Missouri, Arkansas and other sections of the western country: C. Wiley & Co., New York, 299 p.

Sholes, M. A., and **McBride, E. F.**, 1975, Arkansas Novaculite *in* Briggs, G., and others, editors, Sedimentology of Paleozoic flysch and associated deposits. Ouachita Mountains–Arkoma Basin Oklahoma: Dallas Geological Society, Guidebook April 1975. p. 69-87.

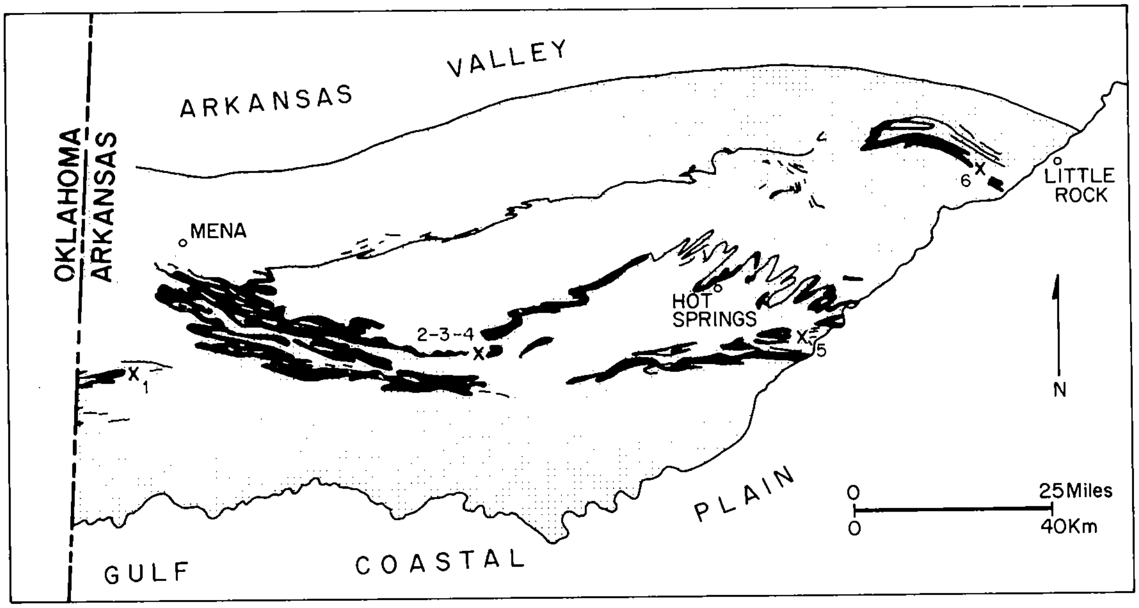


Figure 6. Map of eastern part of Ouachita Mountains (stippled area) showing outcrop of Arkansas Novaculite (black lines) and location of novaculite samples listed in table 1.

TABLE 1.—CHEMICAL ANALYSIS (IN PERCENT) OF SAMPLES AND ADDITIONAL DATA ON SAMPLES (see fig. 6 for location map)

Sample number	SiO_2	Al_2O_3	MnO	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	LOI
1	99.03	0.42	0.01	0.07	0.02	0.03	0.03	0.004	0.10	0.29
2	99.18	0.26	0.07	0.09	0.02	0.03	0.02	0.003	0.03	0.30
3	99.07	0.25	0.01	0.29	0.02	0.03	0.02	0.003	0.05	0.26
4	99.19	0.19	0.03	0.19	0.01	0.03	0.02	0.003	0.05	0.29
5	99.19	0.25	0.01	0.14	0.02	0.02	0.02	0.003	0.05	0.30
6	99.16	0.27	0.04	0.16	0.02	0.03	0.03	0.002	0.01	0.28

Sample number	True thickness (feet)	Division of Novaculite Formation	Location
1	130	Lower	Abandoned quarry, NW¼NW½ sec. 6, T. 5 S., R. 31 W., Polk Co.
2	100	Bottom of Lower	Caddo Gap outcrop, SW¼SE¼ sec. 18, T. 4 S., R. 24 W., Montgomery Co.
3	249	Remainder of Lower	Caddo Gap outcrop, SW¼SE¼ sec. 18, T. 4 S., R. 24 W., Montgomery Co.
4	105	Upper	Caddo Gap outcrop, NW¼NE¼ sec. 19, T. 4 S., R. 24 W., Montgomery Co.
5	210	Lower	Butterfield quarry, SW¼NE¼ sec. 34, T. 3 S., R. 17 W., Hot Springs Co.
6	60	Lower	Lawson Road outcrop, NE¼SE¼ sec. 19, T. 1 N., R. 13 W., Pulaski Co.

THE SIGNIFICANCE OF POROSITY AND SURFACE AREA MEASUREMENTS OF CHERT TO CONCRETE PETROLOGY

WILLIAM A. KNELLER[1] and KARINLEE KNELLER[1]

Abstract—Fifteen samples of chert from seven localities in Ohio were tested for potential durability and reactivity in concrete. The tests determined are porosity, pore-size distribution, relative degree crystallinity, specific surface area, and degree of dissolution according to the ASTM C289-71, *Potential Reactivity of Aggregates, Chemical Methods*. The results of these tests were compared with petrographic, electron optical, physical-chemical, and engineering properties of the chert samples. Based on these tests, the important properties that affect the durability and reactivity of chert in concrete were observed to be: (1) porosity, (2) pore-size distribution or pore spectra, (3) relative degree of crystallinity, (4) grain size, (5) specific surface area, (6) impurities, and (7) amount and species of quartz present—all of which are functions of original composition, time (geologic age), depth of burial, tectonics, and diagenesis.

Preliminary results of this study indicated that the geologic history and physical-chemical properties of chert vary from one sample to another, and any one or combination of these parameters affect the performance of the chert in concrete. These complex interrelationships are difficult to ascertain; if the performance of the chert in concrete is to be predicted, it is necessary to study in detail this enigmatic material.

---

[1] The Eitel Institute for Silicate Research, University of Toledo, Toledo, Ohio.

DOMESTIC PETROLEUM OUTLOOK AND ITS IMPACT ON INDUSTRIAL MINERAL DEVELOPMENT

THOMAS M. GARLAND[1]

Abstract—During the rest of this century, the United States faces no more complex or challenging problem than that of assuring availability of adequate, secure energy supplies in general, and crude oil and natural gas in particular. This talk will present the bare facts concerning where we have been, where we are, and what we can expect, focusing primarily upon consumption and supply of crude oil and natural gas.

---

[1] Bureau of Mines, Dallas, Texas.

ORIGIN AND CHEMICAL EVOLUTION OF BRINES IN SEDIMENTARY BASINS

ALDEN B. CARPENTER[1]

Abstract—Brines (a solution containing more than 100,000 mg/l dissolved solids) in sedimentary basins are genetically related to evaporites in one of three ways: (1) dissolution of evaporite minerals, generally halite; (2) interstitial fluids in evaporites which are expelled from their source rock during compaction; (3) incongruent alteration of hydrous evaporite minerals (carnallite).

Most brines of commercial interest originate as interstitial fluids in halite-rich rocks. These fluids are initially rich in magnesium, sulfate, and potassium but evolve in composition to an Na-Ca-Cl brine during their migration to their present host rock. A particularly important reaction in this process is:

$$2CaCO_3 + Mg^{2+} = CaMg(CO_3)_2 + Ca^{2+} \qquad (1a)$$

This reaction reduces the magnesium content of the brine and ultimately converts it to a calcium-rich brine. The loss of sulfate occurs by two mechanisms. One of these is by direct precipitation as calcium sulfate (either as gypsum or anhydrite):

$$Ca^{2+} + SO_4^{2-} = CaSO_4 \qquad (2a)$$

Additional sulfate may be lost from the brine by sulfate reduction:

$$SO_4^{2-} + 1.33CH_2 + 2H^+ = H_2S + 1.33CO_2 + 1.33H_2O \qquad (3a)$$

The loss of carbonate species occurs by precipitation as carbonates:

$$H_2O + CO_2 + Ca^{2+} = CaCO_3 + 2H^+ \qquad (4a)$$

The net result of reactions 3 and 4 is:

$$Ca^{2+} + SO_4^{2-} + 1.33CH_2 = H_2S + CaCO_3 + 0.33H_2O + 0.33CO_2 \qquad (5a)$$

The loss of potassium from brines is caused by the formation of potassium aluminosilicates:

$$2K^+ + Al_2Si_2O_5\ (OH)_4 + 4SiO_2 = 2H^+ + 2KAlSi_3O_8 + H_2O \qquad (6a)$$

The hydrogen ions produced by this reaction dissolve carbonates:

$$2H^+ + CaCO_3 = Ca^{2+} + CO_2 + H_2O \qquad (7a)$$

The net result of reactions 6 and 7 is:

$$2K^+ + CaCO_3 + Al_2Si_2O_5\ OH)_4 + 4SiO_2 = Ca^{2+} + 2KAlSi_3O_8 + H_2O + CO_2 \qquad (8a)$$

A study of brines from central Mississippi has shown that the composition of these brines is related to the interaction of pore fluids from evaporites with minerals in the enclosing sedimentary rocks.

INTRODUCTION

Occurrences of brines in sedimentary basins containing intervals of bedded halite are known in a number of areas around the world. In many of these locations, certain stratigraphic intervals are important producers of hydrocarbons and, in some cases, contain major base-metal deposits. The purpose of this investigation has been to develop a model for predicting the chemical composition of brines produced by the evaporation of sea water and a model for quantitatively predicting the changes in the composition of these brines as they migrate into sedimentary rocks and react with a variety of common minerals. If the brines

---

[1] Department of Geology, University of Missouri, Columbia, Missouri.

and their associated hydrocarbons in oil-field reservoirs have migrated to their present position along the same path, the ability to determine the point of origin and the migration path of a brine from its chemical characteristics could be a valuable tool in petroleum exploration.

A second goal of this investigation is to establish a basis for estimating the mineralogical and physical changes that are induced in different types of sedimentary rocks by exposure to various types of subsurface brines. Some of these changes result in significant increases in permeability while others result in a loss of permeability. The ability to quantitatively predict the mineralogical and hydrologic changes which will be induced in a rock by interaction with brines may permit better evaluation of the hydrocarbon production potential of a reservoir with data obtainable from a limited number of holes. The development of such a technique would be of value in reducing the cost of petroleum exploration.

CLASSIFICATION AND ORIGIN OF BRINES

There are two general schemes for the classification of water based on the total concentration of dissolved solids (table 1). Davis (1964) has commented that the classification used by Krieger (1963) is difficult to remember being neither arithmetic nor geometric in progression. Davis also noted that the term *brine,* as commonly used, indicates water saturated with or nearly saturated with ordinary salt. A histogram of total dissolved solids in oil-field waters does not provide any indication of a discontinuity in frequency of occurrence in the range 1,000 to 500,000 mg/l dissolved solids (fig. 1). Since the histogram indicates that the classification of these waters into groups is arbitrary, it seems best to adopt the classification proposed by Davis with the modification that the unit of dissolved solids be changed from parts per million (ppm) to milligrams per liter (mg/l). The vast majority of water samples are analyzed on a weight per unit volume basis, and the density of a sample may not have been determined. The modification of units from parts per million to milligrams per liter makes Davis's classification easier to apply to most data.

TABLE 1.—CLASSIFICATION OF WATER BASED ON TOTAL DISSOLVED SALTS (parts per million)

Krieger (1963)		Davis (1964)	
Slightly saline	1,000-3,000	Fresh water	<1,000
Moderately saline	3,000-10,000	Brackish water	1,000-10,000
Very saline	10,000-35,000	Saline water	10,000-100,000
Brine	35,000	Brine	>100,000

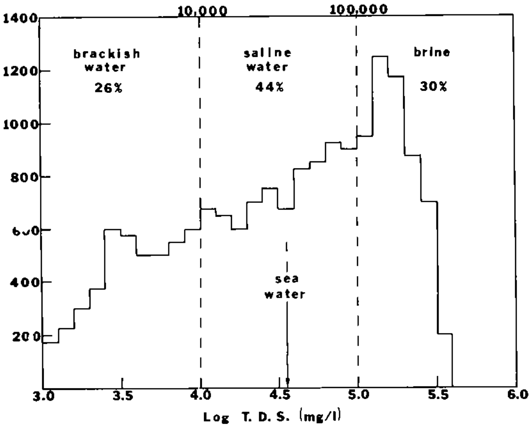


Figure 1. Histogram illustrating the relative abundance of oil-field waters of differing salinities (data courtesy of A. Gene Collins, U.S. Bureau of Mines).

Although the term *brine* in both classification systems is applied to water samples on the basis of a measureable parameter. The usage proposed by Davis has definite genetic implications, whereas that used by Krieger does not. Natural aqueous solutions containing more than 100,000 mg/l dissolved solids appear to originate either as a result of the crystallization of siliceous magma or as a result of some process involving evaporites (table 2). It has been established that most, if not all, porphyry copper deposits contain minerals with inclusions of highly saline solutions containing as much as 600,000 mg/l dissolved salts (Roedder, 1977). Kilinic and Burnham (1972) have shown experimentally that, if an aqueous phase forms during the crystallization of a siliceous magma, much of the chloride in the magma is incorporated into this aqueous phase. As a result of this process, the aqueous fluid can become a highly concentrated brine. Fluid-inclusion studies of brines associated with porphyry copper deposits indicate that these are Na-K-Cl brines.

The association of evaporites and brines in sedimentary basins has been recognized for some time. Although evaporites and brines of nonmarine origin are known to

TABLE 2.—ORIGIN OF BRINES

I.-Crystallization of siliceous magma

II.-Brines in sedimentary basins

- A) Dissolution of evaporite minerals (especially halite)
- B) Evaporation of H_2O from saline water
- C) Incongruent alteration of hydrous evaporite minerals

occur, this review is restricted to evaporites of marine origin. Brines produced by the dissolution of highly soluble minerals such as halite generally have distinct compositions which can be used to determine the mineral or minerals that have been dissolved. Brines produced by the dissolution of halite consist almost entirely of sodium and chloride and have very low concentrations of bromide and calcium. The incongruent alteration of hydrous evaporite minerals to form brines has been described by Braitsch (1971, p. 118-122). These brines are usually very high in calcium and (or) magnesium and relatively low in sodium. Their occurrence is generally restricted to the immediate vicinity of evaporite deposits containing potash salts.

Sodium-calcium chloride brines appear to originate as interstitial fluids in evaporites and are then subsequently expelled as a result of the compaction occurring in response to loading by younger sediments. Landes (1960, p. 60) states that evaporite-mineral accumulations usually have initial porosities in excess of 50 percent which are in considerable contrast to the negligible porosities of ancient evaporites.

The modification of ground-water composition can occur through a variety of mechanisms. Mangelsdorf and others (1970) have reviewed the effects of gravitational settling of ions, ion movement in a thermal gradient (Soret effect), and thermocell diffusion. They concluded that these mechanisms cannot account for the enrichment of dissolved salts commonly found in subsurface brines but may modify ion distributions due to other phenomena. The effect of shale-membrane filtration on the chemistry of brackish water has been studied experimentally by several individuals notably Hanshaw and Coplen (1973) and Kharaka and Smalley (1976). Hanshaw and Coplen demonstrated that the concentration of sodium in brackish water could be increased from 225 to 400 ppm using a montmorillonite clay and a pressure on the residual solution of 330 bars. Kharaka and Smalley conducted experiments with bentonite and fluid pressures of 690 bars and measured the differential mobility of ions in solutions containing up to 6,400 mg/l dissolved solids. However, the formation of a brine from sea water has yet to be demonstrated. Manheim and Horn (1968) have carefully evaluated the difficulties of producing brines by shale-membrane filtration. They concluded that the pressure requirements for appreciable salt filtration remain unsatisfied by known geologic environments. They also noted that a second requirement of a filtration system capable of producing brines is that "enormous volumes of fluids must be pushed through poorly permeable (membrane-active) strata in preference to permeable channels, under virtually leak-free conditions." They concluded that "field evidence of such a system has never been offered and that such systems would appear to defy standard ground water, petroleum engineering and geological engineering and experience."

The majority of oil-field brines appear to be sodium-calcium chloride brines containing significant amounts of bromine. The evidence indicates that these brines originated as interstitial fluids in evaporite deposits. The details of the origin and chemical evolution of these brines are discussed in later sections.

EVAPORATION OF SEA WATER

Attempts to reconstruct the chemical history of subsurface brines derived from sea water require the use of one or more "marker" constituents. Such a constituent must neither precipitate during the evaporation of sea water nor participate in diagenetic reactions with subsequent mineralogical environments. Zherebtsova and Volkova (1966) showed that during the evaporation of sea water essentially all of the potassium, rubidium, lithium, and bromide remain in solution until potash salts begin to precipitate and that most of the lithium and bromide remain in solution during potash-salt deposition. Of these elements, however, only bromine is essentially free from participation in diagenetic reactions. The inert character of bromine makes it ideal for tracing the chemical evolution of brines derived from the sea water. Rittenhouse (1967) has already successfully used bromide concentrations to determine the origin of some oil-field brines.

Although there have been several studies on the evaporation of sea water and the precipitation of evaporite minerals, few of these investigations included the determination of bromide as part of their analytical work. Those investigations that have included data on bromide concentrations suffer from internal inconsistencies in the data. The purpose of this section is to critically review existing data on compositional trends established during the evaporation of sea water and to eliminate the inconsistencies which appear to be present.

In this context, a key aspect of the evaporation of aqueous solutions is worth noting in detail. If a solution containing several different ions is concentrated by evaporation, the ratios of the various ions with respect to each other remain constant except in the cases of ions that are being precipitated or reacting with the substrate in which the brine is contained. This relationship may be expressed in the form:

$$\frac{B}{A} = k \qquad (1a)$$

or

$$B = kA \qquad (1b)$$

where A and B are ions in solution and k is a constant. Using logarithmic form for equation 1b:

$$\log B = \log A + \log k \qquad (2)$$

results in an equation which plots as a straight line with a 1:1 slope, regardless of the numerical value of k. Any ion which deviates from this relationship with other ions in solution as increments of water are removed is being affected by some process other than the removal of water. This very simple test is a powerful method both for checking the validity of analytical data and for detecting the presence of chemical reactions within the system which are not readily apparent.

The study by Zherebtsova and Volkova (1966) on compositional trends during the evaporation of sea water stands out as a classic paper on this subject. Water from the Black Sea was evaporated in flat vinyl tubs, "evaporators," placed at the gates separating the evaporating basins of the Saki saltern. "Brines corresponding to five stages of salt deposition, i.e., deposition of gypsum, halite, magnesium sulfates, potassium salts, and bischofite, were collected and analyzed." Because the Black Sea contains only one half the total dissolved solids of sea water, it is conceivable that contributions from river water cause the Black Sea to have a composition that is different from that of ocean water. A comparison of the compositions of ocean water and Black Sea water is presented in table 3. The data show that, although the Black Sea is slightly enriched in calcium and slightly low in potassium relative to ocean water, the differences are small. Selected data derived from Zherebtsova and Volkova's study are presented in tables 4 and 5.

Four important points are evident from the data:

1)—The ratios of Mg/Br and Mg/K remain constant until a magnesium salt begins to precipitate.

2)—The ratio of K/Br remains constant until potash salts begin to precipitate.

TABLE 3.—COMPARISON OF WATERS FROM THE BLACK SEA WITH WATERS FROM THE OCEAN (MG/L)

	Ca	Mg	Na	K	Cl	Br	SO_4
Black Sea Water[1]	233	679	5,817	192	10,340	35.5	1463
Black Sea water scaled to 19,870 mg/l Cl	448	1305	11,180	369	19,870	68.2	2812
Ocean Water (S = 35 $^{\circ}/oo$) (Riley and Chester, 1971)	422	1326	11,050	416	19,870	68.	2780
Differences between ocean water and Black Sea water	+6.2%	-1.6%	+1.2%	-11.%		+.3%	+1.2%

---

[1] Zherebetsova and Volkova (1966).

TABLE 4.—COMPOSITION OF BRINES PRODUCED BY THE EVAPORATION OF WATER FROM THE BLACK SEA (MG/L) (based on data in Zherebtsova and Volkova, 1966)

Reported Stage of Mineral Deposition	Ca	Mg	Na	K	SO_4	Cl	Br	T.D.S.	Den
Black Sea water	233	679	5,820	193	1,460	10,340	35	18,760	1.014
Beginning of gypsum precipitation	1,040	7,590	59,700	2,220	13,300	107,800	396	192,000	1.131
Beginning of halite precipitation	307	19,600	94,300	5,600	27,700	183,300	1010	331,800	1.227
Halite precipitation	-	50,500	55,200	15,800	76,200	187,900	2670	388,300	1.271
Beginning of Mg-sulfate precipitation	-	56,100	48,200	17,700	82,200	190,500	2970	397,700	1.286
Beginning of K-salts precipitation	-	72,900	22,100	25,900	56,100	224,000	4770	405,800	1.290
Precipitation of K-salts	-	92,600	8,960	18,800	54,200	254,000	6060	434,600	1.318

TABLE 5.—RATIOS OF DISSOLVED CONSTITUENTS TO BROMIDE IN WATER FROM THE BLACK SEA DURING EVAPORATION (based on data in Zherebtsova and Volkova, 1966)

Reported State of Mineral Deposition	Ca/Br	Mg/Br	Na/Br	K/Br	SO_4/Br	Cl/Br	Mg/K
Black Sea water	6.5	19.1	164	5.4	41.2	291	3.5
Beginning of gypsum precipitation	2.6	19.1	151	5.5	33.6	272	3.4
Beginning of halite precipitation	.3	19.5	94	5.5	27.5	182	3.5
Halite precipitation	-	18.9	21	5.9	28.5	70	3.2
Beginning of Mg-sulfate precipitation	-	18.8	16	5.9	27.6	64	3.2
Beginning of K-salts precipitation	-	15.2	4.6	5.4	11.7	47	2.8
Precipitation of K-salts	-	15.3	1.5	3.1	8.9	42	4.9

3)—The sample which was collected when gypsum crystals were first observed was, in fact, collected well after gypsum had begun precipitating. This statement is supported by the fact that the ratios of Ca/Br and SO_4/Br in this sample are considerably different from those in the original solution.

4)—The sample which was collected when halite crystals were first observed was, in fact, collected well after halite had begun precipitating. This statement is supported by the fact that the ratios of Na/Br and Cl/Br in this sample are considerably different from those in the parent solution.

There are two useful principles which emerge from these observations:

1)—Magnesium or potassium concentrations in bodies of evaporating sea water may be used to estimate bromide concentrations if the Mg/K ratio in the water is the same as in normal sea water. This fact is useful in estimating bromide concentrations in samples collected during earlier studies which did not include bromide determinations (for example, Morris and Dickey, 1957). These estimates permit older data to be more readily compared with the results of recent investigations.

2)—Generally speaking, it is difficult to determine by direct observation the point at which a brine begins to precipitate a new phase. However, the precipitation of an ion phase has a drastic effect on the ion ratios involving that element in the aqueous solution. The reason for this effect is that the concentrations of essential constituents in crystals is very much higher than in the parent solution. For example, the maximum concentration of calcium in solution during the evaporation of normal sea water is approximately 1,500 ppm whereas the concentration of calcium in gypsum is 260,000 ppm. Thus, the precipitation of a small amount of gypsum causes a large shift in the Ca/Br ratio of the parent solution. The careful monitoring of ion ratios in aqueous solution is a particularly effective technique for determining water compositions at the beginning of precipitation of solids from complex solutions. The monitoring of ion ratios is also an extremely sensitive method for detecting the addition of soluble salts to a solution and for detecting chemical interactions between a solution and the solids with which it is in contact.

Herrmann and Knake (1973) made an extensive study of the evaporation of water from the Adriatic Sea at the Secovlje salt works, Yugoslavia. These salt works have been in use since the 13th century, and the method of operation has remained essentially unchanged since 1904. The salt works consist of a series of pans (P) connected by canals (C) containing water of increasing salinity. "The bottom and the dams of the individual pans within the salt works consist of the silt and clay of the flysch. . . . The bottoms of the basins are covered with stromatolitic mats of algae, mainly consisting of cyanophyceae and cemented by biogenetically precipitated calcium carbonate. The evaporating pans remain untouched by man for decades. The pans in which NaCl precipitates acquire a new layer of Cyanophyta each year—the so-called 'petola' which is cemented by calcium carbonate and calcium sulphate. This is so strong that workers can walk on it when they heap up the salt. The salt is piled up next to the pans until it is transported in the store houses of Portoroz." The Adriatic Sea water studied by Herrmann and Knake and ocean water are closer in chemical composition than Black Sea water and ocean water. Data derived from Herrmann and Knake's study are presented in table 6.

The data in table 6 have several noteworthy aspects confirming the conclusions derived from the data in Zherebtsova and Volkova's study. The first "event" of interest was the major increases in the Na/Br, Cl/Br, SO_4/Br, and Ca/Br ratios

Table 6.—Ratios of Dissolved Constituents to Bromide in Water from the Adriatic Sea During Evaporation
(based on data in Herrmann and Knake, 1973)

Sample	Sample Location	Remarks	Ca/Br	Mg/Br	Na/Br	K/Br	Cl/Br	SO_4/Br	Mg/K
1	SW	Adriatic sea water	6.3	22.2	163	6.5	303	42.6	3.4
2	P 1		6.5	22.3	168	7.0	312	43.2	3.2
3	P 2		6.2	21.4	166	6.8	305	42.9	3.2
4	P 3		6.5	22.4	164	6.8	305	42.3	3.3
5	P 4		6.6	21.6	165	6.5	305	42.1	3.3
6	C 4		6.4	21.7	176	6.4	322	42.5	3.4
7	P 5		6.4	20.9	171	6.2	310	42.6	3.4
8	P 6		6.5	21.5	169	6.5	310	42.3	3.3
9	P 7		7.0	22.1	190	6.8	342	46.2	3.2
10	P 8		7.1	22.6	189	7.2	340	48.4	3.2
11	C 8		7.0	23.0	191	7.1	345	48.4	3.3
12	P 9		6.4	22.1	178	6.6	323	45.3	3.4
13	P 10		6.8	22.8	179	6.7	326	47.1	3.4
14	P 11		6.8	25.1	183	7.0	339	47.7	3.6
15	P 12	Precipitation of calcite	5.7	24.3	181	6.6	333	44.2	3.7
16	C 12		4.6	25.9	181	7.1	350	46.5	3.6
17	P 13A		3.9	27.0	204	7.4	368	52.4	3.6
18	P 13B	Precipitation of gypsum	1.2	28.3	200	7.6	369	40.6	3.7
19	P 13C		1.1	27.3	197	7.3	363	39.4	3.7
20	P 13D		0.9	27.9	199	7.5	367	40.0	3.7
21	P 13E	Precipitation of halite	0.2	32.8	96	7.1	222	44.0	4.6
22	P 13F		0.2	33.8	69	7.4	186	36.8	4.6
23	P 13G		0.2	32.8	71	7.4	184	37.4	4.5
24	P 13H		0.2	33.3	65	7.5	175	38.8	4.4
25	P 13I		0.2	33.2	65	7.5	175	38.9	4.4
26	P 13K		0.2	33.4	62	7.3	174	34.2	4.6

which occurred between pan 6 and pan 7. These changes were not accompanied by simultaneous increases in the ratios of Mg/Br and K/Br although there is sufficient scatter in the data that this statement may be considered debatable. The essential question, however, is whether the shifts in ion ratios which occurred between pan 6 and pan 7 were a result of the removal of bromide from the water, perhaps by the action of the algae, or whether halite and gypsum were being added to the water in pan 7. The data in table 7 clearly show that the shift in Na/Br and Cl/Br ratios was a result of the addition of halite to the water in pan 7. The concentration of bromide in pan 7 is 1.013 times higher than in pan 6. If the concentrations of sodium and chloride in pan 6 are multiplied by the same factor, the calculated concentrations are 26,240 and 48,050 mg/l, respectively. These concentrations are less than observed concentrations in pan 7 by 3,260 and 5,030 mg/l, respectively. The weight percent sodium in this surplus sodium plus chloride is 39.3 percent, exactly equal to the weight percent sodium in halite. Other calculations show that calcium sulfate was also being added to pan 7. The changes in x/Br ratios between pans 6 and 7 are an excellent demonstration that monitoring ion ratios is a sensitive method for detecting the addition of soluble salts to a solution.

A similar event occurrred between pans 10 and 11 where there was an abrupt rise in the Mg/Br ratio and a corresponding rise in the Mg/K ratio. A soluble magnesium salt was being added to pan 11; although there is no obvious clue to its identity, the most likely candidate is magnesium sulfate.

Pan 12 marks the beginning of a steady decline in the Ca/Br ratio, which Herrmann and Knake attributed to the precipitation of calcium carbonate in pan 12 and the precipitation of gypsum in pan 13b. It is a remarkable coincidence that the composition of the water in pan 12 is essentially the same as Black Sea water which also precipitates gypsum. It is also noteworthy that the rate at which calcium decreases relative to the increase in bromide is identical for both waters. In all probability both gypsum and calcium carbonate began precipitating in pan 12. Unfortunately this hypothesis cannot be tested because of the absence of data on bicarbonate in the water and because of the addition of excess sulfate to the Adriatic Sea water.

TABLE 7.—RELATIONSHIPS BETWEEN BR, NA, AND CL IN PANS 6 AND 7, SECOVLJE SALT WORKS

Location	Br	Na	Cl
Pan 6	153	25,900	47,430
Pan 7	155	29,500	53,080
Pan 6 x 1.013	155	26,240	48,050
Surplus constituent assuming constant x/Br ratios	-	3,260	5,030

Na, Cl surplus

$$\frac{3,260}{3,260 + 5,030} = \begin{matrix}39.3\%\ \text{Na}\\ 60.7\%\ \text{Cl}\end{matrix}$$

halite

$$\frac{22.99}{22.99 + 35.45} = \begin{matrix}39.3\%\ \text{Na}\\ 60.7\%\ \text{Cl}\end{matrix}$$

There is a final point of interest in the abrupt change in the Mg/K ratio which occurred in pan 13e. Herrmann and Knake noted that "From pan 13e onward the Mg/K ratio increases from about 3.7 to 4.6. This means the K content of the solution increases less than its Mg content. Some of the K therefore must be bound up in some way. However, no K mineral has crystallized at this stage of seawater concentration. Some of the K may be adsorbed onto the anaerobic mud in the pans." However, the data in table 6 show no evidence of decrease in the ratio of K/Br as would be expected to accompany the loss of potassium from solution, whereas, there is a distinct increase in the Mg/Br ratio. The obvious explanation for the change in Mg/K ratio is not as a result of the loss of potassium from the solution but rather from the addition of a soluble magnesium salt, again probably magnesium sulfate. There appears to be an increase in the SO_4/Br ratio in pan 13e, but the continued precipitation of gypsum in the succeeding evaporating pans makes this relationship difficult to demonstrate from ratio calculations alone. Herrmann and Knake's unfortunate conclusion that the change in Mg/K ratio was due to a loss of potassium illustrates the importance of selecting a more inert element, such as bromide, in using element ratios to detect and interpret changes in water chemistry.

Clearly, the antiquity, design, and operation of these salt works result in the contamination of the brines by previously precipitated salts. The nature and extent of this contamination can be detected using bromide concentrations and x/Br ratios to monitor changes in the composition of the brines.

The data outlined above are amenable to some very simple but effective graphical and algebraic methods for predicting compositional trends during the evaporation of ocean water. Included in table 3 are data for calcium, sulfate, and bromide in ocean water. From these data and equations 1 and 2, it follows that calcium and sulfate concentrations in ocean water increase during evaporation in a predictable manner, provided that none of these constitutents are added to or removed from the water during this process:

$$\text{Log (Ca)} = \text{Log (Br)} + 0.792 \qquad (3)$$

$$\text{Log (SO}_4\text{)} = \text{Log (Br)} + 1.611 \qquad (4)$$

These relationships are illustrated in figure 2. The data in studies by Zherebtsova and Volkova (1966) and Herrmann and Knake (1973) show that Log (Ca) decreases linearly with respect to Log (Br) during the precipitation of gypsum. The intersection of this line with that represented by equation 3 indicates that the precipitation of gypsum begins when Log (Br) = 2.55 (275 mg/l).

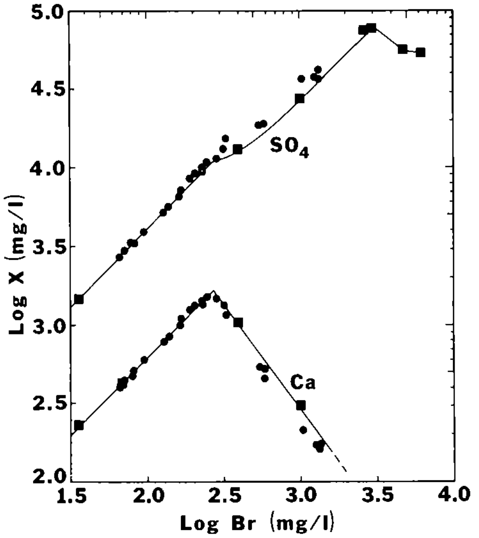


Figure 2. Concentration trends of calcium and sulfate relative to bromide during the evaporation of sea water and the precipitation of calcium sulfate. (Data from Zherebtsova and Volkova, 1966, shown as squares; and from Herrmann and Knake, 1973, shown as circles.) The intersection of the two segments of the calcium-bromide trend line indicates that calcium sulfate begins to precipitate at a bromide concentration of 269 mg/l instead of 395 mg/l reported by Zherebtsova and Volkova or 548 mg/l reported by Herrmann and Knake. The increase in calcium and sulfate relative to bromide at Log Br = 2.22 is a result of the dissolution of calcium sulfate in pan 13B at the Secovlje salt works. Note the excellent agreement between the calculated sulfate-bromide trend line and the experimental observations of Zherebtsova and Volkova in the range Log Br = 2.6–3.5.

The relationships shown in figure 2 may also be used to predict trends in sulfate concentration during the precipitation of gypsum. This is done by extending the lines representing equations 3 and 4 past the point of the initial precipitation of gypsum (fig. 3). These lines indicate what the concentrations of calcium and sulfate would be at a specified bromide concentration in the absence of gypsum precipitation. The difference between the extrapolation of equation 3 and the observed concentration of calcium (line A, fig. 3) is related to the amount of calcium which has precipitated. Since calcium and sulfate are removed from solution in equal molar amounts (whether precipitated as gypsum or as anhydrite) the amount of sulfate precipitated can be calculated (line B, fig. 3). As the process of evaporation and precipitation of calcium sulfate continues, the supply of calcium in the ocean water is exhausted, and the sulfate concentration again rises in 1:1 proportion with bromide. The new equation relating these two parameters can be calculated without any experimental information. Every milligram of calcium precipitated as calcium sulfate is accompanied by 2.397 milligrams of sulfate:

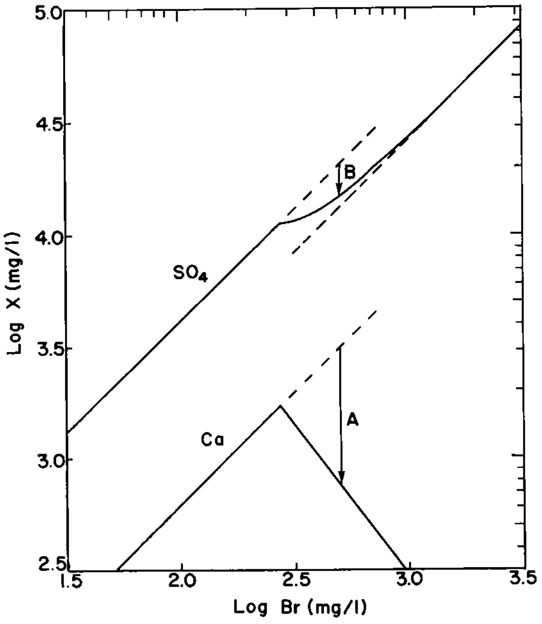


Figure 3. Calculated concentration trend of sulfate relative to bromide during the evaporation of sea water and the precipitation of calcium sulfate. (Concentration trend of calcium relative to bromide is based on data in Zherebtsova and Volkova, 1966, and Herrmann and Knake, 1973.)

$$\frac{\text{molecular weight } SO_4}{\text{molecular weight Ca}} = \frac{96.06}{40.08} = 2.397$$

$$\frac{\text{sulfate-precipitated sulfate}}{\text{bromide}}$$

$$= \frac{2{,}780 - 2.397\,(422)}{68} = \frac{1{,}770}{68}$$

$$\text{Log}\,(SO_4) = \text{Log}\,(Br) + 1.415$$

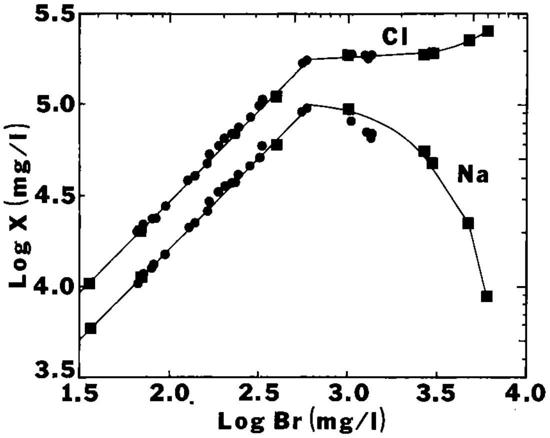


Figure 4. Concentration trends of sodium and chloride relative to bromide during the evaporation of sea water and the precipitation of halite and carnallite. (Data from Zherebtsova and Volkova, 1966, shown as squares; and Herrmann and Knake, 1973, shown as circles.) The intersection of the two segments of the chloride-bromide trend line indicates that halite begins to precipitate at a bromide concentration of 617 mg/l instead of 1,010 reported by Zherebtsova and Volkova or 1,040 mg/l reported by Herrmann and Knake. The increase in sodium and chloride at Log Br = 2.22 is a result of the dissolution of halite in pan 13B at the Secovlje salt works. Note the excellent agreement between the calculated sodium-bromide trend line and the experimental observations of Zherebtsova and Volkova in the range Log Br = 2.7–3.5.

In summary, as shown in figure 3, the rise in sulfate concentration relative to bromide is a 1:1 relationship until the precipitation of calcium sulfate. This relationship then changes in a predictable manner if the decrease in calcium relative to bromide is known from observation. Finally, the trend in sulfate concentration relative to bromide resumes a new predictable 1:1 relationship with bromide when the supply of calcium in the water is exhausted. This new trend line is, of course, parallel to the original line but displaced to lower relative sulfate concentrations. Zherebtsova and Volkova's data shown in figure 2 have excellent internal consistency and are in excellent agreement with the constraints on compositional trends in evaporating ocean water in an inert container.

This technique can be used to predict trends in the concentration of any constituent relative to bromide induced by the coprecipitation of any other constituent. It has been used to determine the effect of chloride on sodium during the precipitation of halite and the effect of sulfate on magnesium by the precipitation of magnesium sulfate. The predicted relationships and observed values are presented in figures 2, 4, and 5. The calcium data for both studies in figure 2 are in relatively good agreement. Figure 2 shows the increase in calcium relative to bromide which occurred in pan 7 and shows that the decrease in Log(Ca) relative to Log(Br) during the precipitation of calcium sulfate is linear. Figure 2 also illustrates that the trend in sulfate concentration in the Secovlje salt pans is in poor agreement with both Zherebtsova and Volkova's data and with trends required during the evaporation of ocean water in an inert environment. Figure 4 illustrates the effects of the addition of sodium chloride to pan 7 at Secovlje. There is good agreement between the two studies on the sodium trend during the precipitation of halite, but the excess chloride in the Secovlje pans is inconsistent with Zherebtsova and Volkova's data and with respect to the 1:1 relationship between chloride and bromide prior to the precipitation of halite. The data for potassium and magnesium for both studies are shown in figure 5. The data for potassium in both salt pan studies are in relatively good agreement. However, there is considerable disagreement with respect to magnesium. Figure 5 shows distinct increases in magnesium relative to bromide in pan 11, just prior to the beginning of gypsum precipitation in pan 12, and again in pan 13e. These data, with the data illustrated in figure 2, strongly suggest that the magnesium was added to the brine in the salt pans primarily as magnesium sulfate.

Figure 6 illustrates the trends in the concentration of the major ions in sea water relative to bromide during the evaporation of sea water in an inert environment. A computer program which generates the trends shown in figure 6 is available from the author.

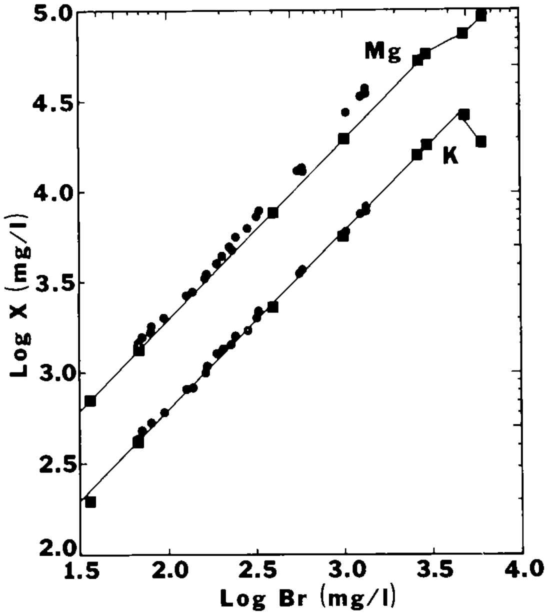


Figure 5. Concentration trends of potassium and magnesium relative to bromide during the evaporation of sea water and the precipitation of magnesium sulfate and carnallite. (Data from Zherebtsova and Volkova, 1966, shown as squares; and Herrmann and Knake, 1973, shown as circles.) The increase in magnesium relative to bromide at Log Br = 3.02 is a result of the dissolution of a magnesium compound in pan 13E at the Secovlje salt works.

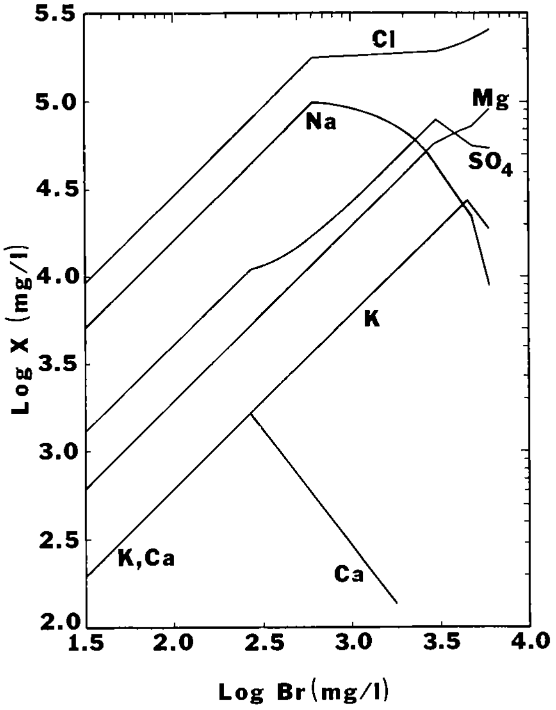


Figure 6. Concentration trends of ions in sea water relative to bromide during the evaporation of sea water and the precipitation of evaporite minerals.

INTERACTION OF BRINES WITH FRESH WATER, SEA WATER, AND HALITE

It is very likely that brines produced by the evaporation of sea water will be moved from their point of origin as a result of sediment compaction, tectonic deformation, and other processes. Figure 7 illustrates the effects of mixing fresh water and sea water with halite-saturated brines that are not in contact with halite. The mixing of such a brine (brine *A*, for example) with fresh water causes the composition of the brine to move along a straight line toward point *B* with a 1:1 slope parallel to the line produced by the evaporation of sea water prior to the precipitation of halite. The mixing of halite-saturated brines with sea water produces trends toward the composition of sea water (fig. 7).

The dissolution of halite in sea water produces brines which are rich in chloride but relatively low in bromine (fig. 8). This diagram is based on the assumption that the halite which is being dissolved by sea water contains 68 ppm bromine in its crystal structure. If the halite contains a larger amount of bromine, the compositional trend will curve more perceptibly toward higher dis-

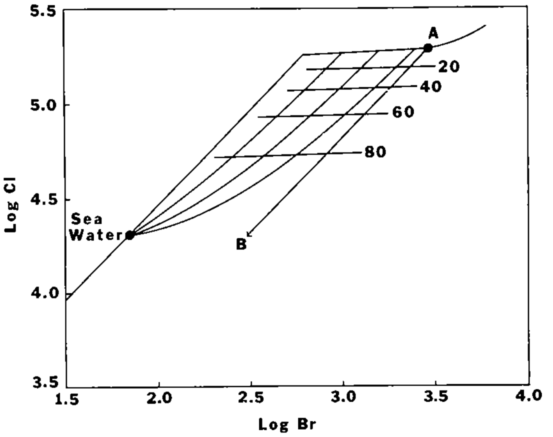


Figure 7. Relationships between chloride and bromide as a result of mixing NaCl-saturated brines with fresh water and with sea water. The addition of fresh water to a brine of composition *A* causes the chloride and bromide concentrations to move along a line with a 1:1 slope toward *B*. The addition of sea water to NaCl-saturated brines causes the chloride and bromide concentrations to move along trend lines which are initially nearly parallel to line *AB* but which converge on sea water as the percentage of sea water becomes large. The percentages of sea water in brine-sea water mixtures are indicated by the nearly horizontal isopleths.

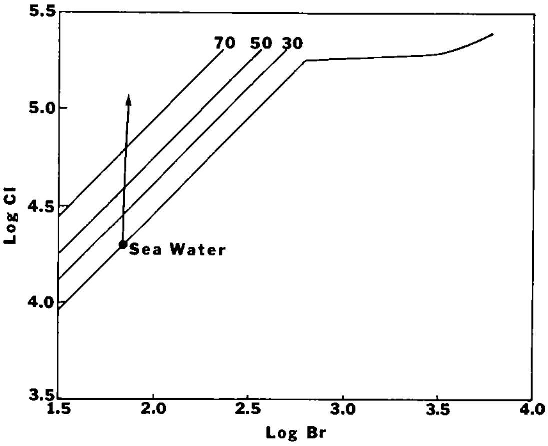


Figure 8. Relationships between chloride and bromide as a result of adding halite (containing 68 ppm bromine) to sea water. The isopleths indicate the percentage of chloride in the brine contributed by dissolved halite.

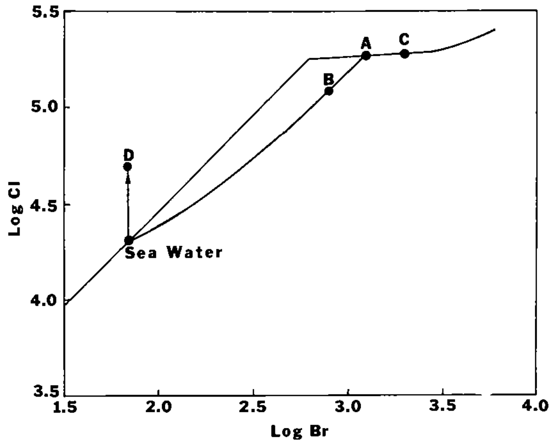


Figure 9. An illustration that a brine of arbitrary composition, *B*, can be produced by different mechanisms. Brines *A* and *C* are produced by the evaporation of sea water and the precipitation of halite. Brine *D* is produced by the addition of 60.4 grams of halite per liter of average sea water. Brine *B* can be produced by mixing 6 volumes of brine *A* with 4 volumes of average sea water. Brine *B* can also be produced by mixing 3.7 volumes of brine *C* with 6.3 volumes of brine *D*. The chemical composition of brine *B* is the same in all respects for the two cases described here.

solved bromide concentrations in the manner illustrated by Rittenhouse (1967).

Samples which contain more bromide and less chloride than would result from the evaporation of sea water are apparently a result of the mixing of waters of different origins and compositions. Unfortunately, it is generally not possible to determine the compositions and proportions of the waters that combine to form the hybrid solution. For example, brine *B* (fig. 9), can be produced by mixing six volumes of brine *A* with four volumes of average sea water. Brine *B* can also be produced by mixing 0.37 liters of brine *C* with 0.63 liters of sea water containing 60.4 grams of added halite in solution (brine *D*). Despite the fact that brine *B* may originate as a result of mixing solutions of differing origin, the interaction of brine *B* with minerals in reservoir rocks will be the same regardless of the mechanism by which the brine was formed.

INTERACTION OF CONCENTRATED SEA WATER WITH SEDIMENTARY ROCKS

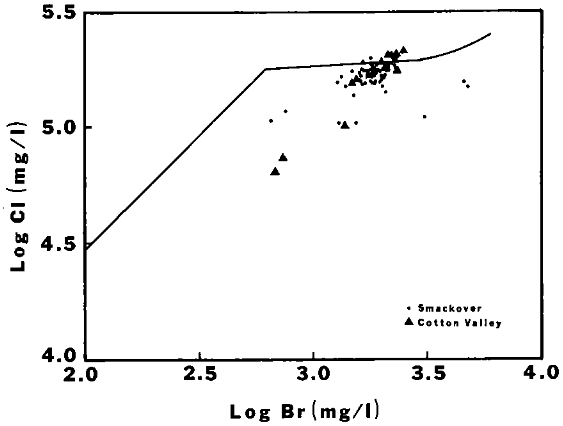


Figure 10. Chloride-bromide relationships in 86 oil-field brines from Jurassic reservoir rocks in Mississippi (Carpenter and others, 1974 and Carpenter, unpublished data). (The chloride-bromide relationships in most samples are close to the chloride-bromide concentration trend produced by the evaporation of sea water and the precipitation of halite.)

Figure 10 illustrates the chloride and bromide concentrations in 86 oil-field brines from Jurassic reservoir rocks in central Mississippi. The data points straddle the chloride-bromide concentration trend line for ocean water, strongly suggesting that these brines are genetically related to concentrated sea water. These brines probably originated as interstitial fluids in the Louann Salt and have been expelled upwards along fracture systems as a result of loading by younger sediments. The expulsion of large volumes of K-Mg-SO_4-rich brines associated with the compaction of thick evaporite sequences produces major changes in the overlying rocks and in the composition of the migrating brines. This section demonstrates that many of the specific changes in the rocks and brines are predictable and that regional data on rock mineralogy and brine chemistry can be used to reconstruct or recognize some aspects of ancient hydrologic systems.

Table 8 presents data on brines from Jurassic reservoir rocks in central Mississippi and from fluid inclusions in ore minerals from the Mississippi Valley region. The major differences between most oil-field brines and concentrated sea water are that oil-field brines contain high concentrations of calcium, appreciable strontium, and are very low in sulfate.

TABLE 8.—COMPOSITION OF BRINES IN FLUID INCLUSIONS, MISSISSIPPI VALLEY REGION (PPM)

	A	B	C	D
Ca	18,000	7,600	20,400	31,200
Mg	2,400	1,300	2,200	2,220
Sr				1,870
Na	57,100	49,000	53,400	65,500
K	2,700	2,800	2,500	713
Cl	124,600	94,000	120,000	161,200
SO_4	<3,000	2,200	1,000	15
T.D.S.[1]	208,000	156,900	199,500	264,700

A. Sphalerite, Tri State district, Ottawa Co., Oklahoma. (Roedder, et al., 1963).

B. Yellow fluorite, Cave-in-Rock district, Illinois. (Hall and Friedman, 1963).

C. Purple fluorite, Cave-in-Rock district, Illinois. (Hall and Friedman, 1963).

D. Metal-rich brine, Raleigh field, Smith Co., Mississippi., (Pb 91 ppm; Zn 296 ppm). (Carpenter et al., 1974).

[1] Total dissolved solids

Divalent Cations

The high calcium content of oil-field brines is undoubtedly due to the conversion of calcite to dolomite by magnesium-rich water:

$$2CaCO_3 + Mg^{2+} = CaMg(CO_3)_2 + Ca^{2+} \qquad (6)$$

Strontium in oil-field brines is most likely related to the recrystallization of aragonite to calcite:

$$(Ca_{1-x}Sr_x)CO_3 + yCa^{2+} = (Ca_{1-x+y})CO_3 + ySr^{2+} \qquad (7)$$

(An excellent summary of the geochemistry of strontium during carbonate diagenesis is available in Bathurst, 1975.) The essential point of this brief discussion is that there are abundant sources of calcium and strontium in sedimentary rocks and that these elements are readily exchanged for magnesium either directly or indirectly.

Some brine samples have characteristics which suggest the formation of authigenic laumontite ($CaAl_2Si_4O_{12} \cdot 4H_2O$). Merino (1975) reported the presence of laumontite in sandstones in the Temblor zone V, Kettleman North Dome, California, and noted that two independent lines of evidence indicate that detrital plagioclase in this reservoir alters to albite plus laumontite. A reaction which may occur in the deeply buried sandstone reservoirs in central Mississippi is:

$$\begin{aligned} &Ca^{2+} + 2NaAlSi_3O_8 + 4H_2O \\ &\quad = CaAl_2Si_4O_{12} \cdot 4H_2O + 2SiO_2 + 2Na^+ \qquad (8) \end{aligned}$$

Laumontite has not been reported in reservoir rocks in Mississippi; this may be because it is present in relatively small amounts and because no one has systematically examined these rocks for the presence of laumontite.

Sulfate

The availability of additional calcium to a brine as a result of dolomitization may result in the precipitation of additional sulfate either as gypsum or anhydrite:

$$Ca^{2+} + SO_4{}^{2-} = CaSO_4 \qquad (9)$$

Additional sulfate may also be lost from the brine by the process of sulfate reduction (Orr, 1974):

$$\begin{aligned} &SO_4{}^{2-} + 1.33CH_2 + 2H^+ \\ &\quad = H_2S + 1.33CO_2 + 1.33H_2O \qquad (10) \end{aligned}$$

Oil-field brines ordinarily contain less than 1,000 mg/l H_2S and are usually very low in both free CO_2 and HCO_3^- (Collins, 1975). The loss of H_2S from the brine may be attributed to precipitation as pyrite. The loss of carbonate species may be attributed to precipitation as carbonates, for example:

$$H_2O + CO_2 + Ca^{2+} = CaCO_3 + 2H^+ \qquad (11)$$

The net reaction involving sulfate reduction then becomes:

$$Ca^{2+} + SO_4{}^{2-} + 1.33CH_2 = H_2S + CaCO_3 + .33H_2O + .33CO_2 \quad (12)$$

Ashirov and Sazonova (1962) have shown experimentally that sulfate reduction in the presence of calcium is, in fact, accompanied by the precipitation of calcium carbonate. A fundamental aspect of the loss of sulfate from brines is the requirement that electrical neutrality in the solution be maintained. Since the loss of sulfate from brines is not accompanied by the addition of equivalent amounts of other anions, it follows that the loss of sulfate must be accompanied by the loss of cations from solution. These cations will be the divalent cations and will be precipitated as gypsum, anhydrite, calcite, and (or) dolomite.

Potassium

Carpenter and others (1974) noted substantial variations in potassium concentrations relative to bromide in central Mississippi brines. Brines stratigraphically just above the Louann Salt, have K/Br ratios similar to the K/Br ratio of sea water. Brines from approximately 5,000 feet above the Louann Salt have lost 90 percent of their potassium relative to bromide. The sandstone intervals for 2,000 feet above the Louann Salt contain abundant authigenic potash feldspar and (or) illite. These data indicate that the loss of potassium is related to such reactions as:

$$2K^+ + 3Al_2Si_2O_5(OH)_4 = 2H^+ + 2KAl_2AlSi_3O_{10}(OH)_2 + 3H_2O \quad (13)$$

$$2K^+ + KAl_2AlSi_3O_{10}(OH)_2 + 6SiO_2 = 2H^+ + 3KAlSi_3O_8 \quad (14)$$

$$2K^+ + Al_2Si_2O_5(OH)_4 + 4SiO_2 = 2KAlSi_3O_8 + H_2O + 2H^+ \quad (15)$$

The loss of potassium from the brine ceases when the K/H ratio reaches the appropriate equilibrium value. The reaction of potassium with low-potassium clay minerals to produce potassium-rich aluminosilicates can release substantial quantities of H^+ to the brine. For example, a brine containing 1,510 mg/l bromide should contain 9,240 mg/l potassium if the K/Br ratio is the same as that in sea water. Lower Cretaceous brines in central Mississippi with this concentration of bromide contain only 900 mg/l potassium (Carpenter and others, 1974). In this instance the formation of potassium aluminosilicates has resulted in the release of 0.24 moles H^+ per liter ($pH<2$). Since the observed pH's of these brines are considerably higher ($pH = 5.4$ at room temperature), it is evident that the H^+ has reacted with some constituent(s) in the rocks, probably carbonate minerals:

$$2H^+ + CaCO_3 = Ca^{2+} + CO_2 + H_2O \quad (16)$$

Thus the sum of equations 14 and 16 can be written:

$$2K^+ + CaCO_3 + KAl_2AlSi_3O_{10}(OH)_2 + 6SiO_2 = Ca^{2+} + 3KAlSi_3O_8 + H_2O + CO_2 \quad (17)$$

Sodium

The volume for volume replacement of detrital plagioclase and the presence of albite overgrowths on altered plagioclase in Tertiary sandstone, Kettleman North Dome, California, have been described by Merino (1975). A similar volume for volume alteration of detrital plagioclase to albite occurs in Jurassic and Cretaceous sandstones in central Mississippi (Carpenter and others, in preparation). This reaction can be expressed schematically as:

$$Na_{.80}Ca_{.20}Al_{1.20}Si_{2.80}O_8 + .2Na + .4SiO_2 + .1H_2O + 2H^+ = NaAlSi_3O_8 + .1Al_2Si_2O_5(OH)_4 + .2Ca^{2+} \quad (18)$$

The decision to express the aluminum released by the alteration of plagioclase as authigenic kaolinite is based on the observations that the reaction proceeds on a volume for volume basis and the dissolved aluminum in oil-field water is generally less than 0.1 mg/l (data from Chevron Oil Company and from Barnes, 1975).

Sodium may also be lost from brines as a result of reaction with clay minerals such as kaolinite to form authigenic albite:

$$2Na^+ + Al_2Si_2O_5(OH)_4 + 4SiO_2 = 2NaAlSi_3O_8 + H_2O + 2H^+ \quad (19)$$

The hydrogen ions released by this reaction presumably react with carbonate minerals in a manner analogous to equation 17 so that the sum of equations 16 and 19 becomes:

$$2Na^+ + CaCO_3 + Al_2Si_2O_5(OH)_4 + 4SiO_2 = Ca^{2+} + 2NaAlSi_3O_8 + 2H_2O + CO_2 \quad (20)$$

Other Considerations

The chemical composition of standard

ocean water is given in table 9. An extremely useful fact illustrated in this table is that regardless of the choice of salts selected to represent the composition of ocean water, a significant amount of divalent cations ($\geq$0.035 moles/liter) must be considered present as chlorides, expressed here as MCl_2. Both $CaCl_2$ and $MgCl_2$ are extremely soluble and do not precipitate from sea water in significant amounts until the deposition of carnallite ($KMgCl_3 \cdot 6H_2O$) This fact provides a basis for determining if a brine has originated from the evaporation of sea water followed by simple diagenetic interactions with sedimentary rocks or whether the brine has had a more complex origin. Table 10 illustrates the relationship of MCl_2 to bromide in evaporating sea water and during diagenesis. This relation may be expressed in the form:

$$R \cong \frac{\text{Ca + Mg + Sr - SO}_4\text{ - HCO}_3\text{ meq/l}}{\text{Br mg/l}} \qquad (21)$$

This equation takes into account any sulfate or bicarbonate present in the brine as a result of inadequate opportunity for magnesium to react with $CaCO_3$, producing dolomite and releasing calcium to be precipitated by reactions involving sulfate. In most oil-field brines the concentrations of sulfate and bicarbonate are very low so that:

$$R \cong \frac{\text{Ca + Mg + Sr meq/l}}{\text{Br mg/l}} \qquad (21a)$$

In fact, Ca> >Mg, Sr in many oil-field brines so that as a crude approximation:

$$R \cong \frac{\text{Ca meq/l}}{\text{Br mg/l}} \qquad (21b)$$

TABLE 9.—CHEMICAL COMPOSITION OF SEA WATER (after Riley and Chester, 1971, p. 64)

Constituent	mg/l	Salt	moles/liter
Ca	422	$CaCO_3$	.0012
Mg	1,326	$CaSO_4$	.0093
Na	11,050	$MgSO_4$	.0196
K	416	NaCl	.4806
Cl	19,870	KCl	.0106
SO_4	2,780	$MgCl_2$	.0349
HCO_3	142		

TABLE 10.—CHEMICAL COMPOSITION OF SEA WATER DURING EVAPORATION AND DIAGENESIS (MOLES/LITER)

Constituent	Seawater	Calcite[1]	Gypsum Anhydrite	Diagenesis[2]	Residue
Ca	.0105	.0012	.0093	.0196	.0349
Mg	.0545				
Na	.4806				.4806
K	.0106				.0106
Cl	.5605				.5605
SO_4	.0289		.0093	.0196	.0000
HCO_3	.0023	.0023			.0000
Br	.00085				.00085
R[3]	1.0265	1.0265	1.0265	1.0265	1.0265

[1] $Ca^{2+} + HCO_3^{-} = CaCO_3 + CO_2 + H^+$

[2] $Mg^{2+} + 2CaCO_3 = CaMg(CO_3)_2 + Ca^{2+}$

$Ca^{2+} + SO_4^{2-} = CaSO_4$

$Ca^{2+} + SO_4^{2-} + 1.33CH_2 = H_2S + CaCO_3 + .33H_2O + .33CO_2$

[3] $R = \dfrac{\text{Ca + Mg + Sr - SO}_4\text{ - HCO}_3\text{ meq/l}}{\text{Br} \qquad \text{mg/l}}$

Anderson and others (1966) noted that there is an approximately linear relationship between calcium and bromine in saline waters. They suggested that this relationship might involve dolomitization followed by the retention of calcium and bromide by a shale-membrane filter. However, the simplest explanation for the high correlation coefficient for calcium and bromide, or total divalent cations (meq/l) and bromide, in subsurface brines is that it is the natural result of dolomitization and the loss of sulfate from solutions produced by the evaporation of sea water.

The parameter MCl_2, Ca+Mg+Sr $-SO_4-HCO_3$ meq/l, appears to be of some value in determining the chemical history of chloride-rich brines. A plot of Log MCl_2 against Log Br in evaporating sea water (up to the point of carnallite precipitation) is a straight line with a 1:1 slope (fig. 11):

$$\text{Log MCl}_2 = \text{Log Br} + 0.011 \qquad (22)$$

Brines which plot above this line, such as point *A*, are enriched in MCl_2 or depleted in bromine relative to sea water. Enrichment in MCl_2 can easily be a result of the formation of potassium aluminosilicates (for example, equation 17) or the albitization of plagioclase (equation 18). Brines which plot below this line, such as point *B*, are depleted in MCl_2 or enriched in bromine relative to

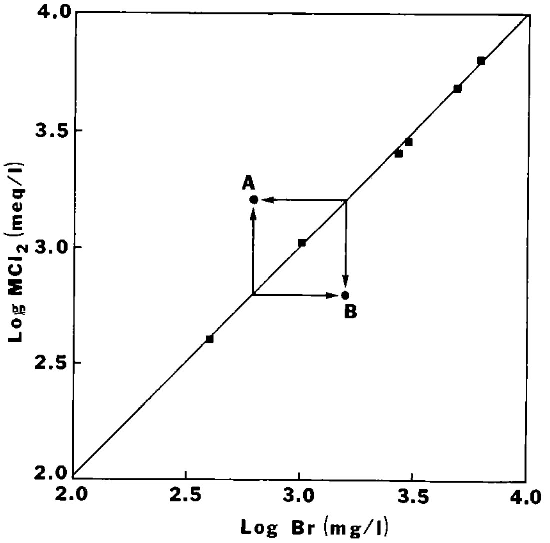


Figure 11. Calculated concentration trend of MCl_2 (meq. M^{2+}/l) relative to bromide during the evaporation of average sea water. (Data points for the evaporation of Black Sea water are from Zherebtsova and Volkova, 1966.) Hypothetical brine *A* is either enriched in MCl_2 or depleted in bromide with respect to brines produced by the evaporation of average sea water. Hypothetical brine *B* is either depleted in MCl_2 or enriched in bromide with respect to brines produced by the evaporation of average sea water.

sea water. One can usually determine which constituent is enriched or depleted with respect to sea water from the relationship of bromide to chloride (fig. 6) or MCl_2 to chloride in evaporating sea water. (The relationship of MCl_2 to chloride in evaporated sea water is essentially identical to that for bromide to chloride.) At least one of these two relationships will generally be in good agreement with that of evaporated sea water and may be used to estimate the concentrations of the major components of the original brine. One relationship, Br-Cl or MCl_2-Cl, may appear to be abnormal; this must be taken into account in attempting to reconstruct the unusual aspects of the original composition and subsequent chemical evolution of the brine.

THE CHEMICAL EVOLUTION OF AN Na-Ca-Cl BRINE

The combined effects of the reactions described above on a brine produced by the evaporation of sea water is illustrated below. This particular brine was collected from a well (Blakeney et al.) in central Mississippi producing from within the Cotton Valley Group (Upper Jurassic) at a horizon approximately 2,400 feet (730 m) above the Louann Salt (table 11). The first step in reconstructing the chemical evolution of this brine is to distribute the charge balance error among the ions in proportion to their concentration in milliequivalents per liter (meq/l). The brine from the Blakeney et al. well contains approximately 6,500 mg/l more chloride than would be expected in an NaCl-saturated marine brine containing 2,300 mg/l bromide. The additional chloride is probably the result of the dissolution of an additional 10,770 mg of halite per liter of brine (table 12). Carpenter and others (1974) noted that undiluted samples of Jurassic and Lower Cretaceous brines in this region usually precipitate readily visible amounts of NaCl within seven days from the time of collection. The additional 970 mg/l sodium may be attributable to the alteration of a small amount of albite to laumontite (equation 8).

The calcium content of the brine can be estimated on the basis of the types of reactions that have occurred (table 13). The most important reaction affecting this constituent is the conversion of calcite to dolomite (equation 6). Additional calcium is brought into solution as an indirect result of the formation of authigenic aluminosilicates (equation 17). Loss of calcium from the brine occurs as a result of exchange for strontium

TABLE 11.—COMPOSITION OF OIL-FIELD BRINE FROM THE BLAKENEY ET AL., UNIT 1, BAY SPRINGS FIELD, JASPER COUNTY, MISSISSIPPI (MG/L)

	Ca	Mg	Sr	Na	K	Cl	Br	SO_4	Error
Raw Data	45,900	2,960	1,740	63,200	6,100	196,100	2,320	< 100	-0.7
Adjusted Data	46,200	2,980	1,150	63,700	6,140	194,700	2,300	< 100	0.0
Evaporated Sea Water	100	44,800	< 1	58,500	14,000	188,100	2,300	60,300	0.0

TABLE 12.—CHEMICAL EVOLUTION OF AN NA-CA-CL BRINE-I (MG/L)

	Na	Cl
Brine	63,660	194,670
Evaporated Sea Water	58,450	188,140
Excess Na, Cl	5,210	6,530
Addition of 10.77 gms NaCl/liter	4,240	6,530
Excess Na	970	
Na from alteration of 11.1 gms of albite	970	

in $CaCO_3$ (equation 7), as a result of the loss of sulfate from the brine (equation 9 or equation 12), and as a result of the formation of a small amount of laumontite or some other calcium aluminosilicate (equation 8).

These reactions also affect the detrital minerals in the rock which are reacting with the brine. In this particular case, 0.10–0.15 moles (26.9–40.4 gms) of kaolinite would be consumed by the growth of authigenic potassium aluminosilicates per liter of brine (equations 13, 14, and 15). In addition, the formation of authigenic K-spar from kaolinite and the alteration of albite to laumontite would result in the conversion of up to 0.56 moles (33.7 gms) of quartz into authigenic alkali aluminosilicate minerals (equations 8, 14, and 15). The calcite produced as a result of sulfate reduction minus the calcite dissolved as a result of the formation of potassium aluminosilicates can be as large as 0.527 moles (52.7 grams of calcite) per liter of brine. The calcium precipitated as a result of sulfate reduction may not actually be present as calcite since the large amount of magnesium in the initial brine is capable of converting 3.44 moles (344 gms) of calcite to dolomite.

The preceeding tables and statements indicate that the potassium-magnesium-sulfate-rich brines produced by the evaporation of normal sea water can significantly alter the mineralogy of the rocks with which they may come in contact. Generally, the product of these reactions will be rocks that have lost much or all of their original calcite and kaolinite and now contain dolomite, and authigenic illite, K-spar, and albite. The brines in the pores of these rocks will be Na-Ca-Cl brines, which are low in potassium and essentially devoid of sulfate. Thus, the migration path of marine brines can be recognized by the spatial variations in the authigenic minerals and brine chemistry within sedimentary basins.

The interaction of brines with the minerals in sedimentary rocks will obviously modify the porosity and permeability of these rocks. However, the magnitude of the changes in porosity (and perhaps permeability) cannot be made without first specifying the initial mineralogy and porosity of the original sediment or rock and without specifying the volume of brine that has reacted with the rock. In some cases, reasonable estimates of these parameters may be available, and the quantitative estimation of brine-rock interaction may be of value in understanding, predicting, or evaluating the characteristics of potential petroleum reservoir rocks.

FUTURE WORK

The logic and procedure for estimating the nature and extent of brine-rock interac-

TABLE 13.—CHEMICAL EVOLUTION OF AN NA-CA-CL BRINE-II (MG/L)

	Ca	Mg	Sr	K
Brine (Blakeney et al. well)	46,200	2,980	1,750	6,140
Evaporated sea water	100	44,800	<1	14,000
Dolomitization	+68,870	-41,780		
Recrystallization of aragonite	-800		+1,750	
Formation of potassium aluminosilicates	+7,190			-7,860
Loss of sulfate	-25,160			
Formation of laumontite	-850			
Reacted sea water	46,200	2,980	1,750	6,140

tion outlined above is a product of an extensive study of the brines and petroleum reservoir rocks of the central Mississippi salt-dome basin. For the most part, the Jurassic and Lower Cretaceous brines in this region are relatively simple, NaCl-saturated, Na-Ca-Cl brines. An investigation of the bromide-rich brines of southern Arkansas (Carpenter and Trout, 1978) has shown that brine-rock interaction in this region may be estimated by a slight modification of the technique outlined here. However, a preliminary study of the very calcium-rich brines of southern Michigan has shown that still other factors, such as the effect of $MgCl_2$ released by the alteration of carnallite, must be taken into consideration in attempting to unravel the origin and chemical evolution of those brines. A procedure for reconstructing the chemical evolution of different types of evaporite-related brines is in progress, but additional work is required before it will be capable of contending with the range of origins and evolutionary paths that appear to exist.

SUMMARY

A brine may be defined as an aqueous solution containing more than 100,000 mg/l dissolved solids. A review of the literature on dissolved salts in subsurface waters indicates that brines in sedimentary basins are genetically related to evaporites. The most common type of brine appears to originate as interstitial fluids in evaporites and is then subsequently expelled as a result of the compaction that occurs in response to loading by younger sediments.

The chemical composition of brines produced by the evaporation of sea water has been studied by Zherebtsova and Volkova (1966) and by Herrmann and Knake (1973). A critical review of this data indicates that bromine is an inert constituent during the evaporation of sea water and that the ratios of other constituents to bromine is a sensitive indicator of the precipitation of evaporite minerals and other reactions.

The interaction of brines produced by the evaporation of sea water with common minerals in sedimentary rocks involves a number of chemical reactions: (1) the conversion of calcite to dolomite that results in an increase in the calcium content of the brine; (2) the precipitation of calcium sulfate; (3) the reduction of sulfate to sulfide accompanied by the precipitation of calcite or dolomite; (4) the formation of authigenic sodium and potassium aluminosilicates accompanied by the destruction of detrital kaolinite and the dissolution of carbonates. In some cases brines are affected by the gain or loss of bromine or magnesium chloride. This type of situation can be detected and taken into account using the relationship of MCl_2 ($Ca + Mg + Sr - SO_4 - HCO_3$, meq/l) to bromide.

Brines from Jurassic and Lower Cretaceous oil fields in the central Mississippi salt-dome basin are generally simple, NaCl-saturated, Na-Ca-Cl brines. The chemical evolution of these brines can be reconstructed with little difficulty.

ACKNOWLEDGMENTS

I wish to thank the members of the Missouri Friends of Oilfield Brines group, James Darr, Laura Fox, James Frank, Michael Garbarini, Bruce Grethen, and Tom Hesemann, for their contributions to and discussion of ideas on the origin and chemical evolution of oil-field brines. Michael Garbarini and Laura Fox were of great assistance in writing the computer programs which were used in the preparation of this report. The illustrations were prepared by Kirk McQuillan. I wish to thank Mecca B. Carpenter for critically reviewing the manuscript. This investigation was supported in part by a grant from the National Science Foundation (NSF-EAR-74-13669-A01- Carpenter).

REFERENCES CITED

Anderson, R. J., Graf, D. L., and **Jones, B. F.,** 1966, Calcium and bromide contents of natural waters: Science, v. 153, p. 1637-1638.

Ashirov, K. B., and **Sazonova, I. V.,** 1962, Biogenic sealing of oil deposits in carbonate reservoirs: Mikrobiologiya, v. 31, p. 680-683.

Barnes, R. A., 1975, The determination of specific forms of aluminum in natural water: Chemical Geology, v. 15, p. 177-191.

Bathurst, R. G., 1975, Carbonate sediments and their diagenesis: Elsevier, New York, 658 p.

Braitsch, O., 1971, Salt deposits their origin and composition: Springer-Verlag, New York, 297 p.

Carpenter, A. B., and **Trout, M. L.,** 1978, Geochemistry of bromide-rich brines of the Dead Sea and southern Arkansas, *in* Johnson, K. S., and Russell,

J. A., editors, Thirteenth industrial minerals forum: Oklahoma Geological Survey Circular 79. p. 78-88.

Carpenter, A. B., Trout, M. L., and **Pickett, E. E.,** 1974, Preliminary report on the origin and chemical evolution of lead- and zinc-rich brines in central Mississippi: Economic Geology, v. 69, p. 1191-1206.

Collins, A. G., 1975, Geochemistry of oilfield brines: Elsevier Scientific Publishing Company, Amsterdam, 496 p.

Davis, S. N., 1964, The chemistry of saline waters by R. A. Krieger—Discussion: Ground Water, v. 2, no. 1, p. 51.

Hall, W. E., and **Friedman, I.,** 1963, Composition of fluid inclusions, Cave-in-Rock fluorite district, Illinois, and Upper Mississippi Valley district: Economic Geology, v. 58, p. 886-911.

Hanshaw, B. B., and **Coplen, T. B.,** 1973, Ultrafiltration by a compacted clay membrane — II. Sodium ion exclusion at various ionic strengths: Geochimica et Cosmochimica Acta, v. 37, p. 2311-2327.

Herrmann, A. G., and **Knake, D.,** 1973, Geochemistry of modern sea water and brines from salt pan: main components and bromine distribution: Contributions to Mineralogy and Petrology, v. 40, p. 1-24.

Kharaka, Y. K., and **Smalley, W. C.,** 1976, Flow of water and solutes through compacted clays: American Association of Petroleum Geologists Bulletin, v. 60, p. 973-980.

Kilinic, I. A., and **Burnham, C. W.,** 1972, Partitioning of chloride between a silicate melt and coexisting aqueous phase from 2 to 8 kilobars: Economic Geology, v. 67, p. 231-235.

Krieger, R. A., 1963, The chemistry of saline waters: Ground Water, v. 1, no. 4, p. 7-12.

Landes, K. K., 1960, The geology of salt deposits, *in* Kaufman, D. W., editor, Sodium chloride: Reinhold, New York, p. 28-69.

Mangelsdorf, P. C., Manheim, F. T., and **Gieskes, J. M. T. M.,** 1970, Role of gravity, temperature gradients, and ion-exchange media in formation of fossil brines: American Association of Petroleum Geologists Bulletin, v. 54, p. 617-626.

Manheim, F. T., and **Horn, M. K.,** 1968, Composition of deeper subsurface waters along the Atlantic coastal margin: Southeastern Geology, v. 8, p. 215-236.

Merino, E., 1975, Diagenesis in Tertiary sandstones from Kettleman North Dome, California. I. Diagenetic mineralogy: Journal of Sedimentary Petrology, v. 45, p. 320-336.

Morris, R. C., and **Dickey, P. A.,** 1957, Modern evaporite deposition in Peru: American Association of Petroleum Geologists Bulletin, v. 41, p. 2467-2474.

Orr, W. L., 1974, Changes in sulfur content and isotopic ratios of sulfur during petroleum maturation: American Association of Petroleum Geologists Bulletin, v. 58, p. 2295-2318.

Riley, J. P., and **Chester, R.,** 1971, Introduction to marine chemistry: Academic Press, New York, 465 p.

Rittenhouse, G., 1967, Bromine in oil-field waters and its use in determining possibilities of origin of these waters: American Association of Petroleum Geologists Bulletin, v. 51, p. 2430-2440.

Roedder, E., 1977, Fluid inclusions as tools in mineral exploration: Economic Geology, v. 72, p. 503-525.

Roedder, E., Ingram, B., and **Hall, W. E.,** 1963, Studies of fluid inclusions III: Extraction and quantitative analysis of inclusions in the milligram range: Economic Geology, v. 58, p. 353-374.

Zherebtsova, I. K., and **Volkova, N. N.,** 1966, Experimental study of behavior of trace elements in the process of natural solar evaporation of Black Sea water and Sasyk-Sivash brine: Geochemistry International, v. 3, p. 656-670.

GEOCHEMISTRY OF BROMIDE-RICH BRINES OF THE DEAD SEA AND SOUTHERN ARKANSAS

Alden B. Carpenter[1] and Michael L. Trout[2]

Abstract—The Dead Sea is the only relatively large body of surface water having bromide concentrations comparable to those in the brines of the Smackover Formation in Arkansas. The Dead Sea, like the Smackover brines, contains a great deal of calcium and is very low in sulfate and iodide. The relationships between potassium, divalent cations, and chloride indicate that over 20 percent of the bromide in the Dead Sea is derived from some source other than by the evaporation of sea water. A similar type of study of the Smackover brines in Arkansas indicates that approximately 60 percent of the bromide has been derived from some source other than sea water. Both the Dead Sea and Smackover brines are very low in iodide suggesting that the excess bromide has not been derived from organic matter. The origin of the excess bromide is probably the same for both of these brines, but the source of this bromide remains unknown.

INTRODUCTION

In 1976 approximately 300 million pounds of bromine were recovered from bromide-rich brines in the Smackover Formation of southwestern Arkansas. This quantity represents approximately 50 percent of world bromine production. The bromide-rich brines of the Dead Sea are another major source of bromine for world consumption. The Dead Sea is estimated to contain one billion tons of bromine. The purpose of this report is to analyze selected aspects of the geochemistry and origin of these bromide-rich brines.

The origins and chemical evolution of brines in sedimentary basins have been summarized by Carpenter (1978). (Brine is an aqueous solution containing more than 100,000 mg/l total dissolved solids.) These brines are genetically related to evaporites although the chemical composition of these brines can be modified to some extent by gravitational settling of ions, ion movement in a thermal gradient, thermocell diffusion, and interaction with minerals in the enclosing rocks. Experimental and field data related to shale-membrane filtration indicate that although these processes are capable of increasing the salinity and modifying the composition of brackish water, it is not a plausible mechanism for producing brines from sea water.

The trends in the chemical composition of sea water during evaporation and during the precipitation of evaporite minerals have been reviewed by Carpenter (1978). The variations in chloride and bromide concentrations during the evaporation of sea water are illustrated in figure 1. The concentrations of chloride and bromide in brines from

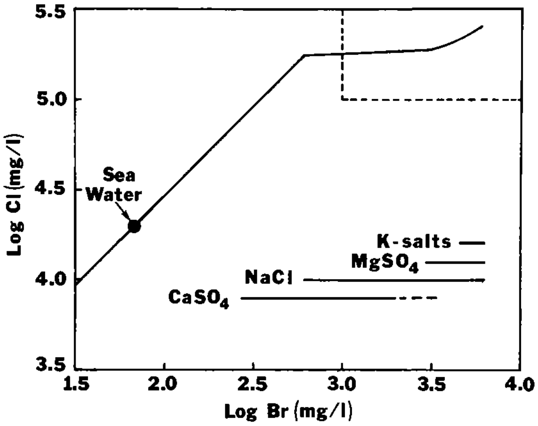


Figure 1. Concentration trend of chloride relative to bromide during the evaporation of sea water and the precipitation of evaporite minerals (from Carpenter, 1978). The precipitation ranges of the common evaporite minerals are indicated by the horizontal bars. The concentrations of chloride and bromide in Smackover brines in Arkansas and Mississippi and brines in the Dead Sea lie in the dashed rectangle in the upper right-hand corner of the diagram.

---

[1] Department of Geology, University of Missouri, Columbia, Missouri.

[2] Phillips Petroleum Co., Bartlesville, Oklahoma.

the Smackover Formation in Arkansas and in brines from the Dead Sea area lie within the dashed rectangle in the upper right-hand corner of the diagram.

DEAD SEA BRINES

The Dead Sea is the only large body of surface water having bromide concentrations comparable to those in the brines of the Smackover Formation in Arkansas. The Dead Sea, like the Smackover brines, contains a great deal of calcium and is very low in sulfate. It seems likely that these two bodies of water had a similar history, and any information on the origin and chemical evolution of the Dead Sea will be of value in reconstructing the history of the Arkansas brines. The most significant recent papers on the origin and geochemistry of the Dead Sea are those by Bentor (1961), Neev and Emery (1967), Lerman (1967) and Zak (1974).

The Dead Sea lies near the center of the Jordan-Arava graben which extends some 600 km from the Red Sea at the Gulf of Eilat to the Mediterranean. According to Bentor (1961), this graben is believed to have originated during the early Tertiary (probably Oligocene); and the central portion was flooded, at least intermittently, with sea water during the Neogene. In the late Pliocene or early Pleistocene, tectonic movements severed the connection of the Dead Sea with the Mediterranean, and the Dead Sea is believed to have been isolated from a source of sea water since that time. During the Pleistocene, the Dead Sea depression was occupied by a fresh water lake, Lake Samra. After a short interval, the water turned brackish; the fresh water lake was replaced by the saline Lisan Lake.

The sedimentology and bromine geochemistry of sediments in the Dead Sea basin have been described by Neev and Emery (1967) and by Zak (1974). More than 2,400 m of Pliocene and earliest Pleistocene halite is known to occur beneath the Dead Sea at two different locations. Zak noted the presence of halite with "rare zones with traces of dispersed and disseminated sylvite and pockets of carnallite and sylvite" at a depth of approximately 1,000 m. The thick salt deposits beneath the Dead Sea are overlain by 900 m of Pleistocene and Recent marls and sand with some evaporite intervals. Zak noted the presence of "small acicular crystals of $CaCl_2$ and $MgCl_2$ salts dispersed in laminated sediments" in the top 400 m of sediment. The laminated sediments consist of aragonite, calcite, dolomite, gypsum, anhydrite, halite, clay, and silt. The halite in the thick salt deposits beneath the Dead Sea contains 40–600 ppm bromine (Zak, 1974). The mean bromine content of the halite generally increases from 100 ppm at a depth of 2,530 m to 290 ppm in the halite of Recent sediments of the Dead Sea.

Reliable estimates of the sources of the dissolved salts in the Dead Sea are not available because of uncertainties in the chemical composition of the Jordan River and uncertainties in the relative discharge from the Jordan River and various salt springs into the Dead Sea. Many geologists agree, however, that most of the salts have been derived from earlier residual marine brines trapped in the evaporite sediments beneath the Dead Sea. The high calcium concentrations in these brines are a result of the dolomitization of calcite and aragonite in sediments of the Dead Sea Group. Low sulfate concentrations are a result of the precipitation of gypsum and anhydrite and of sulfate reduction accompanied by the precipitation of calcium carbonate. The very low SO_4/Cl ratio in the Jordan River, relative to spring water within the same drainage basin but located above the Dead Sea Group sediments, very strongly suggests that the Jordan River salts are also largely of residual brine origin (Neev and Emery, 1967). The chemical composition of brines from various sources in the Dead Sea area are presented in table 1. One of the remarkable features of the Dead Sea brine is its extremely low iodine content (less than 0.1 mg/l) (Bentor, 1961).

BROMIDE-RICH BRINES OF SOUTHWESTERN ARKANSAS

Brines containing more than 4,000 mg/l bromide are present in the Smackover Formation (Jurassic) throughout a 3,000 square kilometer area in southwestern Arkansas. Five companies recover bromine from brine fields in Union and Columbia Counties.

The geology of the bromide-rich area is

TABLE 1.—CHEMICAL COMPOSITION OF BRINE FROM THE DEAD SEA AREA (MG/L)

Brine	Ca	Mg	Na	K	Cl	Br	SO_4	HCO_3	Reference
Dead Sea Water									
(Deep Member)	17180	42430	39700	7590	219,250	5270	420	220	Neev and Emery, 1967
Subsurface Brines									
Sedom I (artesian well)	85200	21100	23100	30100	274,800	3100		trace	Bentor, 1969
Sedom I (artesian well)	80530	18430	17930	27360	255,500	2870	108		
Mumillah Spring, Mt. Sedom	48010	45650	14390	14720	255,300	3060	58		
Avg. of 3 Mt. Sedom Springs	37240	41670	24813	15992	247,720	2900	107	127	
Mayan Ha Reiach, S. (well)	22810	38360	33450	18355	228,600	2330	263	neg.	Mazor, 1962
Tumillet hole	40900	41000	26600	14900	259,080	3310		380	
Well near Mayan Ha Reiach, N.	12860	56220	21620	28780	240,170	3830	134	376	
Jordan River	129	95	224	32	762	9	97	181	Neev and Emery, 1967

summarized in table 2. Brines and petroleum are produced from the upper portion of the Smackover Formation, known locally as the Reynolds Oolite. The oolite consists of calcite with minor amounts of dolomite and anhydrite and trace amounts of quartz, pyrite, sphalerite, and galena. Chemical analyses of Smackover brines from a number of localities in southwestern Arkansas are presented in table 3.

Collins (1974) conducted an extensive investigation of the geochemistry of liquids, gases, and rocks from the Smackover Formation including the bromine-rich region of Arkansas. His data show that iodine concentrations in the bromide-rich brines are typical for brines of that salinity (10-30 mg/l). Collins also determined the bromine concentration in the halite of the Louann Salt which underlies the Smackover Formation in this region. His data show that the bromine content of the halite ranges from 80 to 405 ppm with a mean value of 240 ppm. The data on the bromine content of Louann halite are too limited to determine whether there are any systematic trends in bromine content with respect to stratigraphic position.

DISCUSSION

Figure 2 illustrates the relationships between chloride and bromide concentrations in brines from the Dead Sea area and in brines from the Smackover Formation in southwestern Arkansas. Chloride and bromide concentrations in Smackover brines from central Mississippi are also shown for comparison (Carpenter and others, 1974, and Carpenter, unpublished data). The data points for the Smackover brines in Mississippi are quite close to the chloride-bromide concentration trend produced by the evaporation of sea water. The Smackover brines in Arkansas contain similar chloride concentrations but are very much higher in bromide. In fact, with the exception of one sample from the Arkansas-Louisiana State line, the bromide concentrations of the Arkansas brines are comparable to bromide concentrations in salt pans in which potash salts are being precipitated. The brines from springs and wells in the Dead Sea area contain more chloride than any of the other brines under consideration and have bromide concentrations intermediate between the Smackover brines from Mississip-

TABLE 2.—SUMMARY OF SOUTHWESTERN ARKANSAS STRATIGRAPHY (FROM TROUT, 1974)

SERIES	FORMATION	THICKNESS (ft.)	LITHOLOGIC DESCRIPTION
UPPER JURASSIC	Cotton Valley Group	0-2700	Principally near-shore red beds consisting of varicolored shale, sandstone and basal conglomerate; grading southward to offshore gray shale, sandstone and limestone and the dark shales and sand of the Bossier Formation.
	Buckner	0-274	Red shale grading to red shale with intercalations of anhydrite with dolomitic streaks grading to fairly massive anhydrite.
	Smackover	0-1000	The upper portion is dense dolomite and dolomitic shale "Cap Rock" (lower Buckner of some authors) overlying the Reynolds Oolite zone and lower chalk zone. The lower member is dense, argillaceous limestone.
	Norphlet	0-150	Red and gray shale and sandstone with fluvial gravel and mudstone in the northern part of the area.
MIDDLE OR LOWER JURASSIC	Louann	0-1404	White to gray, coarsely crystalline halite with anhydrite streaks.
	Werner	0-200	Dense granular anhydrite overlying beds of red shale and sandstone, commonly conglomeratic at the base.
UPPER TRIASSIC	Eagle Mills	0-6968	Continental, water-laid deposits; principally red shale mottled gray or green. Also contains sandstones and siltstones with some conglomerate, and nodular limestone, dolomite and anhydrite Pre-Werner diabase intrusions are known.

pi and from Arkansas. The brine from the Deep Member of the Dead Sea Group (Neev and Emery, 1967) contains less chloride and significantly more bromide than the brines collected from the nearby springs and wells. The chloride and bromide content of the Dead Sea brine is comparable to that of some of the Smackover brines in Arkansas.

The relationships between potassium and bromide in sea water during evaporation and in the brines under consideration are shown in figure 3. There is a perceptible degree of scatter in the data points for the Smackover brines. This scatter is probably due to variations in the extent to which these brines have reacted with clay minerals to produce potassium-rich authigenic aluminosilicates:

$$2K^+ + Al_2Si_2O_5(OH)_4 + 4SiO_2 = 2KAlSi_3O_8 + H_2O + 2H^+ \qquad (1)$$

Figure 2 clearly illustrates that the mean potassium concentration of the Mississippi brines is much higher than in the bromide-rich brines of Arkansas and that the potassium-bromide relationships in some Mississippi brines is the same or very similar to the potassium-bromide trend. The brines from springs and wells in the Dead Sea area cluster about the potassium-bromide trend produced by the evaporation of sea water. Although the brine in the deeper portions of the Dead Sea is much richer in bromide, it is much lower in potassium.

TABLE 3.—CHEMICAL COMPOSITION (MG/L) OF SMACKOVER BRINES, SOUTHERN ARKANSAS (FROM TROUT, 1974)

Sample[1]	Well	Type of[2] Sample	Fe	Mn	Pb	Zn	Mg	Ca	Sr	Ba	Li	Na	K	Cl	Br	SO_4	H_2S	TDS	Den.	% Error
Buckner Field, Lafayette and Columbia Cos. (1/9/73)																				
3	McKean B12	WH	31	14	<1	12	3910	41500	2030	<20	92	65300	1810	189,000	6020			309,900	1.212	-0.6
4	McKean D6	WH	34	14	2	24	4030	44200	2030	<20	95	64500	1800	190,800	6160			313,700	1.212	0.0
Cairo Field, Union Co. (1/8/73)																				
5	Edwards D1	WH	<2	4	<1	<1	3550	37600	1910	<20	159	65600	1950	183,900	5490			300,300	1.205	-1.0
6	Murphy-Mckinney	WH	<2	4	<1	<1	3760	38000	2120	<20	175	68700	2120	188,100	5600			308,700	1.210	-0.4
Kerlin Brine Field, Columbia Co. (1/9/74)																				
8	BSW #17	WH	5	37	<.5	.4	3490	44200	2930	38	312	74600	5000	210,900	6130	>100	172	347,600	1.229	-0.4
9	BSW #36	WH	7	17	<.5	.4	3550	45600	2640	20	214	68200	3294	197,000	5830	158	196	326,300	1.223	0.7
Kilgore Lodge Brine Field, Columbia Co. (1/7/74)																				
10	Jameson	WH	15	50	<.5	.7	3480	44500	2760	38	269	80000	4670	209,600	6100	150	215	351,400	1.228	1.8
11	Carter	WH	3	47	<.5	.7	3380	42800	2960	34	302	79400	5060	210,800	6130	150	246	350,800	1.228	0.7
Lewisville Field, Lafayette Co. (1/7/74)																				
12	Beasley et al #1	WH	92	46	<.5	13	3640	39900	2060	13	67	60400	1510	179,300	5780	160	0	292,800	1.203	-1.1
13	Morton	WH	59	16	1.5	15	3680	38400	2080	6	59	65600	1320	183,300	5500	174	0	300,000	1.206	-0.7
Magnolia Field, Columbia Co. (1/8/74)																				
14	Crisp #1	DST	152	11	1.6	.9	3820	42700	2760	11	77	76700	1270	200,800	4370	173		332,600	1.223	1.5
Mt. Zion Field, Union Co. (1/10/74)[3]																				
16	Flournoy #1	WH	3	2	<.5	<.5	3350	28200	1330	<5	56	61000	862	156,800	3940	237	14	255,500	1.177	-0.8
Palm Field, Lafayette Co. (1/7/74)																				
17	Featherstone #2	SP	98	6	<.5	4	4090	35300	1430	7	84	54500	1520	156,200	4550			257,800		1.1
Parker's Chapel Brine Field, Union Co. (1/17/74)																				
18	BSW #7	WH	1	4	<.5	<.5	3300	35800	2080	<5	172	63000	1900	175,200	5100	174	144	286,600	1.199	-0.9
19	BSW #8	WH	3	6	<.5	<.5	3570	40000	2120	<5	173	63500	2050	177,200	5030	174	157	293,700	1.203	1.2

Table 3 (cont.)

Sample[1]	Well	Type of Sample[2]	Fe	Mn	Pb	Zn	Mg	Ca	Sr	Ba	Li	Na	K	Cl	Br	SO_4	H_2S	TDS	Den.	% Error
	Spirit Lake Field, Lafayette Co. (1/16/74)																			
23	Carter-Moore #2	WH	39	38	18	64	3990	44300	2470	20	134	68000	2400	194,600	6360	153		322,400	1.221	0.6
24	Carter-Moore #3	WH	38	37	19	66	4020	43800	2510	13	136	68300	2430	194,600	6360	127		322,800	1.221	0.6
	Village Field, Columbia Co. (1/8/73)																			
27	Lewis D1	WH	1	2	<1	<1	3700	32600	1660	<20	64	65500	1250	176,600	5030		12	286,500	1.196	-1.8
29	Harris E1	WH	196	3	<1	<1	3720	34000	1690	<20	67	65500	1220	176,500	5030			288,100	1.197	-0.9
	Walker Creek Field, Lafayette and Columbia Cos. (1/11/73)																			
30	Hunt-Ham #1	WH	207	9	<.5	17	2710	35300	2900	34	102	62400	1710	178,400	2240	116		286,000	1.198	-2.3

---

[1] Sample numbers are the same as those used in Trout (1974).

[2] Type of Sample (WH, well head; SP, separator).

[3] Sample may be from the oolitic facies of Buckner Formation.

Carpenter (1978) showed that sea water contains a significant concentration of calcium-magnesium chloride and that the concentration of divalent ions electrically balanced by chloride can be calculated by the expression,

$$MCl_2 = Ca + Mg + Sr - SO_4 - HCO_3 \text{ (meq/l)}, \quad (2)$$

where M^{2+} as chlorides is stated in milliequivalents per liter (meq/l). Since the concentration of sulfate and bicarbonate in these brines is extremely low, the concentration of M^{2+} as chlorides becomes

$$MCl_2 = Ca + Mg + Sr \text{ (meq/l)} \quad (3)$$

Carpenter noted that the ratio MCl_2/Br is constant during the evaporation of sea water, and that the ratio,

$$\frac{Ca + Mg + Sr - SO_4 - HCO_3 \text{ (meq/l)}}{Br \text{ (mg/l)}} = R = 1.0265. \quad (4)$$

can be used as the first step of a procedure to determine the nature and extent of the chemical alteration of marine brines. Figure 4 illustrates the relationship between MCl_2 and bromide during the evaporation of sea water. The data points for the Smackover brines in Mississippi straddle the MCl_2-bromide trend line for sea water indicating these brines have not gained or lost significant amounts of MCl_2 or bromide relative to sea water. The brines from the springs and wells in the Dead Sea area have compositions that plot to the left of the trend line indicating that these brines are enriched in MCl_2 or depleted in bromide relative to sea water. The brine in the deeper portions of the Dead Sea and the Smackover brines in Arkansas have compositions that plot to the right of the trend line indicating that these brines are depleted in MCl_2 or enriched in bromide relative to sea water.

A solution to the problem of which brines have gained or lost which constituents can be obtained by a comparison of the brine data with the MCl_2-chloride trend line shown in figure 5. In this figure the data points for all of the brines lie relatively close to the trend line. The data points for the Smackover brines from both Mississippi and Arkansas plot within a common region along the trend line. The relatively good agreement between the MCl_2-chloride data

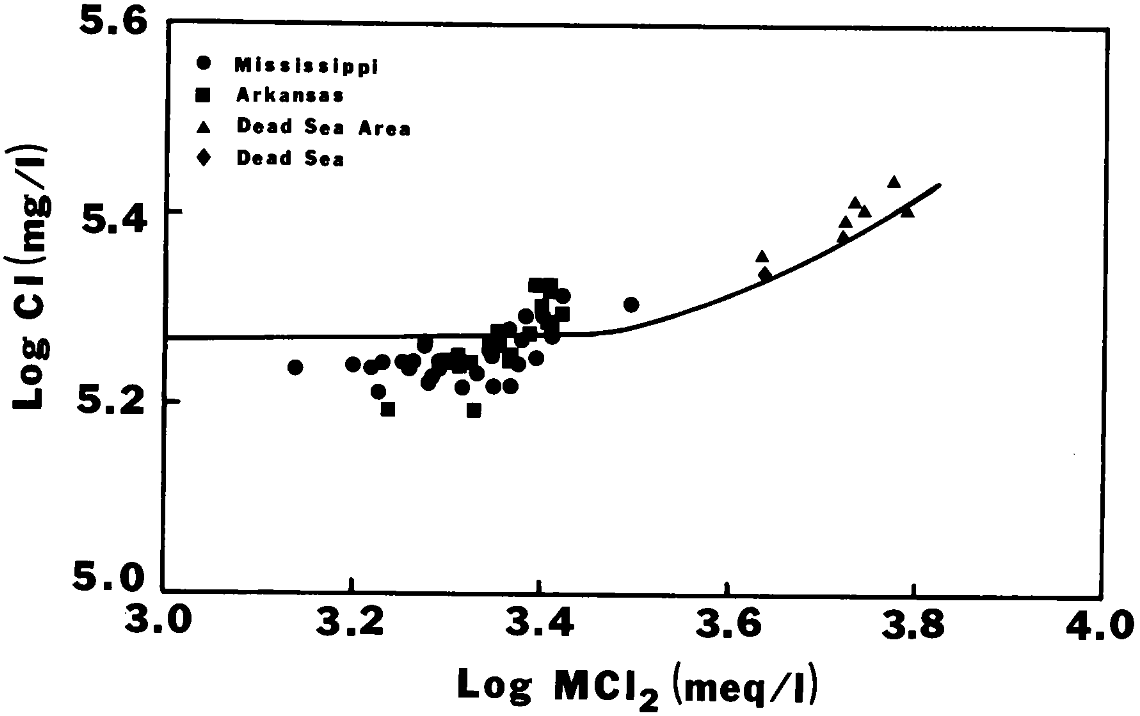


Figure 2. Concentration trend of chloride relative to bromide during the evaporation of sea water and the precipitation of halite and carnallite. Halite is present along the full length of the trend line. The precipitation range of carnallite is indicated by the horizontal line.

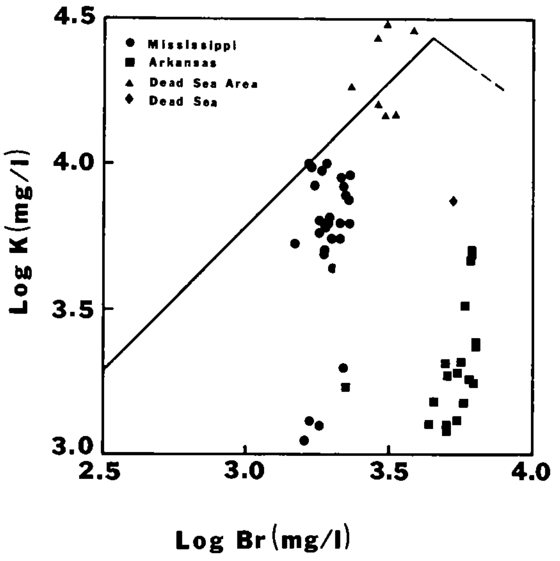


Figure 3. Concentration trend of potassium relative to bromide during the evaporation of sea water and the precipitation of carnallite. The precipitation of carnallite begins at the point where the trend line changes from a positive to negative slope.

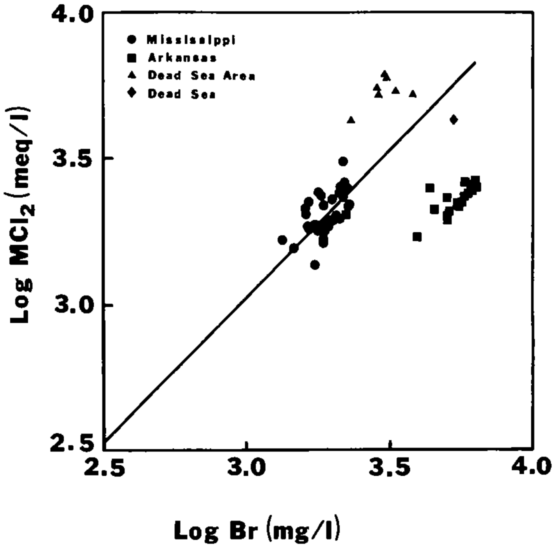


Figure 4. Concentration trend of MCl_2 (meq/l) relative to bromide during the evaporation of sea water.

TABLE 4.—EXCESS BROMIDE IN BROMIDE-RICH BRINES (MG/L)

Sample	Well	Arkansas Total Bromide	Bromide From Sea Water	Excess Bromide	Percent Excess Bromide[1]
3	McKean B12	5970	2330	3650	61
4	McKean D6	6150	2450	3700	60
5	Edwards D1	5420	2120	3290	61
6	Murphy-Mckinney	5560	2150	3410	61
8	BSW #17	6080	2440	3640	60
9	BSW #36	5850	2480	3380	58
10	Jameson	6190	2400	3790	61
11	Carter	6150	2340	3810	62
12	Beasley *et al* #1	5710	2240	3470	61
13	Morton	5450	2160	3290	60
14	Crisp #1	4430	2340	2090	47
16	Flournoy #1	3900	1630	2270	58
17	Featherstone #2	4590	2000	2590	56
18	BSW #7	5040	2010	3030	60
19	BSW #8	5070	2190	2880	57
23	Carter-Moore #2	6390	2450	3940	62
24	Carter-Moore #3	6380	2410	3970	62
27	Lewis D1	4930	1900	3030	61
29	Harris E1	4970	1960	3010	61
30	Hunt-Ham #1	2180	2000	180	8
Dead Sea - Deep Member		5280	4110	1170	22
		Mean[2]			59%

---

[1] Excess bromide (percent of total bromide).

[2] Excluding sample 30 and the Dead Sea.

points for the Arkansas brines and the sea-water trend line contrasts with the disagreement present in the chloride-bromide and MCl_2-bromide relationships (figs. 2 and 4). In figures 2 and 4, the Arkansas samples contain more bromide than expected based on the amount of chloride or MCl_2 present. This phenomenon is undoubtedly due to the presence of bromide in these brines from some source other than sea water. The amount of "excess" bromide can be estimated from the relationship between MCl_2 and bromide in sea water (fig. 3). The concentration of bromide derived from sea water is calculated using equation 4; the excess bromide is the difference between total bromide and the bromide derived from sea water. The results of these calculations are presented in table 4. These data show that the mean excess bromide amounts to 60 percent of the total bromide in these brines. Arkansas sample 30 was collected from an oil field to the south of the high bromide brine region and has a composition similar to the Smackover brines in Mississippi.

The origin of the major chemical features of the brines from the Dead Sea area can be estimated by the same technique. Using the concentration of MCl_2 as a reference, the excess bromide in the Dead Sea is estimated to amount to 22 percent of the total bromide (table 4). The data on the composition of brines from springs and wells in the Dead Sea area indicate that these brines may be regarded as being either enriched in MCl_2 or depleted in bromide. The data in figure 2 indicate that, if the character of the brine is due to the loss of bromide, the initial concentration of bromide must have been 6,100 mg/l and that approximately half of this bromide has been subsequently lost from the brine. A concentration of 6,100 mg/l bromide in evaporated sea water would be characteristic of brines that have precipitated considerable amounts of potash salts and is equal to the maximum bromide concentration achieved by Zherebtsova and Volkova (1966) in their study on the brines produced by the evaporation of water from the Black Sea. The relationship between MCl_2 and chloride in these brines shows a close similarity to the MCl_2-chloride trend line of sea water (fig. 5) although there does appear to be some excess chloride in some samples. If the bromide in the springs and wells is assumed to be entirely of marine origin, the amounts of excess dissolved MCl_2, KCl, and the deficiency of dissolved NaCl can be estimated (table 5). The source of the excess MCl_2 and potassium chloride may be due to the alteration of the carnallite and $CaCl_2$-$MgCl_2$ minerals noted by Zak (1974). Braitsch (1971) has described the incongruent alteration of carnallite,

$$KMgCl_3 \cdot 6H_2O \rightarrow KCl + KCl\text{-saturated } MgCl_2 \text{ brine} \qquad (5)$$

in response to an increase in temperature and by the action of NaCl-saturated brines.

The source of the excess bromide in the Smackover brines of southwestern Arkansas and in the Dead Sea appears to be an unsolved problem at the present time. Day (1974) reviewed the geochemistry of the halogens and noted that bromine is enriched in a few varieties of marine organisms and plants. However, marine organisms and plants usually contain even higher concentrations

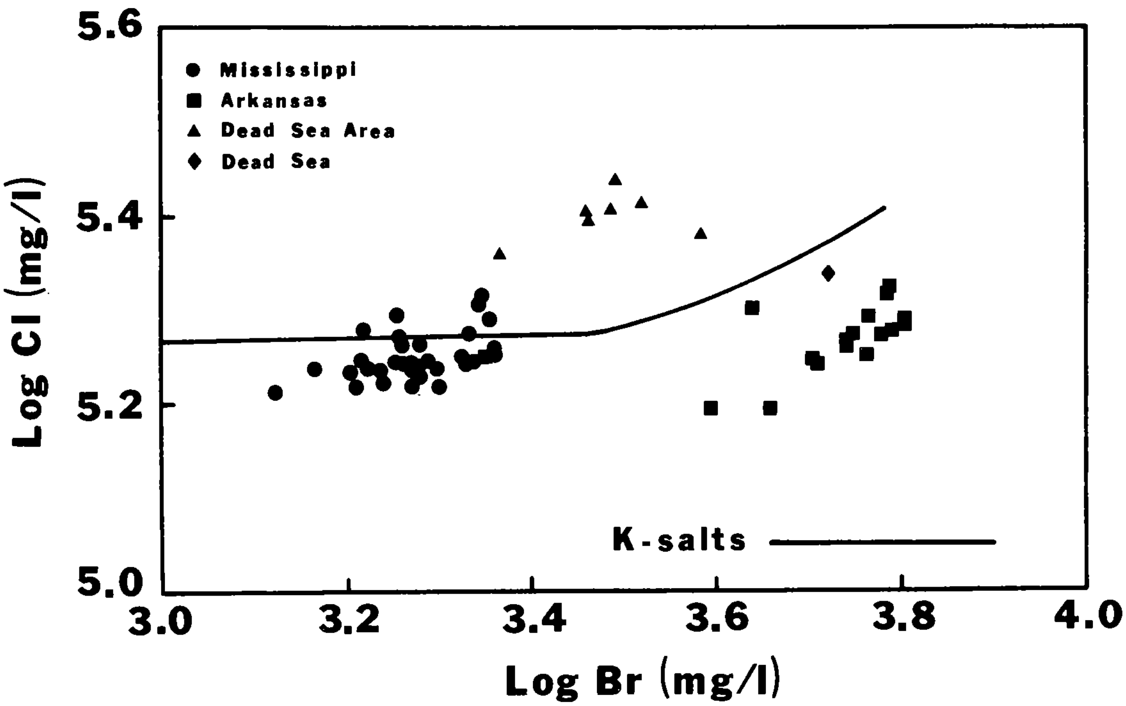


Figure 5. Concentration trend of chloride relative to MCl_2 (meq/l) during the evaporation of sea water.

of iodine. Organic-rich sediments (> 1 percent organic carbon) of the Barents Sea contain 44-84 ppm bromine. These sediments also contain 130-280 ppm iodine and have an iodine/bromine ratio of approximately 3:1 (Price and others, 1970). The low iodide content of the bromide-rich brines in Arkansas and in the Dead Sea indicates that the excess bromide has not been supplied as a result of the degradation of organic matter. The recrystallization of bromide-rich halite to low-bromide second-generation halite has been described by Holser (1966). However, the halite beneath the bromide-rich brines in Arkansas and in the Dead Sea generally appears to be relatively rich in bromide, and there is no indication that any significant amount of these halite deposits have been altered in a manner that could account for the high bromide content of the stratigraphically higher brines. The data on the bromide content of the Louann Salt in Arkansas are such as to suggest that some of this halite originally precipitated from a brine that was abnormally rich in bromide. Scattered occurrences of brines containing more than 3,000 mg/l bromide have recently been discovered in west-central Mississippi and in the Florida panhandle. Possibly, the determination of the geologic setting of these brines will provide clues to the origin of the excess bromine in bromide-rich brines.

ACKNOWLEDGMENTS

We wish to thank E. E. Pickett and the staff of the University of Missouri Environmental Trace Substances Center for their assistance in the chemical analysis of brine samples from southwestern Arkansas. We also wish to thank Laura A. Fox and J. Michael Garbarini for their assistance in writing the computer programs used in the preparation of this report. The illustrations were prepared by Laura A. Fox and Kirk McQuillan. We wish to thank Mecca B. Carpenter for critically reviewing the manuscript. This investigation was supported in part by financial assistance from the St. Joe Minerals Corporation and a grant from the National Science Foundation (NSF-EAR-74-13669-A01-Carpenter).

REFERENCES CITED

Bentor, Y. K., 1961, Some geochemical aspects of the Dead Sea and the question of its age: Geochimica et Cosmochimica Acta, v. 25, p. 239-260.

Braitsch, O., 1971, Salt deposits their origin and composition: Springer-Verlag, New York, 297 p.

Carpenter, A. B., 1978, Chemical evolution of brines in sedimentary basins, *in* Johnson, K. S., and Russell, J. R., editors, Thirteenth industrial minerals forum: Oklahoma Geological Survey Circular 79, p. 60-77.

Carpenter, A. B., Trout, M. L., and **Pickett, E. E.**, 1974, Preliminary report on the origin and chemical evolution of lead- and zinc-rich brines in central Mississippi: Economic Geology, v. 69, p. 1191-1206.

TABLE 5.—GEOCHEMISTRY OF BRINE FROM WELL NEAR MAYAN HA REIACH, N., DEAD SEA AREA (FROM MAZOR, 1962) (Concentrations are in mg/l, except as noted.)

	M^{2+}[1]	Na	K	Cl	Br
Brine from well[2]	5,220	21,430	28,530	242,300	3864
Brine produced by evaporation of sea water	4,086	28,920	23,540	209,200	3867
Excess constituent	1,134	-7,490	4,990	33,100	-
Percent excess constituent	22	-26	17	14	

---

[1] meq/l.

[2] chemical analysis adjusted to eliminate charge balance error.

Collins, A. G., 1974, Geochemistry of liquids, gases, and rocks from the Smackover Formation: U.S. Bureau of Mines Report of Investigation 7897, 84 p.

Day, F. H., 1964, The chemical elements in nature: Reinhold Publishing Corporation, New York, 372 p.

Holser, W. T., 1966, Bromide geochemistry of salt rocks, *in* Rau, J. L., editor, Second symposium on salt: Northern Ohio Geological Society, v. 1, p. 248-275.

Lerman, A., 1967, Model of chemical evolution of a chloride lake: Geochimica et Cosmochimica Acta, v. 31, p. 2309-2330.

Mazor, E., 1962, Radon and radium content of some Israeli water sources and a hypothesis on underground reservoirs of brines, oils, and gases in the rift valley: Geochimica et Cosmochimica Acta, v. 26, p. 765-786.

Neev, D., and **Emery, K. O.**, 1967, The Dead Sea, depositional processes and environments of evaporites: Israel Geological Survey Bulletin, v. 41, 147 p.

Price, N. B., Calvert, S. E., and **Jones, P. G. W.**, 1970, The distribution of iodine and bromine in the sediments of the southwestern Barents Sea: Journal of Marine Research, v. 28, p. 22-34.

Trout, M. L., 1974, Origin of bromide-rich brines in southern Arkansas: M..A. thesis, University of Missouri-Columbia, 79 p.

Zak, I., 1974, Sedimentology and bromine geochemistry of marine and continental evaporites in the Dead Sea basin, *in* Coogan, A. H., editor, Fourth symposium on salt: Northern Ohio Geological Society, v. 1, p. 349-361.

Zherebtsova, I. K, and **Volkova, N. N.**, 1966, Experimental study of behavior of trace elements in the process of natural solar evaporation of Black Sea water and Sasyk-Sivash brine: Geochemistry International, v. 3, p. 656-670.

IODINE IN NORTHWESTERN OKLAHOMA

HOWARD M. COTTEN[1]

Abstract—Early in 1977, Amoco Production Company and Houston Chemicals, a subsidiary of Pittsburg Plate Glass (PPG) Industries, started producing iodine commercially in northwestern Oklahoma. This is significant because it is the first plant in over 40 years to be built in the United States with iodine as its sole commercial product. With the exception of a limited amount of iodine produced by Dow Chemical in Michigan, the United States is dependent upon imports from Chile and Japan for its iodine needs. The two million pounds of iodine produced annually from the Woodward plant will supply over one-third of the United States' requirements.

Routine analysis of subsurface brines by the Formation Water Lab at the Amoco Production Company Research Center in Tulsa, Oklahoma, revealed unusually high concentrations of certain potentially economic minerals. Investigations determined that, of the minerals in question, iodine appeared to offer the best potential. The brines in question are located in the Morrow sands (basal Pennsylvanian) at a depth of 7,175 to 7,400 feet, in an area where Amoco has been active in a gas play for the past 20 years. The regional iodine concentration ranges from 10 to 700 ppm and averages around 300 ppm with the project area. The project is located 8 miles north and slightly east of the town of Woodward, where the well-developed, porous, and permeable sands of the Woodward trench contain large volumes of brine.

BACKGROUND ON IODINE

A brief look at the history of iodine, some of its uses, where it is found, and how it is recovered might give a better understanding as to why and how this project came about. Iodine is the heaviest of the halide series, and, like other halides, it is very reactive. In fact, iodine is never found in the elemental state in nature. Iodine was discovered by Bernard Courtois in 1811 and identified as a new chemical-element by Gay-Lussac in 1813. Immediately, chemists and medical men found uses for this new element. Eight years after its discovery, a Swiss, Dr. Coindet, determined that iodine was lacking in the drinking water in a certain area of France, and he began the treatment of goiter with tincture of iodine. In less than 20 years, iodine tincture was being used to treat wounds, with its first battlefield application during our Civil War. In 1928 the first production of iodine in the United States was from oil-field brine in Louisiana. The first gasoline antiknock compound found before TEL (tetra-ethyllead) was developed was iodine. A minor problem developed—the corrosion rate was so great the engine lasted only long enough to run a single test series.

Table 1 shows seven categories under which iodine is classified for use in today's market. As you can see, no single category accounts for more than 25 percent of the total, and each category can also be further subdivided. The only category to be discussed is the last one on the list. This miscellaneous category includes some of the more unique uses of iodine that are becoming more and more essential. Quartz-iodine lights are finding increased usage in photography and television studio lighting, as automobile headlamps, and as floodlamps in sports stadiums and drilling rigs. Scintillation crystals of sodium iodide are used in geiger counters and in airport luggage scanners. Although not yet commercial, two uses that have future potential for utilizing large quantities of iodine are water purification and coal liquefaction.

The free world's total consumption of iodine is about 20 million pounds per year. Prior to about 1950, the demand was increasing at the rate of 2 to 3 percent per year. Since then, the rate has been about 15 percent per year. The United States presently consumes approximately 9.5 million pounds of iodine per year and depends on foreign supply for about 95 percent of this.

---

[1] Amoco Production Company (Research), Tulsa, Oklahoma.

TABLE 1.—CURRENT AND PROJECTED USES OF CRUDE IODINE IN UNITED STATES

Use	Percent of Total	Thousand lbs. 1974	Growth Rate (percent per year) 1973-77	Thousand lbs. 1977
Catalysts	25	1,750	15	3,060
Animal feed supplements	20	1,400	7	1,840
Nylon stabilizers	15	1,050	0	1,050
Pharmaceuticals	13	910	5	1,110
Inks and dyes	13	910	4	1,060
Sanitation	7	490	10	720
Other	7	490	7	640
Totals	100	7,000	48	9,480

The price of iodine has gone from $1.18 a pound in 1968 to $2.59 a pound in February 1977. The price is expected to continue to rise.

As shown in figure 1, the world's iodine market is supplied by two countries at present—Chile and Japan. Japan accounts for about three-fourths of the world's supply of iodine, while Chile produces the other one-fourth. Dow Chemical, in Michigan, produces a limited amount for sale. Indonesia produces a few thousand pounds a year, which is consumed domestically. Russia and several eastern European countries produce small amounts, but they are also net importers of iodine. In Chile, iodine is a byproduct of the nitrate industry, which is located in the Atacama Desert in northern Chile. Iodine occurs as sodium or calcium iodate crystals in the evaporite deposits of Chile. In contrast to the Chilean deposits, where iodine is present in the oxidized or iodate form as a solid salt, iodine in the United States and Japan is produced from subterranean brines, where it occurs in the reduced form as sodium iodide and is most probably of organic origin. Both Chile and Japan have been having problems in meeting iodine demands. The Chilean production has fallen, primarily because of the political situation, while the Japanese producers have land subsidence problems created by the withdrawal of the brine.

Iodine was recovered from seaweed commercially from its discovery in 1811 to about 1940. Seaweed is no longer a commercial source of iodine anywhere in the world. However, seaweed in the diet does supply much of the nutritional need for iodine for a large part of the world's population. The average person requires about 75 mg of iodine

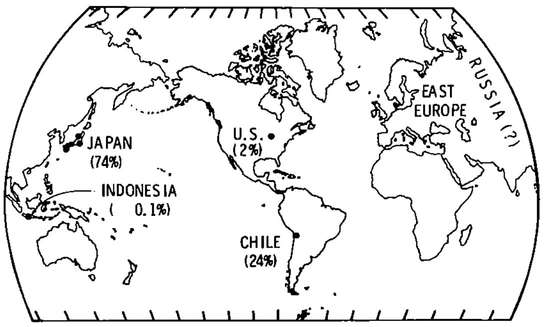


Figure 1. Countries in the free world producing iodine.

per year. In this respect, 18 tons would supply the total United States' need for a year. If this 75 mg of iodine were in the solid state, it would be a piece about the size of a BB or small buckshot.

WOODWARD IODINE PROJECT

The Woodward iodine project is unique in that it was both conceived and developed by a research organization. This means that for the past several years Amoco Research Center, through normal operational channels, has been purchasing acreage and drilling wells.

This project had its origin as a byproduct of a hydrocarbon exploration study that started about 12 years ago. In the process of reporting the analytical results of surface and subsurface water samples that had been submitted to the Formation Water Lab, unusually high concentrations of certain potentially economic minerals were noted. As a result of investigations into the feasibility of developing several or possibly all of these minerals, it was determined that iodine appeared to offer the best potential for diversification at this time. Based on the United States being almost completely dependent upon foreign imports for this vital resource, plus the fact that our annual consumption of iodine is steadily increasing, the time appeared right for a local iodine supplier to enter the market.

Figure 2 shows the location of some of the unusually high iodine concentrations in the United States. With concentration highs of 1,560 ppm in the Chesterian (Mississippian) and 700 ppm in the Morrowan (Pennsylvanian), it is obvious why Amoco concentrated its effort in northwestern Oklahoma. Unfortunately, the Chesterian (Mississippian) does not normally contain large volumes of brine, nor is it generally capable of delivering large volumes of water to the surface; rocks of the Chesterian series will not be discussed in this report. Based on analyses run on drill-stem tests and produced waters, plus a few from the U.S. Bureau of Mines, two areas of unusually high iodine concentrations within the Morrow Formation were isolated. The concentrations within these two areas range from 10 to 700 ppm and average around 300 ppm. Subsequent drilling has substantiated this concentration. Table 2 shows a comparison of the average concentration within the project area with other commercial plants.

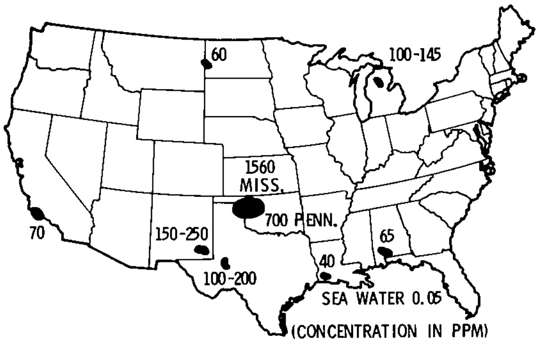


Figure 2. Areas of known iodine concentrations in the United States.

To determine how much brine was needed, an investigation was made of iodine supply and demand as it affected the world market. This investigation indicated that there would be no major problem in marketing an initial 2,000,000 pounds of iodine per year. At a concentration of 300 ppm, a 42-gallon barrel of brine contains 0.105 pound of iodine. Therefore, it takes 10 barrels of brine to produce 1 pound of iodine. To produce 2,000,000 pounds of iodine would require 20,000,000 barrels of brine. That is, for one year, with a 10-year plant life, it would take 200,000,000 barrels. This is produced brine delivered to the surface. Since we can expect to recover only about 50 percent of the brine in-place, it will require reserves of approximately 400,000,000 barrels in the formation. Based on this, the daily requirement for the plant is approximately

TABLE 2.—CONCENTRATION OF IODINE FROM COMMERCIAL PLANTS AND SEA WATER

Plants	Parts Per Million (ppm)
Japan	60 - 120
Chile	400 (in the ore)
Michigan	40
Oklahoma	300
Others	10 - 40
Seawater average	0.05

60,000 barrels. The processed brine is reinjected into the Morrow Formation to maintain reservoir pressure.

Two obvious questions had to be resolved: first, is there sufficient brine in place to supply the plant; and, second, is the Morrow Formation capable of delivering 60,000 barrels a day of 300 ppm brine to the surface for a period of 10 years from a limited number of wells? This paper deals primarily with the first question—do we have sufficient reserves? To answer this question, electric logs were examined over a large area of northwestern Oklahoma covering the areas of high concentration. Calculations were made on the Morrow Formation in each well to determine the number of feet of water-bearing sands with porosities greater than 10 percent. Using these data, reserves were calculated for each well. Since most wells in the area are drilled on 640-acre spacing, these conditions were assumed to extend over the entire section. Primary interest was on areas of thick, porous sands that could contain large volumes of brine. Based on this work, it soon became apparent that the Woodward trench, a recognized subsurface geologic feature in the area with an average width of about 1 mile and a known length of about 70 miles, had well-developed Morrow sands that contained an unusually high concentration or volume of brine. There is a vast difference between the Morrow sands of the wells drilled in the trench and those in the wells drilled in the flood plains on either side. This is considered reasonable since the trench is apparently an ancient, meandering river channel that cut a gorge down into the top of the underlying Chesterian limestones (Mississippian). This north-south trending channel or gorge was in turn filled with well-developed, porous, and permeable sands and shales of Morrowan age.

Cross sections *A* and *B* in figure 3 illustrate the development of sands within the trench as compared to the flood plains on either side. The Morrowan interval in this area dips and thickens to the south-southwest, which is downdip into the Anadarko basin. The Morrow sands pinch out to the east of the trench by truncation. Section *A-A'* shows one well with an abnormally thick sand interval as compared to wells on either flank. The thick sand is in the trench. Section *B-B'*, located approximately 15 miles south of section *A-A'*, illustrates the same thing—a well in the trench with thick, well-developed sands compared to poor or no sands on either side. Section *C-C'* in figure 3 illustrates the sand development down what appears to be the center of the trench in a localized area northeast of Woodward. The well on the extreme left or the downdip end of the section is located on the edge of the trench, which accounts for its thin sand section. This section also demonstrates one of the most critical factors of the project, and why Amoco zeroed in on the Woodward trench. This factor is the continuity or continuous nature of the Morrowan sands in the trench.

Based on the geological evaluation, there are adequate brine reserves in-place to support a plant capable of producing 2,000,000 pounds of iodine per year for 10 years. To determine if the Morrowan sands were capable of delivering this much brine to the surface, wells were drilled and sufficient testing was done to satisfy the criterion that a limited number of wells could deliver the necessary brine. Table 3 gives a brief summary of test results.

A total of 14 wells has been drilled in parts of T. 24 and 25 N., R. 20 W. in conjunction with this project—nine producers and five injectors. The production wells are located in Woodward and Harper Counties, with brine production coming from depths ranging from 7,175 to 7,400 feet in various wells. Figure 4 shows the locations of the wells and the plant site superimposed on the generalized configuration of the Woodward trench.

Early in the evaluation, Amoco's management decided that it wanted a partner in this project. Following negotiations, Pittsburgh Plate Glass (PPG) was selected, and a joint-venture agreement was made. It was felt that a joint venture would bring together the expertise required to develop this project. Amoco would be responsible for the field well development, and PPG, through their Houston Chemical Company subsidiary, would develop the plant and market the product.

While Amoco was drilling wells, PPG was designing a pilot plant for the recovery process. Over the years, recovery plants have been built which use certain chemical and physical properties of iodine. These properties are shown by the three column headings in table 4. No attempt is made to

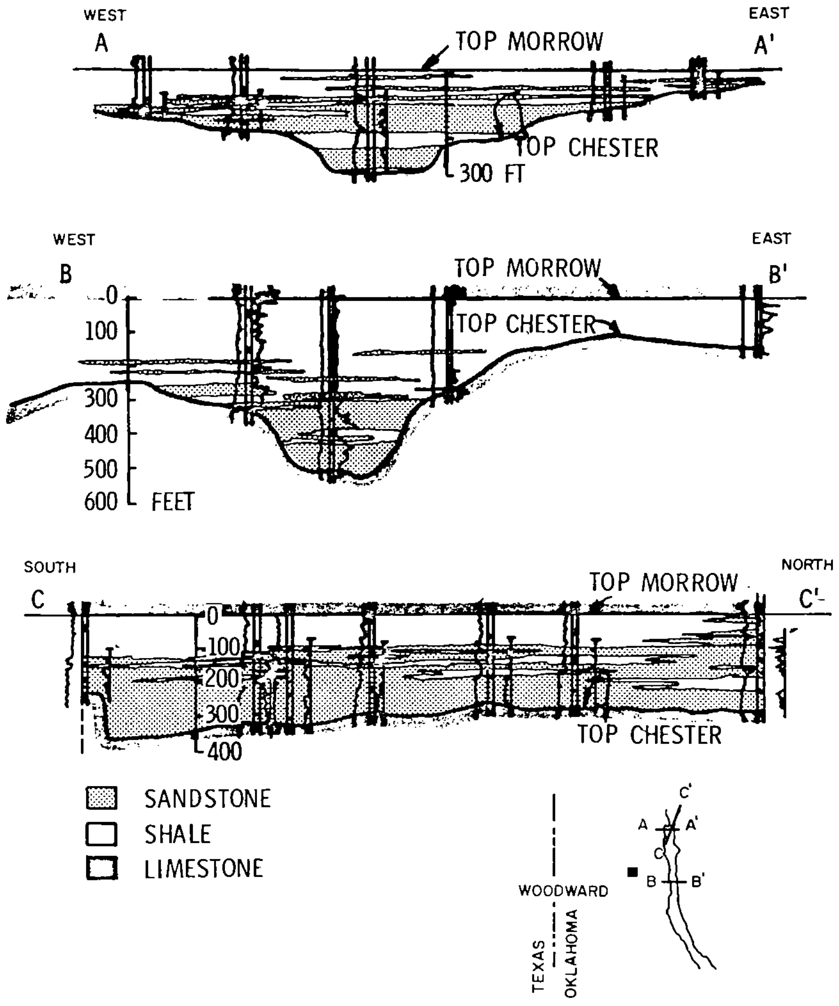


Figure 3. Cross sections across the Woodward trench.

Table 3.—Summary of Results of Reservoir Tests

I.	Iodine concentration	310 ppm average
II.	Reservoir porosity	15 percent
III.	Formation continuous	Yes, 6,000 feet
IV.	Production rate from each producer	5,000 - 15,000 bbl/day avg. 7,500
V.	Production depths	7,175 - 7,400 feet

discuss the first two columns. However, vapor stripping, or the blowout process, which is the one being used at Woodward, is briefly discussed. This process is based on the fact that even though iodine is a solid at room temperature, it has a high vapor pressure and will pass directly from the solid to vapor state without going through the liquid phase. High operating costs, low recovery efficiency, and pollution problems have forced the closing of all the silver, copper, and activated carbon plants. One Japanese ion-exchange plant, built about ten years ago, is still operating. However, because of high investment and operating costs, no new ones will be built. All new Japanese plants use some form of vapor stripping, but each company has its own version that is kept confidential.

Figure 5 is a flow sheet of the process used in Woodward, Oklahoma. It is a vapor stripping process that was developed by the

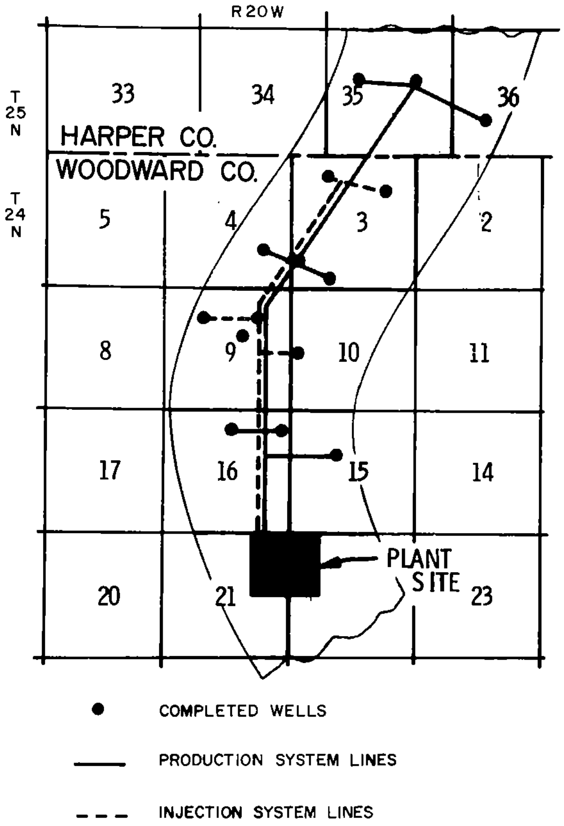


Figure 4. Map showing wells and production system for iodine plant at Woodward.

TABLE 4.—PROPERTIES OF IODINE AS USED IN THE RECOVERY PROCESSES

Insoluble Salts	Adsorption	Vapor Stripping
silver	activiated carbon	air
copper	ion exchange	steam
		air & steam

PPG Industries Research Center in Corpus Christi, Texas. Brine is pumped from the wells to the plant surge tank. The iodine-rich brine is fed into the first column, where it is oxidized under close control. The iodine vapor stripped from the brine passes to a second column where it is reduced and adsorbed in an iodine solution. This solution advances to a final recovery section where it is oxidized to form a solid iodine crystal, which is purified and packaged for shipment. This design is environmentally acceptable. The only net withdrawal from the system is the iodine product. Nothing is added to the brine. The spent brine returns to the same formation from which it is withdrawn.

The Woodward Plant is not a big project by large corporation standards. However, the 2,000,000 pounds being produced annually will cover about one-third of the needs of the United States. Also, by developing a natural resource that we have here in Oklahoma, the petroleum industry can contribute to making the United States a little less dependent upon foreign imports.

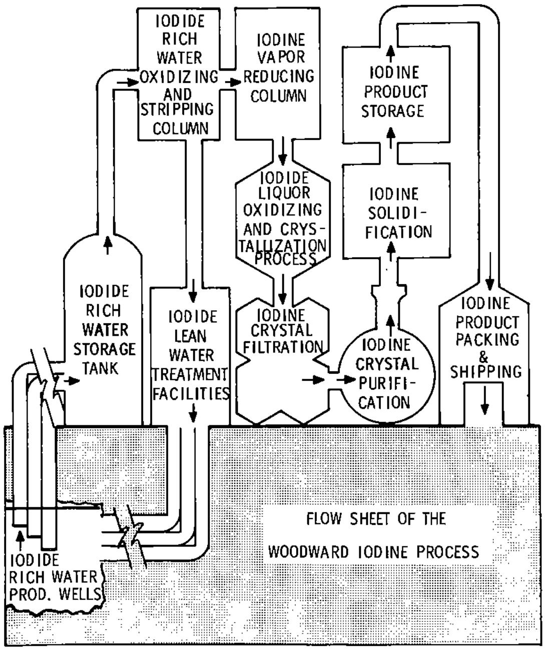


Figure 5. Flow sheet of the iodine process from the Woodward plant.

GEOCHEMISTRY OF ANOMALOUS LITHIUM IN OIL-FIELD BRINES

A. Gene Collins[1]

Abstract—The demand for lithium may increase because of its potential use in lithium batteries and in the generation of electrical power by fusion. Therefore, lithium abundance in some United States oil-field brines was surveyed. Oil-field brines from numerous locations were found to contain more than 100 mg/l lithium and several exceeded 500 mg/l. An area of 25,000 km^2, with a reservoir thickness of 60 m, an effective porosity of 5 percent, and a brine with a specific gravity of 1.2 containing 100 mg/l of lithium, contains about 0.75×10^6 tonnes (1 tonne = 1 metric ton = 1,000 kg) of lithium in 7.5 km^3 of brine. It is postulated that the brines were enriched in lithium by lithium-rich spring water or lithium leached from volcanic rocks followed by evaporation sequences.

INTRODUCTION

The demand for lithium may increase because of its use in the manufacturing of lithium batteries and in the generation of electrical power by controlled thermonuclear power. Electric batteries used to power vehicles require about 45 kg of lithium in the electrolyte and electrodes. Batteries in only 130,000 vehicles would have consumed the entire 1974 U.S. production of lithium (about 6,000 tonnes). Thermonuclear power plants, now being designed, will require lithium to produce tritium, the prime fuel. The required amount of lithium is dependent upon the design but could be of the order of 3 to 900 kg of lithium per megawatt of electrical power. Lithium is used in several other industries such as ceramics, glass, greases, air conditioning, brazing, welding, and metallic alloys (Cummings, 1970). Subsurface brine in Clayton Valley, Nevada, has been the major source of lithium since about 1967; however, the economic life of this deposit is limited to only a few more decades at the present rate of production. The concentration of lithium in Clayton Valley brine is about 300 mg/l.

LOCATIONS OF OIL-FIELD WATERS WITH > 50 MG/L OF LITHIUM

Most oil-field waters contain lithium, and some studies indicate that lithium concentrations can be used to explore for petroleum (Miodrag, 1975). Several oil-field waters contain more than 50 mg/l of lithium.

Table 1 lists the state, county, location, depth, geologic formation, specific gravity of the water, and concentrations in mg/l of lithium, sodium, potassium, rubidium, cesium, and fluoride for several oil-field waters in the United States. Lithium concentrations up to 692 mg/l were found in the Smackover Formation, 118 mg/l in the Saskatchewan Formation, 400 mg/l in a Devonian formation, 345 mg/l in the Madison Formation, 164 mg/l in the Rival Formation, 70 mg/l in the Wilcox Formation, and 51 mg/l in the Arbuckle Formation.

The analyses shown in table 1 were derived from an oil-field-water data bank at the Department of Energy (formerly ERDA), Energy Research Center in Bartlesville, Oklahoma. Although several oil-field waters have been analyzed for lithium, there are many other oil-field water systems that have not been analyzed for lithium. Therefore, it is possible that an oil-field water exists that contains lithium in excess of 700 mg/l.

GENERAL GEOLOGY OF THE SMACKOVER FORMATION

Because more data concerning lithium concentrations in the Smackover water are available, with respect to the other formations shown in table 1, it was decided to try to determine the origin of the lithium in the Smackover. According to Imlay (1940), the

---

[1] U.S. Energy Research and Development Administration, Bartlesville Energy Research Center, Bartlesville, Oklahoma.

TABLE 1.—LIST OF GLASS-SAND PRODUCERS
(Does not include all producers of quartz-bearing, melting materials)

State	County	Location, section-township-range	Depth, feet	Formation	*Specific gravity	Milligrams per liter					
						Li	Na	K	Rb	Cs	F
Alabama	Choctaw	35-11N-4W	11,974	Smackover	1.222	61	75,370	8,000	-	-	-
Arkansas	Columbia	23-19S-23W	10,913-11,038	...do.....	1.197	86	66,100	163	3.75	4.0	3.6
...Do......	...do....	8-18S-20W	8,540- 8,750	...do.....	1.231	462	70,200	4,670	13.8	7.0	3.1
...Do......	...do....	31-17S-20W	8,438- 8,732	...do.....	1.231	481	77,900	6,950	14.5	9.0	6.9
...Do......	...do....	2-18S-20W	8,345- 8,645	...do.....	1.229	423	78,400	5,640	12.0	6.0	3.4
...Do......	...do....	11-18S-20W	8,310- 8,600	...do.....	1.229	404	75,700	5,330	12.5	6.0	7.6
...Do......	...do....	7-18S-20W	8,656- 8,926	...do.....	1.230	481	73,800	5,260	14.0	6.0	7.5
...Do......	...do....	1-18S-21W	8,608- 8,902	...do.....	1.231	519	73,000	7,460	16.0	8.0	3.2
...Do......	...do....	5-18S-20W	8,490- 8,800	...do.....	1.128	481	71,400	5,550	15.5	10.0	6.4
...Do......	...do....	5-18S-20W	8,475- 8,777	...do.....	1.230	442	74,000	4,410	15.0	9.0	7.1
...Do......	...do....	32-17S-20W	8,396- 8,708	...do.....	1.231	462	64,900	6,230	14.5	8.0	4.7
...Do......	...do....	6-18S-20W	8,564- 8,850	...do.....	1.230	462	64,200	11,100	14.5	10.0	7.1
...Do......	...do....	23-18S-20W	8,501- 8,575	...do.....	1.221	308	84,400	5,790	9.5	3.0	4.8
...Do......	Lafayette	12-15S-25W	6,552- 6,556	...do.....	1.183	75	59,400	720	3.5	2.0	5.1
...Do......	Union	13-17S-13W	6,224	...do.....	1.157	50	55,470	614	-	-	-
Florida	Santa Rosa	21-5N-29W	15,692	...do.....	1.226	102	73,100	7,650	-	-	-
...Do......	...do....	40-5N-30W	15,550	...do.....	1.209	81	79,200	5,360	-	-	-
Louisiana	Webster	10-23N-9W	11,032-11,052	...do.....	1.227	66	113,000	616	-	-	-
...Do......	Claiborne	10-23N-6W	10,000	...do.....	1.186	101	87,400	1,090	-	-	-
...Do......	...do....	19-23N-6W	10,000	...do.....	1.191	80	82,800	1,380	-	-	-
Mississippi	Jones	22-9N-10W	12,990	...do.....	1.209	75	70,947	800	-	-	-
...Do......	Smith	9-1N-9E	15,860	...do.....	1.188	67	55,200	4,260	-	-	-
...Do......	Wayne	26-10N-6W	12,688	...do.....	1.210	80	74,500	650	-	-	-
North Dakota	Divide	3-152N-96W	10,882-10,903	Saskatchewan	1.223	118	51,300	13,400	-	-	-
...Do......	Williams	6-155N-95W	10,190-10,530	Devonian	1.238	400	58,200	9,500	-	-	-
...Do......	Burke	10-162N-92W	6,350- 6,373	Madison group	1.210	345	106,000	633	-	-	-
...Do......	...do....	15-162N-92W	6,200	Rival	1.231	164	115,000	3,850	-	-	-
Oklahoma	Noble	22-20N-2W	5,131	Wilcox	1.161	70	74,400	860	-	-	-
...Do......	Carter	4-4S-3W	3,090	Arbuckle	1.140	51	56,700	1,340	-	-	-
Texas	Cass	Sur. G. J. Aerrod	10,050	Smackover	1.105	473	26,800	280	-	-	-
...Do......	...do....	Bryan Mills Unit	10,492	...do.....	1.211	404	69,300	6,390	-	-	-
...Do......	Franklin	B.J. Putoff	12,180	...do.....	1.129	293	49,000	4,660	-	-	-
...Do......	Hopkins	W.L. Houghton Sur.	9,474	...do.....	1.160	99	53,600	2,400	-	-	-
...Do......	Van Zandt	M. Dewberry	12,784	...do.....	1.081	100	25,300	2,860	-	-	-
...Do......	Robertson	-	14,274	...do.....	1.237	624	90,000	15,820	-	-	-
...Do......	Rains	B Deosinia survey	13,740-13,800	...do.....	1.233	224	75,500	6,645	-	-	-
...Do......	Wood	Oscar Engledow Sur.	12,765-12,797	...do.....	1.210	692	75,400	7,430	25.0	25.0	-
Utah	Daggett	22-3N-24E	-	Madison	1.044	85	15,000	1,700	-	-	-
...Do......	San Juan	16-30S-24E	8,376	Mississippian	1.049	56	21,400	1,400	0.5	0.2	-
...Do......	...do....	19-43S-22E	4,849	Ismay	1.052	58	19,700	1,010	-	-	-
...Do......	Grand	16-23S-17E	8,605	Leadville	1.148	53	59,600	2,400	5.0	1.0	-
...Do......	Duchesne	2-15N-2W	5,902	Green River	1.064	68	28,900	408	-	-	-
Wyoming	Campbell	16-47N-70W	9,642	Minnelusa	1.103	90	52,400	2,100	-	-	-
...Do......	...do....	16-17N-70W	9,943	...do.....	1.082	75	41,800	950	-	-	-
...Do......	Sweetwater	1-12N-107W	8,780	Rock Springs	1.106	93	54,830	700	-	-	-
...Do......	Campbell	16-47N-70W	9,642	Minnelusa	1.103	70	52,800	2,100	-	-	-
...Do......	...do....	16-47N-70W	9,943	...do.....	1.082	75	41,820	950	-	-	-

Smackover Formation was named after the Smackover oil field in Arkansas. In that area it is composed of 213 m of oolitic limestone. Smackover time equivalents have been identified in Mexico, Texas, Arkansas, Louisiana, Mississippi, and Alabama. These rocks are definitely Jurassic age (Imlay, 1945) with good paleontological correlations with the Argovian strata of Late Jurassic age in England.

The Smackover Formation is the equivalent of the Zuloaga Formation in Mexico. The Zuloaga carbonate outcrops west of the Tamaulipas Peninsula in northwest Mexico. The Smackover in the United States covers a salt-dome basin in the western part of the Rio Grande embayment in southwest Texas. It crosses the crest of the San Marcos arch, the northwest part of the east Texas salt basin, the northern portion of the north

Louisiana-Arkansas salt basin, then southeast over the north area of the central Mississippi salt basin, and under the Florida panhandle and offshore areas, as illustrated in figure 1. The Smackover Formation does not outcrop anywhere within the continental United States.

The Smackover (Zuloaga) equivalent lies below Cotton Valley (La Casita) or Buckner (Olivido) equivalents in northwest Mexico. The updip limits of the Zuloaga are west of a parallel to the Tamaulipas Peninsula.

A pure coarsely crystalline salt (Louann Salt) is found below the Jurassic sediments in Milam County, Texas. The Smackover Formation in Texas usually consists of an arenaceous basal zone, a microcrystalline middle zone, and a top zone of oolitic limestone or dolomite.

ORIGIN OF LITHIUM IN THE SMACKOVER WATER

Correlation coefficients of the Smackover-brine data show a high degree of intercorrelation among K, Rb, Li, and B. Iodide does not correlate. Combining data from the Smackover with data from an altered relict bittern produced a high correlation between K and B and between Li and Rb. This suggests that a mechanism in addition to sea water evaporation is involved in producing the high concentration of Li and Rb in the brines.

Data shown in table 2 indicate the relative concentrations of various constituents in the Smackover brine. The excess factors were obtained by assuming that bromide, which does not form minerals, is the best single indicator of the degree to which sea water was concentrated. As shown in table 2, about 80 percent of the original K is missing and 40 percent of the original B is missing, whereas there is about 18.1 times as much Li and about 10.4 times as much iodide.

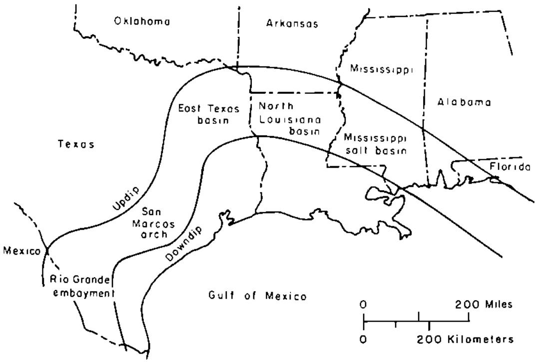


Figure 1. Approximate geographic extent of the Smackover Formation in the Gulf Coast basin.

The anomalous iodide can be reasonably explained as a result of bioconcentration (Collins, 1969). However, a similar mechanism to explain all of the anomalous lithium is not available. It has been postulated that lithium enrichment results at least in part from exchange reactions with clays because lithium has a small radius, a low atomic number, a larger hydrated number than sodium, and a larger polarization than sodium. Therefore, its replacing power in the lattices of clay minerals is low. Other ions such as Ba, Sr, Ca, Mg, Cs, Rb, K, and Na will preferentially replace Li in clay minerals thus releasing Li to solutions. Also the solubility products of most lithium compounds are higher than those of other alkalies or alkaline earths, so lithium tends to stay in solution (Collins, 1975).

A plausible source of some of the anomalous lithium is continental drainage of lithium-enriched solutions into an evaporating sea such as is now occurring at the Great Salt Lake. The effect of this mechanism can be determined. For example, assume that continental water with the approximate composition of Clayton Valley, Nevada, spring water were mixed with a brine and subjected to evaporation similar to that of the Great Salt Lake. The Clayton Valley spring water contains about 4 mg/l of bromide and 55 mg/l of lithium.

Table 2 indicates that bromide in the Smackover water is concentrated about 48 times relative to sea water; therefore, as shown in table 3, in nine assumed evaporations the lithium concentration in the brine is greater than 500 mg/l. If the fresh water source were river water containing 0.02 mg/l of lithium rather than spring water, nine evaporations would yield a lithium concentration of only 9.76 mg/l.

To determine how long such evaporation sequences might take under optimum conditions, again consider the Great Salt Lake. With a volume of 12 km^3 and an annual inflow and evaporation of 3 km^3, each equal volume dilution and evaporation would require only 4 years, or a total of only 36 years for nine cycles.

This evaporation sequence assumption is too simplistic for total direct application,

TABLE 2.—CONCENTRATION RATIOS AND EXCESS FACTOR RATIOS FOR SOME CONSTITUENTS IN SMACKOVER BRINES

Constituent	Average composition, mg/l		Concentration ratio[1]	Excess factor[2]	Number of Smackover samples
	Seawater	Smackover brines			
Lithium......	0.2	174	870	18.1	71
Sodium......	10,600	66,973	6	.1	283
Potassium....	380	2,841	8	.2	82
Calcium.....	400	34,534	86	1.8	284
Magnesium...	1,300	3,465	3	.1	280
Strontium....	8	1,924	241	5	85
Barium......	.03	23	767	16	73
Boron.......	4.8	134	28	.6	71
Copper......	.003	1.1	359	7.5	64
Iron.........	.01	41	4,049	84.2	90
Manganese...	.002	30	14,957	311	69
Chloride.....	19,000	171,686	9	.2	284
Bromide.....	65	3,126	48	1	74
Iodide.......	.05	25	501	10.4	73
Sulfate......	2,690	446	.2	.003	271
Mg'[3]........	1,543	24,362	16	.3	284

[1] Amount in brine/amount in seawater.
[2] Concentration ratio of a given constituent/concentration of bromide.
[3] Mg' = (24.31/40.08) × mg/l calcium + mg/l magnesium.

TABLE 3.—COMPOSITIONS OBTAINED BY SUCCESSIVELY MIXING ONE VOLUME OF CLAYTON VALLEY SPRING WATER WITH ONE VOLUME OF BRINE AND THEN EVAPORATING TO THE ORIGINAL BRINE VOLUME

Item	Bromide mg/l	Lithium
Seawater	65	0.2
48X Seawater	3,120	9.6
Spring water	4	55
One volume each of 2 and 3	1,562	32.3
Evaporate 4 to one-half volume	3,124	64.6
Add second volume of 3 and evaporate to one-half	3,128	119.6
Add third volume of 3 and evaporate to one-half	3,132	174.6
Add fourth volume of 3 and evaporate to one-half	3,136	229.6
Add fifth volume of 3 and evaporate to one-half	3,140	284.6
Add sixth volume of 3 and evaporate to one-half	3,144	339.6
Add seventh volume of 3 and evaporate to one-half	3,148	394.6
Add eighth volume of 3 and evaporate to one-half	3,152	449.6
Add ninth volume of 3 and evaporate to one-half	3,156	504.6

but it can be used to postulate a plausible theory for anomalously high concentrations of lithium in the Smackover brine.

The probable origin of the lithium-rich Smackover brine was an influx of continental water, enriched in lithium either from spring water or leached from volcanic rocks, into the Smackover Sea in the vicinity of the Mexia-Talco fault system as shown in figure 2. The Smackover Sea was subjected to evaporation sequences, and volcanism occurred during the Triassic in the Gulf Coast area.

ESTIMATE OF LITHIUM CONTENT IN SMACKOVER BRINE

The amount of lithium in Smackover brine can be estimated. Assume that an area of 25,000 km^2 has a reservoir thickness of 60 m with a porosity of 5 percent, and that the 1.2 specific gravity brine contains an average of 100 mg/l of lithium. The total volume of brine in the sedimentary rock is about 7.5 km^3 and contains about 0.75 × 10^6 tonnes of lithium. The total area of the Smackover more nearly approximates 250,000 km^2 than 25,000 km^2. However, the concentration of lithium in the brine and the thickness and porosity of the strata are not constant.

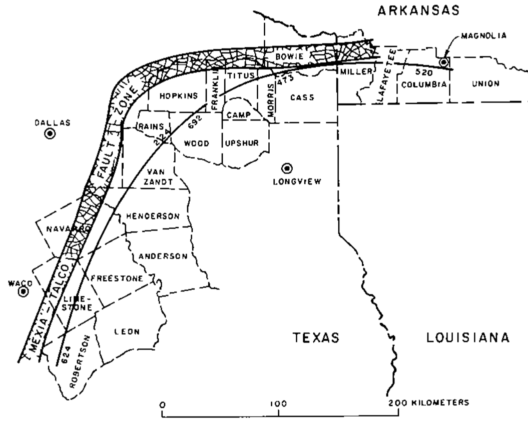


Figure 2. Map showing the concentrations of lithium (in mg/l) in the Smackover waters in Arkansas and Texas along an arcuate contour line parallel to the truncated outcrop of the formation and their relation to the Mexia-Talco fault zone.

REFERENCES CITED

Collins, A. G., 1969, Chemistry of some Anadarko basin brines containing high concentrations of iodide: Chemical Geology, v. 4, no. 1/2, p. 169-187.

———, 1975, Geochemistry of oilfield waters: Elsevier Scientific Publishing Co., New York, 496 p.

Cummings, A. M., 1970, Lithium, *in* Mineral facts and problems: U.S. Bureau of Mines Bulletin 650, p. 1073-1081.

Imlay, R. W., 1940, Lower Cretaceous and Jurassic formations of southern Arkansas and their oil and gas possibilities: Arkansas Geological Survey Information Circular, no. 12, 65 p.

———, 1945, Jurassic fossils from the southern states: Paleontology, v. 19, p. 253-276.

Miodrag, S., 1975, Should we consider geochemistry as an important exploratory technique?: Oil and Gas Journal, v. 73, no. 31, p. 106-110.

PRELIMINARY DESIGN AND ANALYSIS OF RECOVERY OF LITHIUM FROM BRINE WITH THE USE OF A SELECTIVE EXTRACTANT[1]

VI-DUONG DANG[2] and MEYER STEINBERG[2]

Abstract—Lithium requirements in the next few decades for batteries and controlled thermonuclear fusion reactors (CTR) may exceed the availability of the current mineral and brine reserves. It is thus prudent to search for new reserves and resources to satisfy these and future lithium applications. The lithium content of the waters from the Smackover oil field, located in the Gulf Coast region of the United States, ranges from 100 to 500 mg/l and could represent a substantial new reserve.

Experimental evidence described in the literature indicates that a specific chelating agent dipivaloylmethane (DPM), of the diketone type, has a specific selectivity toward lithium in the presence of other metal ions in aqueous solutions. Based in part on this unique property of dipivaloylmethane, a conceptual design of a full-size plant to extract lithium from the Smackover brine is presented in this paper. This study includes alternate flow-sheet development, design information on the major units of the process, energy requirements, and an economic analysis of a facility capable of producing 10^6 kg of lithium per year. The economics of three different process concepts depend primarily on the amount of water needing to be evaporated from the initial oil-field feed waters in concentrating the brine. The results, as a function of production rates, are indicated only in a general manner.

INTRODUCTION

The requirement of lithium for energy applications, such as those for a lithium battery and for the blanket region of controlled thermonuclear fusion reactors (CTR), were presented in a previous symposium (Vine, 1976). Several of the papers in this previous symposium presented assessments of the reserves, resources, and requirements of lithium by the year 2000.

Estimates of the amount of lithium required beyond the year 2030 for the blanket region of controlled thermonuclear fusion reactors are between 4.3×10^7 and 4.3×10^9 kg (Energy Advisory Panel, 1973; and Steinberg and Dang, 1976). Present lithium reserves are about equal to the estimated demand for lithium required for fusion-reactor and battery applications (Chilenskas and others, 1976; Cooper and others, 1976). An ultimate resource of lithium could be sea water which contains a total quantity of lithium of about 2.5×10^{14} kg. The lithium concentration in sea water, however, is very dilute, 170 ppb (Steinberg and Dang, 1976).

The lithium concentration in Smackover oil-field brine is about 174 mg/l. This concentration is about three orders of magnitude higher than in sea water. Smackover brine is water which is associated with petroleum produced from the Jurassic Smackover Formation in the Gulf Coast region. The total quantity of lithium in the brine is estimated to be 6.3×10^{10} kg (Collins, 1976). Extracting lithium from brines should be easier than extracting lithium from sea water because of the existing drilling technology and the higher lithium concentration in brines.

Ion-exchange methods have been proposed to extract lithium from sea water (Steinberg and Dang, 1976). These processes have the disadvantage of needing a larger quantity of ion-exchange resins to extract the dilute concentration of lithium from sea water. From a literature search, a diketone-type chelating agent, identified as dipivaloylmethane (DPM), was found capable of separating lithium from alkali metal ions in aqueous solutions. A specificity for extraction of lithium from other ions was indicated; an application of this chelating agent for studying lithium transfer across red blood cells was reported (Martin and others, 1973). Although additional information is needed for process design purposes, a

---

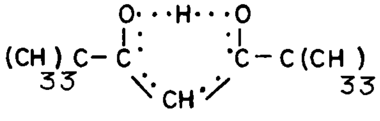
[1] This research was performed under the auspices of the United States Energy Research and Development Administration under Contract No. EY-76-C-02-0016.

[2] Process Technology Division, Brookhaven National Laboratory, Upton, New York.

preliminary design can be undertaken for initial evaluation.

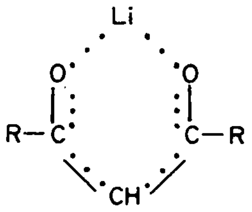
CHEMISTRY OF SEPARATION

Guter and Hammond (1956) reported that based on experiments lithium can be selectively extracted from aqueous solution by dipivaloylmethane (DPM). Dipivaloylmethane (2, 2, 6, 6–tetramethyl–3, 5–heptanedione) is a chelating agent and is a colorless oil with a specific gravity of 0.883. It exists almost entirely in the form of the symmetrical enolic modification I in pure liquid and in organic solvent:



Structure I

When combining with lithium, the chelate probably has the following structure II:



Structure II

The specificity of DPM for lithium ion in the presence of sodium, potassium, and other ions is due to the small radius of the lithium ion (0.60 Å). Although sodium ions may interfere with lithium ions in the process of extraction (Guter and Hammond, 1956), careful successive extractions show that lithium can be recovered to the extent of 97 percent. Without further experimental results, the following process analysis and design will be based on the work of Guter and Hammond (1956).

CONCEPTUAL PROCESS DESIGN FOR EXTRACTION OF LITHIUM FROM SMACKOVER BRINE

The process concept for the extraction of lithium from brine includes a number of unit operations including evaporation, mixing-settling, electrolysis, distillation, and drying. The key step is the liquid-liquid extraction of lithium from the brine by means of DPM in ether. Process analysis depends also on the initial concentration of the constituents in the feed brine. Table 1 is a list of the composition of Smackover brine taken from the work of Collins (1976). Table 2 is a compilation of the analyses of lithium concentration in a number of oil-field and geothermal waters from various locations around the country, which were determined in the Brookhaven National Laboratory. About 50 percent of the samples taken from Texas contained less than about 10 mg/l of lithium and were not listed in the table.

TABLE 1.—CONCENTRATION OF SOME CONSTITUENTS IN SMACKOVER BRINES (after Collins, 1976, p. 119)

Constituent	Average composition (mg/l)	Number of samples
Lithium	174	71
Sodium	66,973	283
Potassium	2,841	82
Calcium	34,534	284
Magnesium	3,465	280
Strontium	1,924	85
Barium	23	73
Boron	134	71
Copper	1.1	64
Iron	41	90
Manganese	30	69
Chloride	171,686	284
Bromide	3,126	74
Iodide	25	73
Sulfate	446	271

TABLE 2.—LITHIUM CONCENTRATION IN SMACKOVER OIL-FIELD AND GEOTHERMAL WATER FROM VARIOUS LOCATIONS (analysis determined at Brookhaven National Laboratory)

State	Field	County	Lithium Concentration (mg/l)
Arkansas	Section 1, Township 18 South, Range 21 West	Columbia	310
Texas	Bryans Mill Unit #1, Bryans Mill	Cass	550
Texas	Currie Plant, Currie	Navarro	370
Arkansas	Dow Chemical Co., Magnolia		280
California	East Mesa 6-1, Holtville	Salton Sea	33
Texas	Chitsey #1, Chitsey	Wood	103
Texas	Buchanan #1, Alba	Wood	72
Texas Tex	Fred Gregg #1A, Birthright	Hopkins	190
Texas	Seager #1, East Yantis	Wood	36
Texas	Teas Plant, Teas 8, Carter Bloxom	Freestone	25

Different process concepts were developed depending on the amount of water evaporated from original oil-field brine.

Referring to process flow diagram in figure 1, Smackover water is first pumped out from the well and separated from the associated oil and gas at the well head in a separation tank. After the initial separation, further separation can be achieved in skimming tanks. The separated brine is passed into an evaporator to precipitate out the sodium chloride and evaporate a large part of the water. The concentrated bittern is then mixed with ether and DPM in a mixer-extraction vessel. Part of the separated sodium chloride is redissolved and the aqueous sodium chloride is electrolyzed to produce hydrogen and chlorine. The latter is then burned to produce hydrogen chloride which is subsequently used to recover the DPM from the metal chelate lithium DPM. Bittern and DPM in ether are then mixed in a mixing tank. After rigorous stirring, the mix is transferred to a settling tank to separate the water layer and the lithium DPM in the ether layer. Part of the ether may remain in the water layer as a result of incomplete separation and partial miscibility between ether and water. At room temperature 1-1.5 percent of the ether dissolves in water, and 7.5 percent of water dissolves in ether. Therefore, the water layer from the settling tank is transferred to a distillation tower where ether and water are separated and recovered. The top layer, which is lithium DPM in ether from the settling tank, is fed into the lithium extraction tower together with the recycled water and hydrogen chloride from the HCl burner. Inside the lithium-extraction tower, water and lithium DPM in ether is well mixed in order to ensure improved extraction of lithium from the organic phase into the aqueous phase. The extraction process is further facilitated by the presence of HCl. The aqueous and organic phases are then separated in the separation tank. The organic phase will be recycled to remix with the bittern for lithium extraction. The aqueous lithium chloride is transferred to the drying tower to evaporate the water, and the lithium chloride is then electrolyzed to produce lithium and chlorine.

The major reactions of the process are:

$$\mathrm{NaCl + H_2O \rightarrow NaOH + \tfrac{1}{2}H_2 + \tfrac{1}{2}Cl_2} \qquad (1)$$

$$\mathrm{\tfrac{1}{2}H_2 + \tfrac{1}{2}Cl_2 \rightarrow HCl} \qquad (2)$$

$$\mathrm{HDPM + Li \rightarrow LiDPM + H}$$

$$\mathrm{\hookrightarrow \tfrac{1}{2}H_2} \qquad (3)$$

$$\mathrm{LiDPM + HCl \rightarrow HDPM + LiCl} \qquad (4)$$

$$\mathrm{LiCl \rightarrow Li + \tfrac{1}{2}Cl_2} \qquad (5)$$

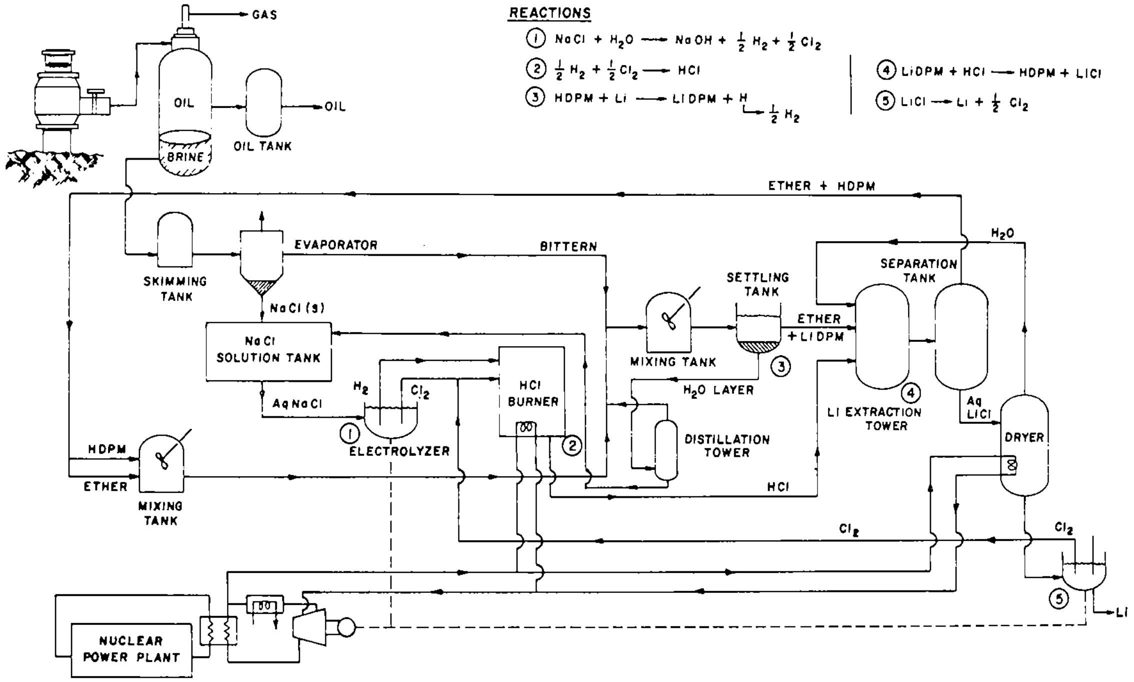


Figure 1. Flow diagram for lithium production from Smackover oil-field water.

PROCESS DESIGN AND ECONOMIC ANALYSIS

Process design and analysis are based on the flow diagram in figure 1. The design calculation is based on the production of *W* gm Li/yr. The first step in the separation process is the separation of other metal ions from lithium, which is similar to a previous method described by Steinberg and Dang (1976) for extraction of lithium from sea water. There are particular advantages of separating out the sodium ion first: (1) sodium may interfere with lithium for chelating with DPM, and (2) sodium chloride separated out from the brine can be used in electrolysis to produce hydrogen and chlorine, and subsequently, for production of hydrogen chloride, which can be used as a neutralization agent for recovery of DPM from its chelating salt. The carbonate precipitation method used in extraction of lithium at Silver Peak, Nevada, cannot be easily applied here because the concentration ratio of magnesium to lithium in Smackover brine is high, about 20 compared to about 1 in Silver Peak. The lithium ions may be adsorbed to magnesium hydroxide when the latter is precipitated, resulting in a large bittern loss.

The following discussion will describe the calculation of the important operations of the process. The first two items are the oil tank and the skimming tank; the volume of the skimming tank has to be at least 2,000 *W* cm^3 based on the storage capacity of the brine.

Evaporator—In contrast to solar evaporation previously used for crystallization of other salts like sodium chloride, the present method employs evaporators to concentrate the solution because the volume processed is much reduced. The composition of various salts in the bittern is given in table 3.

TABLE 3.—ESTIMATED CONCENTRATIONS OF THE MAJOR CONSTITUENTS IN BITTERN

Constituent	Concentration gm constituent \ gm water
Sodium	0.151
Calcium	5.794×10^{-5}
Magnesium	0.134
Potassium	0.194
Lithium	0.0136
Chloride	0.176
Sulfate	1.388×10^{-4}

Brine of 2,000 *W* g/hr flows to the evaporators. Assuming 2 ppm of water are left after evaporation, bittern of 0.00286 *W* g/hr will be obtained after evaporation. Selection of this concentration level is based on a compromise of capital investment and thermal energy required for evaporation. These evaporators use triple effect backward feed. Heat-transfer coefficient of the steam tubes of the evaporators is 0.0678 cal/sec-cm^2-°C. Saturated steam from nuclear power plant at 9.843 kg/cm^2 and 196°C is used, and water is evaporated as superheated steam at 67.78°C and saturation temperature at 63.89°C. Total energy needed to evaporate the water is 308.37 *W* cal/sec. If we use a steam economy (ratio of total water evaporated to total steam supplied) of three, the actual energy required for evaporation is 102.79 *W* cal/sec. Taking the maximum possible heat flux for the evaporator as 8.665 cal/cm^2-sec, the total area needed for the evaporator is estimated as 35.58 cm^2.

NaCl solution tank—Using the average concentration of sodium and chloride ions given by Collins (1976), the concentration of sodium chloride in Smackover brine is determined as 205,659 mg/l. The requirement for the design of the NaCl solution tank is the volume of the tank. In order to obtain that, the total flow rate of sodium chloride, which is 412 *W* g/hr based on 2,000 *W* g/hr of brine, is needed. After water is evaporated, the rate that sodium chloride crystallizes is almost complete, about 412 *W* g/hr. To saturate this quantity of sodium chloride, the volume of the solution tank should be at least 1,073 *W* cm^3.

NaCl electrolyzer—There are many kinds of NaCl electrolyzers available commercially. The present design will be based on the current information with possibly some scale-up or application of more units. One suitable type of NaCl electrolyzer is the De Nora vertical cell[3] with dimensions of 1.2 m × 1.1 m × 3 m (Mantell, 1960) that has a capacity of chlorine production of 100 tons/day or 165 tons/day sodium chloride

---

[3] Any use of trade names is for descriptive purposes and does not constitute endorsement by the Oklahoma Geological Survey.

required. Based on several calculations, the number of electrolyzers needed to produce W g/hr of lithium follows the expression $5.34 \times 10^{-3}\ W$.

HCl burner—Determination of a burner or furnace usually depends on the heat requirement of the reaction. The exothermal heat of reaction of hydrogen chloride is 22.1 kcal/g mole. If the production rate of sodium chloride from the NaCl solution tank is 412 W g/hr, hydrogen can be produced at a rate of 7.043 W g/hr from the NaCl electrolyzer. The rate of hydrogen chloride produced in the HCl burner is 257.06 W g/hr. Hence, the total heat released from the burner is 43.23 W cal/sec which is an important value for determination of the capital investment of the unit.

Mixing tank, settling tank, Li-extraction tower, and Li-separation tank—These four units are similar in the present process in the sense that they serve as storage units. The determination of these units will be based on their volumes. In order to allow for sufficient capacity, a safety factor of 2.5 to 3 is used here. The volume of a mixing tank and settling tank is evaluated as $6.6 \times 10^{-7}\ W$ gallon, while the volume of the Li-extraction tower and Li-separation tank is calculated to be $7.9 \times 10^{-7}\ W$ gallon.

LiCl drying tower—Commercial drying towers are available in several dimensions. One type has a diameter of 182.9 cm and a depth of 60.96 cm. Several of these dryers can be directly applied to the present process, or the unit can be scaled-up to larger dimensions in order to reduce the number of units required. The number of drying towers needed can be readily calculated by knowing the production rate of lithium, which then determines the evaporation rate of water in the drying tower and the dimension of the selected dryer.

The rate of water evaporation in the dryer can be determined by using 6.145 W g/hr as the flow rate of lithium chloride (in the bittern) to the dryer. In this flow stream, the concentration of lithium chloride is 20.36 percent (by weight), based on 20 percent (by weight) of HCl from the separation tank. The dryer has to be designed so that 3.912 gm H_2O must be evaporated per gram LiCl input. Hence, the total rate of water that has to be evaporated in the dryer is 24.04 W g/hr. This quantity is a basis for determining the number of drying towers.

LiCl electrolyzer—Commercial electrolyzer for LiCl has been reported by Hader and others (1951). The electrolyzer is rectangular with a graphite mode, 883.9 cm long with a diameter of 38.1 cm supported from above the cell, and it also has a steel cathode. These commercial electrolyzers can be scaled for use in the present process. For example, the scale-up of the conventional cell with dimensions of 121.9 cm × 182. 9 cm × 91.4 cm can serve the present process well. An electrolyzer cell of 8.7×10^7 cm^3 (3.5 times of the above cell dimension) can handle 1.34×10^8 gm/hr lithium. For a higher production rate of lithium, one can increase the number of unit cells.

Distillation tower for ether—Ethyl ether can be distilled out from water by means of a tray tower. Solubility of ethyl ether in water is 7 percent or 0.01798 by mole fraction. Assume the ether concentration is 97 percent at the top product stream and water concentration is 98 percent (by weight) in the bottom stream. The average molecular weight of the feed is 19.01. Once the feed rate into the tower is specified, the top recycle stream and the bottom reboiler stream can be determined. Using a reflux ratio of 3.5, the number of plates required by a standard method such as Ponchon-Savarit are determined. As an example, a feed rate of 754 g-moles/hr will give a top product stream of 11.18 g-moles/hr and a bottom stream of 742.82 g-moles/hr. The diameter of the tower can be determined by the Sanders-Brown method (Ludwig, 1964). For the present case, the diameter is 30.48 cm, and the height of the tower is 152.4 cm. The operating pressure can be 2.84 atmospheres.

A summary of the dimensions and number of units needed for any production rate of lithium and an example for a lithium production rate of 1.25×10^5 g/hr is presented in table 4. The dimensions of equipment chosen are either of a commercial size or a reasonably practical size. Since the capacity of the LiCl electrolyzer can produce more than 1.25×10^5 g/hr Li, the number of electrolyzers needed is only one. The dimensions and the number of distillation tower units are not listed because these values usually have to be designed for each production rate of lithium.

ENERGY REQUIREMENT AND ECONOMIC ANALYSIS

The energy balance of the process, and for each piece of equipment, is also an important factor in the process. Thermal energy in the form of steam is required to evaporate water. Thermal energy (t) required by the evaporator is 1.291 W kwh (t)/hr. Dissolution of sodium chloride requires the heat of solution, and the total heat required for the process is 1.639×10^{-2} W kwh(t)/hr. Electrical energy (e) required for electrolysis of sodium chloride is estimated to be 8.48×10^{-3} W kwh(e)/hr taking into account the inefficiency of the cell. The HCl burner will release heat due to the recombination reaction of hydrogen and chlorine. Total heat released in the burner is 0.181 W kwh(t)/hr, and this heat is assumed to be recoverable. The energy required for the dryer to evaporate to dryness is estimated to be 1.551×10^{-2} W kwh(t)/hr. Electrical energy supplied to electrolyze LiCl in the electrolyzer is 1.796×10^{-2} W, taking into account the inefficiency. The distillation tower requires a small energy input to the bottom reboiler, and the overall energy balance shows that only 4.86×10^{-8} kwh(t)/hr is needed. Mechanical energy requirement for pumping and transporting liquid and solid in the process is considered to be small, and hence no further detailed calculation is performed. A summary of the energy requirement for process is shown in table 5. The energy required for production of 1 gm Li is very small as compared to the energy value of 3,400 kwh(e)/gm Li which can be produced in the fusion process.

The preliminary economic analysis was performed as follows: Cost data and information were obtained from Peters and Timmerhaus (1968) and Popper (1970). If information was not available from these two references, cost estimation was based on raw material and construction cost of the equipment. Estimates of the cost of the LiCl electrolyzer was obtained in this manner. Correlation of the cost of the equipment with the production rate of lithium has been established for several important pieces of equipment. This cost correlation is based on 1968 dollars, and a conversion factor was applied to obtain 1976 dollars.

Cost-scaling correlations for the HCl burner was determined to be $184.6\ W^{0.85}$ (in dollar units); for the LiCl electrolyzer it is $0.3\ W$; and for the evaporators it is $32.25\ A^{0.8}$ (where A is the heat transfer area needed for evaporation). Cost correlations for the other equipment such as drying towers, mixers, aqueous NaCl electrolyzers, and drilling devices are not available; these were determined analytically.

TABLE 5.—ENERGY REQUIREMENT FOR THE PROPOSED PROCESS

Equipment or unit	Energy Required Thermal energy kwh(t)/hr	 Electrical energy kwh(e)/hr
Evaporator	$1.291\ W$	
NaCl solution tank	$1.639 \times 10^{-2}\ W$	
NaCl electrolyzer		$8.48 \times 10^{-3}\ W$
HCl burner	$-0.181\ W$	
Dryer	$1.551 \times 10^{-2}\ W$	
LiCl electrolyzer		$1.796 \times 10^{-2}\ W$
Distillation tower	$4.86 \times 10^{-8}\ W$	
Subtotal	$1.142\ W$	$2.644 \times 10^{-2}\ W$

Total energy
(thermal & electrical 0.400 W[1] & 0.026 W = 0.426 W (e)

---

[1] Thermal to electrical conversion efficiency = 35%

TABLE 4.—EXTRACTION OF LITHIUM FROM BRINE: SUMMARY OF DIMENSIONS AND NUMBERS OF MAJOR PIECES OF EQUIPMENT

Equipment	Evaporator	NaCl solution tank	NaCl electrolyzer	Mixing tank & settling tank	Li-extraction tower and separation tank	Drying tower	LiCl electrolzyer
Dimensions	6.35×10^5 cm^2 each	5.12 m x 5.12 m x 5.12 m	78 DeNora Cells of 1.2 m x 1.1 m x 3 m	5.12 m x 5.12 m x 5.12 m	5.12 m x 5.12 m x 5.12 m	182.88 cm (dia) x 60.96 cm (length)	426.7 cm x 640 cm x 320 cm
Number of Units (N)	$N = \frac{38.58\ W}{6.35 \times 10^5}$	$N = \frac{1073\ W}{512^3}$	$N = 5.34 \times 10^{-3}\ W$	$N = \frac{2.5 \times 10^{-9}\ W}{5.2^3}$	$N = \frac{3 \times 10^{-9}\ W}{512^3}$	$N = \frac{4\ W}{\pi d^2 1}$	N = 1
Example Tabulation for $W = 1.25 \times 10^5$ g/hr	N = 1	N = 1	8.56 sets of 78 DeNora Cells	N = 1	N = 1	N = 1	N = 1

Capital investment for a 10^6-kg/hr Li-production plant from the brine is given in table 6. The largest capital equipment cost is the evaporator, which has to handle a great deal of brine to produce concentrated bittern. Use of solar ponds could decrease the capital investment, however, as discussed previously, solar ponds are not always feasible for evaporating water from brine. Initial inventory and recycling cost of ethyl ether and DPM are also taken into account. In addition to the major pieces of equipment, piping and other unlisted equipment, service facilities, site preparations, and electrical instrumentation have also been included.

The production cost for the 10^6-kg Li/yr plant is given in table 7. Yearly charge, maintenance, electrical and steam costs are taken to be similar to those previously reported (Steinberg and Dang, 1976) and as indicated in table 7. The production cost for this plant is 5.52 cents/gm, which is in the order of magnitude of the present cost of lithium of 3.3 cents/gm (verbal communication, Foote Mineral Co., Exton, Pennsylvania). With this cost information the present process appears to be feasible.

Since the most capital-intensive item in table 6 is the evaporator, alternative method for lithium production using the present general process is to evaporate less water or

TABLE 6.—CAPITAL INVESTMENT FOR A PLANT THAT EXTRACTS LITHIUM FROM BRINE (concentrate brine by evaporating to 2 ppm water)

	Capital Investment		Cost ($\$10^6$)[1]
(1)	Equipment (itemized)		29.04
	Drilling device	0.60	
	Aqueous NaCl electrolyzer	0.60	
	Evaporator	15.19	
	HCl burner	6.90	
	Mixing, settling, and separation tank	1.50	
	Drying tank	0.65	
	LiCl electrolyzer	0.10	
	Ether and DPM	3.50	
(2)	Piping, 29% of item 1		8.42
(3)	Service facilities, 56% of item 1		16.26
(4)	Unlisted equipment and misc., 10% of items 1-3		5.37
(5)	Installation of equipments, 35% of items 1-4		20.68
(6)	Site preparations and buildings, 20% of items 1-5		15.95
(7)	Electrical and instrumentation, 20% of items 1-6		19.14
	Subtotal		114.86
(8)	Engineering, construction, overhead, and contingency		114.86
	Total		229.72

---

[1] Basis: 10^6 kg Li/yr plant, 300 days operation, 1976 dollar

TABLE 7.—PRODUCTION COST FOR A PLANT PRODUCING 10^6 KG OF LITHIUM PER YEAR (concentrate brine by evaporating to 2 ppm of water)

	Items	Cents/gm[1]
(1)	Annual depreciation, 13%	2.98
(2)	Electrical energy cost (for pumping and electrolysis) 1.5 cents kwh	0.04
(3)	Steam cost 0.249 cents/1000 gm	0.21
(4)	Raw material	0.00
(5)	Maintenance, labor, and similar items	2.29
(6)	Ether and DPM loss	0.01
	Total	5.53

---

[1] 1976 dollar

TABLE 8.—CAPITAL INVESTMENT FOR A PLANT THAT EXTRACTS LITHIUM FROM BRINE (concentrate brine by evaporating to 50 percent of initial water)

	Capital Investment		Cost ($\$10^6$)[1]
(1)	Equipment (itemized)		41.15
	Drilling device	0.60	
	Aqueous NaCl electrolyzer	0.60	
	Evaporator	3.35	
	HCl burner	6.90	
	Mixing, settling, and separation tank	5.14	
	Drying tank	1.46	
	LiCl electrolyzer	8.60	
	Distillation tower	8.00	
	Ether and DPM	6.50	
(2)	Piping, 29% of item 1		11.93
(3)	Service facilities, 56% of item 1		23.04
(4)	Unlisted equipment and misc., 10% of items 1-3		7.61
(5)	Installation of equipments, 35% of items 1-4		29.31
(6)	Site preparations and buildings, 20% of items 1-5		22.61
(7)	Electrical and instrumentation, 20% of items 1-6		27.13
	Subtotal		162.78
(8)	Engineering, construction, overhead, and contingency		162.78
	Total		325.56

---

[1] Basis: 10^6 kg Li/yr plant, 300 days operation, 1976 dollar

TABLE 9.—PRODUCTION COST FOR A PLANT THAT PRODUCES 10^6 KG LITHIUM PER YEAR
(concentrate brine by evaporating to 50 percent of initial water)

	Items	Cents/gm[1]
(1)	Annual depreciation, 13%	17.00
(2)	Electrical energy cost (for pumping and electrolysis) 1.5 cent/kwh	0.60
(3)	Steam cost 0.249 cent/1000 gm	0.05
(4)	Raw material	0.00
(5)	Maintenance, labor, and similar items, 10%	6.04
(6)	Ether and DPM loss	2.76
	Total	26.45

[1] 1976 dollar

TABLE 10.—CAPITAL INVESTMENT FOR A PLANT FOR THE EXTRACTION OF LITHIUM FROM BRINE
(no concentration of brine)

	Capital Investment		Cost ($$10^6$)[1]
(1)	Equipment (itemized)		76.68
	Drilling device	0.60	
	Liquid-liquid extraction tower	59.11	
	Drying tank	1.46	
	LiCl electrolyzer	8.60	
	Ether and DPM	6.91	
(2)	Piping, 29% of item 1		22.23
(3)	Service facilities, 56% of item 1		42.94
(4)	Unlisted equipment and misc., 10% of items 1-3		14.19
(5)	Installation of equipments, 35% of items 1-4		54.61
(6)	Site preparations, buildings, 20% of items 1-5		42.13
(7)	Electrical and instrumentation, 20% of items 1-6		50.56
	Subtotal		303.34
(8)	Engineering, construction, overhead, and contingency		303.34
	Total		606.68

[1] Basis: 10^6 kg Li/yr plant, 300 days operation, 1976 dollar

to use the raw brine without evaporation for liquid extraction. If 50 percent of water in the initial brine is evaporated in the evaporation process, the same procedure of calculation as previously discussed for this process (fig. 1) can be followed. The capital investment and production cost of this method are given in tables 8 and 9. The other process is to use the brine directly with DPM in ether for liquid-liquid counter current extraction. Subsequently, lithium is extracted from the ether phase to the aqueous phase in another liquid-liquid extractor. The flow diagram of this process is shown in figure 2. Process calculations have been performed, and the results of economic analysis are given in tables 10 and 11. In comparing tables 6 through 11, the most economical process involves evaporating water to give two parts of brine from an initial million parts of Smackover oil-field water. Further laboratory process bench scale work will have to be performed to determine operational feasibility especially concerning losses of lithium and the specificity of lithium extraction with a chelating agent such as DPM.

TABLE 11.—PRODUCTION COST FOR A PLANT THAT PRODUCES 10^6 KG LITHIUM PER YEAR
(no concentration of brine)

	Items	Cents/gm[1]
(1)	Annual depreciation, 13%	4.22
(2)	Electrical energy cost (for pumping and electrolysis) 1.5 cents kwh	0.40
(3)	Steam cost 0.249 cents/1000 gm	0.05
(4)	Raw material	0.00
(5)	Maintenance, labor, and similar items, 10%	3.24
(6)	Ether and DPM loss	1.38
	Total	9.29

[1] 1976 dollars

CONCLUSION

Data from the literature are used as the basis for a preliminary process design and analysis of the extraction of lithium from Smackover oil-field brine by means of the chelating agent dipivaloylmethane (DPM). Assuming the feasibility of the scale-up of the process chemistry, process-design calculation was performed as a production rate of lithium. A typical example of lithium production rate of 10^6 kg/yr is tabulated. The major pieces of equipment needed are described. Energy requirement (converted from thermal to electrical energy) for the process is low, 0.426 kwh(e)/gm. Production cost of the most economic process investigated is 5.52 cents/gm (1976 dollar) for a production plant of 10^6 kg/yr. This price is compatible with the present cost of lithium of 3.3 cents/gm.

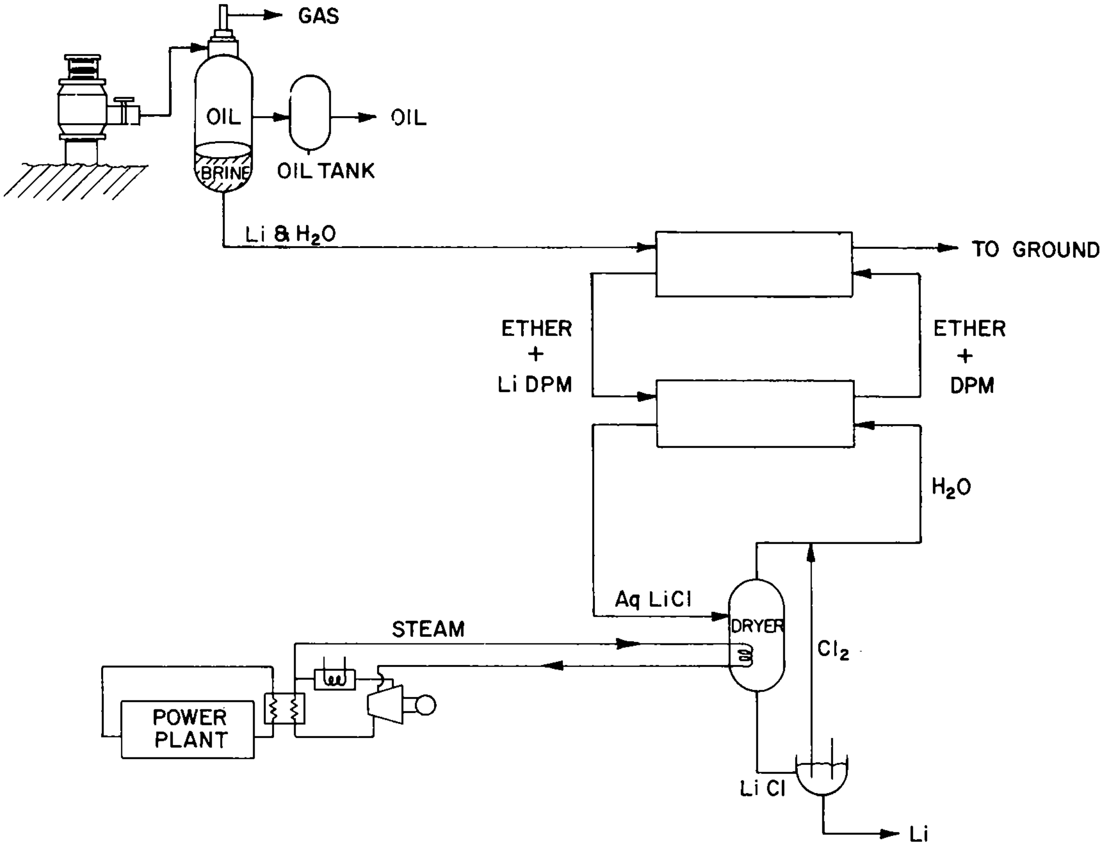


Figure 2. Flow diagram for lithium production from Smackover oil-field water using direct liquid-liquid extraction with water evaporation.

REFERENCES CITED

Chilenskas, A. A., Bernstein, G. J., and **Ivins, R. O.,** 1976, Lithium requirements for high-energy lithium-aluminum/iron-sulfide batteries for load-leveling and electric-vehicle applications, *in* Vine, J. D., editor, Lithium resources and requirements by the year 2000: U.S. Geological Survey Professional Paper 1005, p. 5-9.

Collins, A. G., 1976, Lithium abundance in oilfield waters, *in* Vine, J. D., editor, Lithium resources and requirements by the year 2000: U.S. Geological Survey Professional Paper 1005, p. 116-123.

Cooper, J. F., Borg, I. Y., O'Connell, L. G., Behrin, E., Rubin, B., and **Wiesner, H. J.,** 1976, Lithium requirements for electric vehicles using lithium-water-air batteries, *in* Vine, J. D., editor, Lithium resources and requirements by the year 2000: U.S. Geological Survey Professional Paper 1005, p. 9-12.

Energy Advisory Panel, 1973, An assessment of new options, *in* Energy Research and Development: AET-9, (Assessment Energy Technology-Brookhaven National Laboratory), November, p. 217.

Guter, G. A., and **Hammond, G. S.,** 1965, The separation of lithium from alkaline metal ions: Journal of American Chemical Society, v. 78, p. 5166.

Hader, R. N., Nielsen, R. L., and **Herre, M. G.,** 1951, Lithium and its compounds: Industrial and Engineering Chemistry, v. 43, no. 12, p. 2636-2646.

Ludwig, E. E., 1964, Applied process design for chemical and petrochemical plants: Gulf Publishing Co., Houston, v. 2, p. 101.

Mantell, C. L., 1960, Electrochemical engineering: McGraw-Hill Co., New York, p. 266.

Martin, D. F., Heyl, M. G., and **Doig, M. T., III,** 1973, Effect of selected β-diketones on lithium fluxes of bovine red blood cells: Life Science, v. 12, p. 241-251.

Peters, M. S., and **Timmerhaus, K. D.,** 1968, Plant design and economics for chemical engineers, 2d edition: McGraw-Hill Co., New York, 850 p.

Popper, H., 1970, Modern cost-engineering techniques: McGraw-Hill Co., New York, 538 p.

Steinberg, M., and **Dang, V. D.,** 1976, Preliminary design and analysis of a process for the extraction of lithium from seawater, *in* Vine, J. D., editor, Lithium resources and requirements by the year 2000: U.S. Geological Survey Professional Paper 1005, p. 79-88.

Vine, J. D., editor, 1976, Lithium resources and requirements by the year 2000: U.S. Geological Survey Professional Paper 1005, 162 p.