Ernest E. Angino
Ronald G. Hardy } Editors

A SYMPOSIUM ON INDUSTRIAL MINERAL EXPLORATION AND DEVELOPMENT

Proceedings of the Third Forum on Geology of Industrial Minerals

April 5-7, 1967
The University of Kansas
Lawrence, Kansas

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Previous Forums

1. A Symposium on Geology of Industrial Limestone and Dolomite (1965) published in: Ohio Journal of Science, 1966, vol. 66, pp. 97-224.

2. A Symposium on Geology of Cement Raw Materials (1966) published by: Indiana Geological Survey, 1966, 197 p.

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EDITOR'S COMMENTS

The title of this volume reflects the general theme of the Third Forum on the Geology of Industrial Minerals. In actuality, the Forum itself was subdivided into three sessions, titled respectively: Exploration and Evaluation, Applications of Geochemistry to Industrial Mineral Development, and Practical Examples of Industrial Mineral Development. The continuity of subject matter is retained in this volume, i.e. the papers are arranged in the order presented at the meeting. The papers have been edited only insofar as necessary to present a unified style and format. A large part of the everyday work of typing and preparing the manuscripts for the printer was handled by Mrs. Diana Coleman. Her diligence has in no small way contributed greatly to the early publication of the Forum Proceedings.

July 1967
Lawrence, Kansas

Meetings such as the Forum are designed to stimulate conversation and thinking among people with different backgrounds, but at the same time with similar interests. The technical sessions themselves though only a part of the value of such meetings are, of course, the key to this stimulation. The "keynote" address by Dr. Campbell set the stage for a stimulating meeting, the promise of which was borne out by the quality of the papers presented herein. Judging from comments and discussions made both during and since the meeting, the papers presented in this volume help to serve the purposes for which the Forum was designed. The authors are to be congratulated for both the quality and stimulation of ideas that their papers provided and will continue to provide to the readers of this volume.

Ernest E. Angino
Ronald G. Hardy

FOREWARD

This third annual Forum on the Geology of Industrial Minerals records the rapid evolution of the Forum and the growing recognition of the significance of the so-called industrial minerals. The annual Forum began with a group representing especially the mid-west states. The 1967 meeting has dropped mid-west from its title and has become international in scope. Registrants come from 30 states and 2 foreign countries and inquiries were received from several others.

Why is the term "industrial mineral" used for nonmetallic mineral deposits? To some it carries, I am afraid, a connotation of low value and lack of glamour, but it should be a term of honor and significance. This Forum and those to follow should do much to recognize the indispensible role of the Industrial Minerals in world development.

Frank C. Foley, Director
State Geological Survey of Kansas

INTRODUCTION

The traditional academic course in the geology of industrial minerals, especially nonmetallic minerals, stressed occurrence, uses, production data, limits of permissable use of deleterious materials, and standard tests that seemingly relate to the durability of these materials. The subject was distinctly lowbrow, and most academic institutions generally held, and still hold, the view that any reasonably intelligent student could make his way in the field of industrial minerals provided that the engineer with whom he had, unfortunately to work, would take the trouble to learn a little geology. The student by being alert, could acquire the necessary level of competency through experience. In fact, the whole field of industrial minerals was regarded as an aspect of applied geology, and scarcely worth the attention of academia, which should concentrate on basic research. Unfortunately, the same attitude was prevalent in other disciplines. The economist, for example, judged that any reasonably well-educated economist could deal with mineral resource economics if he simply put his mind to it. The engineer, with a few good reference tables, a superior knowledge of design, and a 100-percent safety factor, could surmount any problems presented by the raw materials with which he had to work.

Fresh winds of change have begun to blow through this subject. Exponential growth in populations has placed tremendous demands on raw materials for construction and food production. Terms like "econometrics of mineral resources," "optimization of return on investment through optimization of exploration, production, processing, and sales," "stewardship of land," and "dynamic conservation" began to appear in print. Optimized return on land for society and regional zoning became subjects for conversation. One began to hear about transportation algorithms for location of plants that used industrial minerals, to read reports about mathematical models of exploration, tight standards for highway materials, resource satellites, and sophisticated instrumental analysis. Terms like "quality of the environment" entered the scene.

It has become evident that the field of industrial minerals has acquired a high level of sophistication and draws heavily upon many disciplines: engineering systems analysis, econometrics, geochemistry, and the like, contribute. Many state and federal agencies, working in close collaboration with industry, have recognized these important changes. Few academic institutions have recognized either the change or the need to look anew to the kind of academic instruction that is necessary if the graduating student is to move with confidence into this field of applied research and development. Thus, this Third Forum on the Geology of Industrial Minerals, held as before on a university campus, not only serves to bring together practi-

tioners in this important field, but also as a locus for a changing profession that relates directly to the problems of modern society. Held in a university setting, the Forum gently nudges the university in the direction of relevance to society's problems and toward applied research. The subject matter of the Forum, ranging widely through geochemical studies, beneficiation techniques, remote sensing, zoning statutes, product development, statistical and computer techniques, and instrumental analysis serves to reveal and emphasize the changing character of industrial mineral studies, and the importance of a new approach in education and research. The State Geological Survey of Kansas is pleased to assist in hastening the process.

William W. Hambleton, Associate Director
State Geological Survey of Kansas

SECTION ONE

EXPLORATION AND EVALUATION

THE INDUSTRIAL MINERALS: IN RETROSPECT, INTROSPECT, AND IN PROSPECT

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ABSTRACT

The Industrial Minerals -- a grouping essentially synonymous with "the nonmetallics" -- include a wide variety of minerals possessing some highly diverse features. They include, for example, the hardest of all minerals (diamond) and the softest (talc); the whitest (magnesite) and the blackest (graphite); among the toughest (jade) and among the most brittle (sulphur), besides many others that exhibit equally great contrasts, not only in mineralogical parameters, but also in geologic occurrence and in geologic distribution. Yet, despite this diversity, the industrial minerals possess certain features, both geologic and economic -- common to most that, in the past, have justified and perhaps still continue to justify treating them as a special group.

Some fifty years ago some 25 to 30 minerals were recognized in the United States as industrial minerals. Their annual value then amounted to a little over $500,000,000. In 1965, the number of the industrial minerals had increased to over 40 and their value to more than $4,600,000,000. By comparison, the metallic "ore minerals" in 1915 numbered some 15 or more, with an annual value almost of $1,000,000,000. Fifty years later the number of ore minerals being produced had increased to nearly 30; their value, to slightly over $2,250,000,000 -- an increase of 230 percent. Yet the industrial minerals, in this same period had enjoyed an increase in value of nearly 900 percent!

Thus, whereas fifty years ago it was understandable in terms of the total economy why "the nonmetallics" were considered "the poor relations" of the mineral kingdom (there were geological and professional reasons that also contributed to this attitude), today the picture is greatly changed -- changed so much in fact, that major metal mining companies and even major petroleum companies are ardently wooing (some have already wedded!) the once despised "nonmetallics".

Projecting such trends gives an encouraging picture of the future of the industrial minerals. There is additional sound basis for such roseate projections in the fact that so many of them -- especially the "bread and butter" minerals (salt, limestone, sand and gravel, the fertilizer minerals, etc) are so closely tied to growth of population. Unquestionably some industrial minerals will face competition from alternative sources, including synthetics. Yet consideration of the "conservation of matter" indicates that the source material, whether natural or syntehtic, will for the foreseeable future have to come very largely from terrestrial sources. Hence mining in one form or another will continue, and continue to expand. Increasingly, too, the industrial minerals -- especially the low-cost, large-bulk minerals that require surface mining -- are going to face competition for land use. Operators to be successful, will have to pay increasing attention to conservation practices and to long-range planning with government agencies. Further, more rigorous specifications for many minerals will require more, better and (hopefully) newer beneficiation methods and these in turn may well lead to more and better and newer by-products, with potential for increased profits.

The touchstones for the future of the industrial minerals therefore lie in research (research in exploration, beneficiation, transportation and applications), in innovative thinking and planning, and in social and political cooperation.

INTRODUCTION

Mr. Chairman, members and guests of the Industrial Minerals Forum: On my way here, in the course of reviewing the correspondence on this Forum, I discovered -- with something of a shock -- an item I had previously overlooked, viz., that my comments this morning are to be in the nature of a "keynote talk". Now, although I come from a state that has recently seen much political activity, I must confess that I am myself totally unfamiliar with the requirements for a "keynote speech"!

Perhaps therefore it will suffice if I recount a recent -- and I think significant -- incident that transpired at the national meeting of AIME in Los Angeles a few weeks ago. In order that you may fully appreciate this, I must go back some three or four years in AIME history, when the Long Range Planning Committee of the Society of Mining Engineers proposed that a restructuring of the Society, whereby all of the Divisions would be based on functional (rather than partly on topical) factors, might be desirable. Thus SME would be re-designed to consist of an Exploration Division, a Mining Division, a Beneficiation Division, and perhaps a Marketing and/or an Economics Division. Despite some obvious logic and appeal in this general pattern, a number of us were not only reluctant, if only for old times' sake, to see the Industrial Minerals Division dissolved, but we felt there were positive values in retaining the Division, as a Division of SME, that outweighed any gains from adopting a wholly functional pattern for the Society.

Because so many of you are members of AIME, and because it bears directly on this matter, it may be appropriate to quote here a portion of my 1964 report to SME's Long Range Planning Committee:

A Look to the Future in the Light of the Past

Although the Industrial Mineral Division is one of the smaller divisions of SME, with only some 700 members listing this Division as their "primary affiliation", it ranks high in "second choice", with well over 3000 such designations. And, in fact, some of the very important work of the Division has always been carried on by SME members who have not been listed among the Division's primary affiliates. The Division has been in successful operation for close to thirty years. Its programs are always among the big drawing cards at annual and regional meetings in which it shares. Increasingly, too, the programs have been successfully coordinated and on appropriate occasions even integrated with those of related groups within SME and within the Institute.

Even before the organization of SME, and more so since, there has been much thought given as to whether SME might not best be organized wholly along functional lines rather than, as at present, partly on functional and partly on topical lines. Thus Mining & Exploration and Minerals Beneficiation Divisions are functional categories; Coal and Industrial Minerals are more topical. In theory there may seem to be advantages in a "more streamlined" organization for SME. In practice many of the members have expressed grave doubts as to the desirability of any such reorganization -- certainly as it would apply to the Industrial Minerals Division. To be sure, industrial minerals involve exploration, and mining, and beneficiation, and processing, and marketing -- broad categories of interest which the Division shares with coal, with the metallic minerals, and even with petroleum. Nevertheless, the kinds of exploration, of mining, of beneficiation, of processing, of fabrication and of marketing that the industrial minerals call for are in general sufficiently different (if not in a number of instances, unique) that the Division has its own special interests in each of these fields. Moreover it is perhaps a reasonable generalization to state that, in organizations operating in the industrial minerals field, there is a greater degree of vertical integration than commonly exists for other minerals. By way of example, the same company that explores for and mines crude gypsum, continues through to make and market wall-board. By

contrast, a lead miner most likely sells his concentrate directly to a smelter or refinery; a gold miner to the mint! This being the case, it is important that the geologist in an industrial minerals organization, no matter where within the spectrum his interest focuses and no matter whether he be primarily in exploration or in marketing, should know at least something about, and attempt to keep somewhat abreast of developments in all related "functions". It is this feature that provides attraction to and benefit from the Industrial Minerals Division programs, and that accounts for the desire of many in the Division -- while contributing to the full to the advancement of SME -- to retain essentially the present Divisional entity.

There were lengthy discussions in SME, following the submission of this and other reports, leading -- we felt at times -- to the probable demise of the Industrial Minerals Division. But to cut a long story short, and jump to the Los Angeles meeting of AIME earlier this year, the final dicision there was unanimously in favor of retaining the present structure of SME which, as you know, provides for a Mining and Exploration Division, a Minerals Beneficiation Division, a Coal Division and an Industrial Minerals Division. In view of the careful studies that preceded this decision, I think this assurance that we now have, that the Industrial Minerals Division will continue as such, as as cheerful a "keynote" as could be sounded! There is an assured place for the Division, there is justification for a continuation of interest in the industrial minerals, and, by the same tokens, there should certainly continue to be a place for these present Forums.

Although this recount, involving as it does "retrospect" and "prospect", might be sufficient justification for my title, some further comments may be in order. In retrospect, we can all recall the time when the industrial minerals were so negatively regarded that they were most commonly referred to as "the nonmetallics"; when they were considered the "poor relations" of the minerals world; and when a geologist working for a limestone company, or a sand and gravel plant, or a clay producer was made to feel "a second class citizen"; and when, indeed, few such companies, confident as so many were of their "inexhaustible reserves" and of the simplicity of the geology and of the processing of the raw materials, even thought of employing a geologist. It may have been, as some have alleged, that it was because we constituted a minority group that we were driven together and that a community of interest developed in the industrial minerals. Rather, I think it was because a few resolute spirits and such able men as Oliver Bowles, Sam Dolbear, Joe Gillson, Ray Ladoo and others saw far enough into the future to recognize that geology was going to be increasingly important in the industrial minerals field, that in recent years we find ourselves no longer "second class citizens" but at times even the envy of those who are more subject to the unfortunate and too violent vagaries of the metal markets, and that programs and forums on the industrial minerals bring out the kind of interest and enthusiasm that we see at this meeting. And we find metal mining companies and even petroleum companies eager today to diversify into production of industrial minerals -- a field that would have been scorned by many a generation ago.

Let that suffice by way of "retrospect". Concerning "introspect" (being neither a psychologist or myself sufficient of an introvert!) I will say little. If we as industrial mineralogists ever really had an "inferiority complex" (personally I suspect this was more figment of the imagination than fact) we should certainly now shed it. Yet in shedding it, and in taking pride in our present status and achievements, let us take care that we do not develop a pride based only on a habit of casting admiring backward looks at the route we have come, or the pride that leads to isolation and the inability and the lack of opportunity to learn from others working in related, or even very different, endeavors. Let us rather, humbly yet seriously, consider the prospects -- first by projecting from the past.

Some fifty years ago some 25 to

30 minerals were recognized in the United States as industrial minerals. Their annual value then amounted to a little over $500,000,000. In 1965, the number of the industrial minerals had increased to over 40 and their value to more than $4,600,000,000. By comparison, the metallic "ore minerals" in 1915 numbered some 15 or more, with an annual value of almost $1,000,000,000. Fifty years later the number of metallic ore minerals being produced had increased to nearly 30; their value, to slightly over $2,250,000,000 -- an increase of 230 percent. Yet the industrial minerals, in this same period, had an increase in value of nearly 900 percent! One of the more trenchant discussions of mineral trends in recent years, especially in comparison to other aspects of the economy, is to be found in a Resources for the Future publication, "Trends in Natural Resources Commodities" by Potter and Christy (1962). There it can be seen that whereas over some 90 years, the per capita consumption of agricultural products has increased only slightly, and over the past decade has actually declined (testimony perhaps to the growing "weight consciousness" of the average American!), and while per capita consumption of forest products has significantly declined, mineral consumption, per capita, has shown a notable and consistent increase through these many decades. If one takes into account also the continuing growth in population, we obviously have a multiplier effect that is consistent with the enormous demands that today's mineral producers must meet: 900,000,000 short tons of sand and gravel in 1966; 775,000,000 short tons of stone; 36,000,000 short tons of salt; 31,000,000 long tons of phosphate rock (up 17% since 1965!). Truly, it calls for imaginative and effective geology even to keep pace with such demands -- to say nothing of developing the reserves that we should have.

Another "prospect" that should be recognized by geologists is the trend to more rigorous specifications for many industrial minerals. Whereas at one time it sufficed to have a few bulk samples of a deposit, tomorrow we may need a detailed pattern of the geochemistry of what would earlier have been regarded as a "uniform and inexhaustible" body of -- this, that, or the other industrial mineral or rock. And closer quality control and tighter specifications will call for more, better, and hopefully also newer beneficiation methods and these in turn may well lead to more and better and newer by-products or co-products, with potential for increased profits.

Projecting such trends gives an encouraging picture of the future of the industrial minerals. There is an additional sound basis for such roseate projections in the fact that so many of them -- especially the "bread and butter" minerals (salt, limestone, sand and gravel, the fertilizer minerals, etc) -- are so closely tied to growth of population. Unquestionably, some industrial minerals will face competition from alternative sources, including synthetics. Yet, consideration of the "conservation of matter" indicates that the source material, whether natural or synthetic, will for the foreseeable future have to come very largely from terrestrial sources. Hence mining in one form or another will continue and continue to expand. Increasingly too, the industrial minerals -- especially the low-cost, large-bulk minerals that require surface mining -- are going to face stiffening competition for land use. In Los Angeles County last year the per capita consumption of sand and gravel was 4.3 tons. If trends of population and demand continue, it is estimated that by 1980 it will require annually 300 acres, quarried to depths of 100 feet, to meet the local needs. There is, to be sure, a bright side to this picture. In our metropolitan areas a hole in the ground (mere "emptiness" if you like) is coming to be worth more than the material extracted to make the hole -- so great is the need for "dumping space". A recent study made by the Aerojet General Corp. for the San Francisco Bay area indicates that in the next 25 years population will have increased 53 percent, but the volume of liquid waste production will be up 78 percent, and of solid waste by a staggering 210 percent! More and bigger holes are assuredly going to be needed, or else we must have a

real break-through in man's attempts to annihilate matter.

Mining operators, to be successful, will have to pay increasing attention to conservation practices and to long-range planning with government agencies, at all levels: city, county, state and federal. For truly it is government decisions that call the turn on many a mining operation today and that determines what will or will not be economically feasible. But make no mistake: although at times a decision may seem to be an arbitrary ruling by "one of those bureaucrats", ultimately in our democracy it is we the people -- you and I and our employers and our neighbors down the street -- who make the decisions.

Mining has too long tended to be an isolated endeavor. Mining must learn to live compatibly with people. And I think we may take pride in the fact that it is in the field of the industrial minerals that we have soonest come to recognize this most important point. Let us nevermore forget or overlook it!

The future of the industrial minerals is indeed bright, and the touchstones for assuring and further brightening that future lie in research (research in exploration, mining, beneficiation, transportation and applications), in innovative thinking and planning, and -- most important of all -- in social and political cooperation.

REFERENCES

Potter, N., and Christy, F. T., Jr., 1962, The Johns Hopkins Press, Charts 23, 29 and 31 are particularly instructive.

INVENTORY OF CONSTRUCTION MATERIALS BY PHOTO INTERPRETATION IN KANSAS

Alvis H. Stallard
State Highway Commission of Kansas
Topeka, Kansas

ABSTRACT

Because the Kansas highway construction program extends over hundreds of miles, the exploration and production of useable construction material is a formidable task. Different types of material are available in different regions and the design of highway construction projects may vary from one area to another in order to utilize, as much as possible, local material and to make the project economically feasible. An inventory of the existing construction material in a given area provides the materials engineer with an indispensable tool to aid him in the utilization of local sources of material, to manage and plan the overall material requirements of a project, and to provide a means of estimating the cost of such a facility. Aerial photographic interpretation techniques provides an economical and expedient aid in conducting such investigations.

The photo interpreter identifies and maps important source units on aerial photographs. A knowledge of the geology of the area is used to determine the thickness uniformity of the source units and previously obtained quality data, along with lithological characteristics, are used to determine the quality consistency of the various producing units.

Although many perspective sites are located by photo interpretation techniques, the system does not eliminate field investigations. It does reduce the extent of such work by eliminating certain areas which are not potential producers as evidenced by the established relationship between the geomorphology and the known material sites. Sampling and testing of the materials must be performed to fulfill specification requirements and to obtain more detailed information concerning the quality and quantity of material available for production purposes.

INTRODUCTION

Kansas is divided naturally into seven physiographic provinces which are characterized by distinctive geologic features. Inasmuch as the state has nearly 11,000 miles of highways in its road system, a wide variation of geologic conditions are encountered. Because highways extend over hundreds of miles, the materials problem is constantly changing and the design of the highway may be altered in order to utilize local sources of material and to compensate for changes in traffic load and in some cases, changes in terrain and climatic conditions.

The State Highway Commission of Kansas has divided the state into six divisions for administrative and operational purposes. With the exception of the two western divisions, each division generally includes separate and different physiographic units and consequently, are characterized by different construction materials resources. The two western divisions are in the same physiographic unit but have different material problems primarily because of different surface drainage systems.

Each division has a materials engineer whose responsibility is to handle all material needs of the highway commission in the respective divisions. In order to manage and plan the overall material requirements of a construction project effectively and to estimate the cost of such a facility, the division materials engineer must have information concerning the location, quality and quantity of construction material

available throughout his area of responsibility.

Time and cost precludes the possibility of inventorying construction materials using conventional ground survey methods. In order to provide such information, the State Highway Commission of Kansas has initiated a state wide inventory of construction materials by using aerial photographic interpretation as the means of accomplishing the project on a county basis.

NATURE OF THE PROJECT

The objectives of the county inventory program are to map and describe all geologic source units exposed in the counties that have been used or may be used in the future for the various types of highway and road construction. In addition, a separate geo-engineering section is included to describe geologic units that exhibit poor engineering properties under the climatic and ground-water conditions that exist in the county. The quality of water available for concrete mix water is also reported.

PROCEDURES

Research and Review of Existing Data

In order to accomplish a materials inventory by photo interpretation, the interpreter must have a good knowledge of the geology of the area and the environmental and climatic conditions that exist in the county. The amount of detailed information that can be included in the final report is contingent, for the most part, on the knowledge that the interpreter has pertaining to the geology and its relationship to the construction materials resources of the county. The geology of the county is the basis by which the project is completed and photo interpretation is the means by which it is accomplished. In essences, the interpreter studies and maps select geologic units on aerial photographs for quantitative data, and available engineering data are correlated with the various geologic source units for qualitative information. Qualitative data are obtained by research and review of geologic and soil maps and reports, results of quality tests, and geologic profiles that have been compiled for the major highways in the county.

Photo Interpretation

The value of photo interpretation is realized in the accuracy and speed that material source units can be mapped over a large area. Because most of the geology of Kansas is readily adaptable to photo interpretation techniques, the mapping process is a relatively easy task and the inventory, for the most part, is a manner of extending geologic and engineering data over the area being investigated. Occasionally, a potential material source has not been exploited in a given area and as a result of the materials inventory investigation, a new source unit is introduced.

In some parts of eastern Kansas, individual source units are highly variable in thickness and quality. In northeastern Kansas, some of the source units are covered by variable thicknesses of glacial drift. The drift is a heterogenous mixture of clay, silt, sand and gravel and is a source of sand and gravel at various horizons. In such areas, additional field investigation must be accomplished to supplement the data derived from the aerial photographs. Color aerial photography has been used to good advantage in these areas but elsewhere, where the geology is relatively consistent, the objectives of the inventory are obtained by using black and white photography. The photography is flown at a scale of 1:24,000 by the State Highway Commission using a Wild RC-8 aerial camera.

Many of the photo interpretation techniques that are applied to materials investigations are generally known. Information concerning pattern elements such as photographic tone, landforms, gullies and others have been described in various publications and text books. Usually two or three pattern elements are utilized during a photo analysis of a given area. It should be noted, however, that even though the pattern elements are observed and studied singly, they are utilized with other clues and a gener-

al knowledge of the area to arrive at a conclusion. It is the task of the photo interpreter to ascertain the significant clues that are discernible which will achieve the objectives of the investigation. Of equal importance, the interpreter must recognize the amount and type of information that can be derived from the aerial photographs.

All sites which are producing or have produced material in the past are located and correlated to the geology of the county. Geologic material source units are mapped and prospective sites are selected. The general quality of material that might be produced from a prospective site can be ascertained providing the same source unit has been sampled and tested in a near-by location and if the geologic unit is consistent in thickness and lithology. In some counties, large areas can be delineated as being void of any type of rock or granular construction material. For example, 70 to 80 percent of some western Kansas counties are covered by thick loess deposits and granular material can be produced only along the major drainage channels where the overburden has been removed.

PRESENTATION OF DATA

The length and detail of a materials inventory will vary with the photo interpreter, the complexity of the geology of the area being investigated, the amount of ground information available, and the amount of time spent compiling the report. There are certain items of information that should be included in the inventory report. They are: 1. a map portraying the geographic extent of source units and negative areas (areas where no material will be found) or where overburden is excessive; 2. a map depicting the location of open and prospective construction material sites; 3. a description of each source unit concerning quality, quantity and general accessibility; and 4. a detailed description and map or sketch or each specific site (open and prospective).

All information should be presented in terms that are meaningful to the materials engineer. The nomenclature and methodology that is used in the investigation may be foreign to the engineer. Although geologic nomenclature is used to classify the source units, the description of the material must be in meaningful engineering terms. In essence, a sufficient amount of geological data must be included for correlation purposes and to aid in future investigations but the pertinent materials information must be presented in significant and meaningful engineering terms.

THE USE OF STATISTICAL ANALYSIS IN QUARRY EVALUATION

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ABSTRACT

The evaluation of quarried stone to determine its acceptability as a highway construction material has long been a problem of interest. Laboratory tests, run on quarry-ledge samples or stockpile samples, are used to evaluate the stone in relation to the prevailing aggregate specifications.

Questions often raised in conjunction with such evaluation include: what degree of mixing of rock units occurs during blasting, loading, and hauling (in regard to the possible dilution of minor amounts of poor material in the remaining, better quality material) and what changes, if any, occur in aggregate quality during crushing and sizing?

A study of an Indiana quarry with three distinct formational units was made using the Los Angeles abrasion test as a basis for comparison. Samples were obtained in the quarry and at several locations during aggregate processing. Analysis of Variance and Multiple Correlation and Regression Analysis were used to determine the degree of mixing and the changes in quality and rock unit contribution during processing.

INTRODUCTION

The information in this report was obtained by the authors during the summers of 1965 and 1966 as a portion of a comprehensive study on aggregate degradation for the National Cooperative Highway Research Program. The purpose of this facet of the overall study was to gain knowledge concerning mixing and beneficiation of aggregates during crushing and milling.

After considering a number of Indiana quarries, one was selected which best filled the needs of the study. The quarry selected is located in flat lying sedimentary rocks in central Indiana. This quarry lacks complicated or discontinuous sedimentary or deformational structures but does possess obvious variations in lithologies in the vertical direction. The major lithologic differences are relatively easy to identify in small fragments and can be traced to their stratigraphic position in the quarry face.

The quarry contains three limestone formations of Meramecian (Mississippian) age. They are from oldest to youngest, the Harrodsburg Limestone, the Salem Limestone, and the St. Louis Limestone. It is relatively rare to find these three formations in a single quarry but it is even more rare to find a quarry containing all three which, as a group, qualify as class A stone according to the Indiana Highway Commission specifications. As far as aggregate quality is concerned, this means the aggregate has less than 40% abrasion loss, less than 15% sulfate soundness loss, and less than 3% absorption. A geologic description of the rock units in this quarry are presented in Appendix A, Table A1.

SAMPLING AND LABORATORY TESTING

The quarry was divided into units A through H on the basis of lithologic difference. Three vertical sections were sampled by obtaining 50 pound samples from each unit in the section. On a subsequent day these vertical sections were resampled to obtain companion samples for comparison. The sampling designations are shown in Appendix A, Table A2. On each sample a Los Ange-

les abrasion test, Grading B, was performed. For a description of the Los Angeles abrasion test method see ASTM C 131-66 (American Society for Testing and Materials, 1966). The information obtained using the Los Angeles abrasion apparatus is shown in Table 1, for the three vertical sections tested.

It can be observed in Table 1 that zones A, B, C are Harrodsburg, D and E are Salem, and F, G, and H are St. Louis formations. In the quarry, the distribution of the formations according to measured thicknesses was Harrodsburg 34.9%, Salem 34.3%, and St. Louis 30.8%. The mean (average) of the abrasion values listed in Table 1 is Harrodsburg 32.0%, Salem 29.4%, and St. Louis 27.6% loss.

STATISTICAL ANALYSIS

Analysis of Variance

A One Way Analysis of Variance test was used to compare the differences (or variance) in abrasion loss in the vertical direction with that in the horizontal direction, and in turn compared with the total variance. The results show that there is no significant difference in variation from one column to another, that is, there is no significant variation from one sample location to another within the same lithologic unit. There is, however, a significant difference between the rock units in the vertical direction. This indicates that a significant change in Los Angeles abrasion accompanies the change in lithologic appearance as expressed by the various bedding units of the quarry. The Analysis of Variance calculations for the quarry face samples are presented in Appendix A, Table A3.

The durability of the various formations during processing was also examined. Before discussing this, however, it is necessary to describe the quarrying and milling operation employed at this location.

The quarry is shot full face (about thirty feet) using delayed shooting to pitch the bottom portion out and drop the top downward. The rock is loaded onto trucks by diesel powered shovels and transported to the mill.

The trucks dump the rock into the primary crusher (a jaw crusher) after which the rock is fed by a conveyor belt onto a conical-shaped surge pile. A steady flow of rock is vibrated out of the bottom-center of this pile to feed the secondary crusher. After secondary crushing the aggregate is sized by vibrating screens. The oversize material is recirculated for further crushing and the undersize is fed to a hammer mill for agricultural lime production.

Samples were initially taken at three locations during processing. These were, 1) after primary crushing, 2) at the base of the surge pile, and 3) after the secondary crushing and sizing of the finished product. The samples were divided into the three formations of origin (Harrodsburg, Salem, and St. Louis), on the basis of lithologies.

The first location below the primary crusher was abandoned after only two samples were taken, as sampling at this point was somewhat dangerous and was strongly discouraged by the plant superintendent. The bulk of the samples were taken at the base of the surge pile (termed P for "in progress" samples) and also after secondary crushing and sizing. Two sizes were being made during the sampling operation, Ind. No. 9's and Ind. No. 11's. Ind. 9's have the following gradation: 100% passing the 3/4" screen, 65-90% passing the 1/2" screen, 0-10% passing the No. 4 screen, and 0-2% passing the No. 30 screen. Ind. 11's have 100% passing the 1/2", 75-95% passing the 3/8", 5-20% passing the No. 4, and 0-5% passing the No. 8 screens.

An Analysis of Variance test was applied in two different ways to determine what if any changes had occurred during processing. In the first analysis (termed Analysis A), using one formation at a time, the change in percentage of each formation present from the P samples to the number 9's and number 11's was determined. For example, the percent Harrodsburg in the P samples was compared to its percentage in the number 9 and 11 sizes. Then the Salem and St. Louis formations were compared in the same manner.

Table 1. Percent loss, Los Angeles abrasion, quarry samples.

TOP OF QUARRY

St. Louis	H	24.5 28.1	25.1 26.6	24.4 28.2
	G	27.4 28.1	28.2 28.8	25.3 27.2
	F	31.4 27.8	30.9 29.2	29.1 28.1
Salem	E	36.3 37.0	35.5 32.0	33.0 36.9
	D	24.7 24.0	22.5 25.3	25.9 26.0
	C	20.3 24.6	30.7 28.2	34.0 26.7
Harrods-burg	B	31.2 36.9	29.8 33.3	31.2 37.0
	A	36.2 37.7	37.5 33.2	33.9 34.5

BASE OF QUARRY

The results show a significant reduction in the percentage of Harrodsburg material between the P samples and the No. 9 and the No. 11 samples. However, no significant change occurred in the Salem and St. Louis percentages relative to the total variability. This suggests that the less durable Harrodsburg material decreased in percentage of representation in the sizes retained on screens during processing. The analysis of variance calculations are presented in Appendix A, Table A4.

In the second application of the Analysis of Variance, Analysis B, the calculation was used to determine the contribution of the three formational units in the P samples, the No. 9 samples and the No. 11 samples. For example, the percent of Harrodsburg, Salem, and St. Louis fragments in the P samples was analyzed to see which predominated.

For the P samples, it was found that the Harrodsburg is the major contributor percentagewise, followed by the St. Louis, and Salem in that order. A statistically important difference is noted. For the No. 9 samples, the St. Louis is the major contributor with Harrodsburg second and salem last; again this order is significant statistically. In the No. 11 samples the same order as in the P samples, that is first (most abundant) Harrodsburg, second St. Louis, and third (least abundant) Salem, is recorded but the order is not statistically significant. The analysis of variance calculations are presented in Appendix A, Table A5.

These results suggest that the percentage of Harrodsburg decreased between the P and No. 9 samples. The No. 11 being of smaller size maintained a higher percentage of the less durable Harrodsburg material although no statistically significant value was obtained. Interestingly enough, the order of formational percentages in the P samples is not the same as in the quarry taken as a whole. This suggests that mixing in the quarry, including blasting and handling prior to crushing, was not complete. A complete listing of the mill samples with abrasion values and formational percentages is given in Appendix A, Table A6.

Multiple Correlation and Regression Analysis

A further comparison of the data on the processed aggregate was made using a multiple correlation and regression analysis. This technique is used to determine the contribution of several variables in the determination of the value of the remaining variable.

Los Angeles abrasion loss for the processed samples was compared to the relative amounts of the three formational units present. The procedure was applied to the P samples and to the No. 9 samples but not to the No. 11's. The gradation of the No. 11 aggregate is such that the rock particles are too small to run the B grading, Los Angeles abrasion test.

Simple correlation for the P samples suggest that as the St. Louis percentage increases, the percentage of Harrodsburg decreases and vice versa. This can be seen in Figure 1 on the following page. Reasons are: 1. The two units are located at extreme positions in the quarry, with the Harrodsburg at the bottom and the St. Louis at the top, and mixing during blasting and loading is difficult to accomplish. 2. The Harrodsburg appeared to break into larger pieces than did the other formations when shot and may have been concentrated into some individual P samples during crushing.

A strongly negative correlation between the Harrodsburg percentage and the Los Angeles abrasion has not been explained. Because the Harrodsburg is the weakest material, the reverse would normally be expected.

For the No. 9 samples, the negative correlation between the Harrodsburg and St. Louis has increased showing a stronger association of lesser amounts of Harrodsburg with greater amounts of St. Louis, and vice versa. In view of the apparent reduction in the amount of Harrodsburg during processing, it seems that the Harrodsburg is removed most readily and the St. Louis is the most durable.

Two equations were obtained for the P and No. 9 samples using regression analysis. In these equations the Los Angeles abrasion value was predicted based on the percentage of the various formational units present. The equations for each are shown below:

For the P samples:

$$LA = -511.61 + 5.3\%\ \text{Harr.} + 5.46\%\ \text{Salem} + 5.38\%\ \text{St. Louis} \quad R^2 = 0.321$$

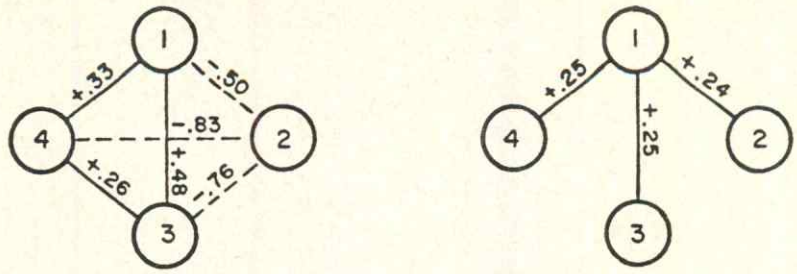
R is the multiple correlation coefficient and is a measure of how well the estimating equation accounts for the variation in the data. The square of R is commonly used for statistical purposes. Krumbein and Graybill (1965) can be consulted for further clarification, if needed. This R^2 value means only 32% of the variation is explained by the equation, which is not particularly high.

By contrast, for the No. 9 samples:

$$LA = -1391.4 + 14.19\%\ \text{St. L.} + 14.13\%\ \text{Harr.} + 14.24\%\ \text{Salem} \quad R^2 = 0.883$$

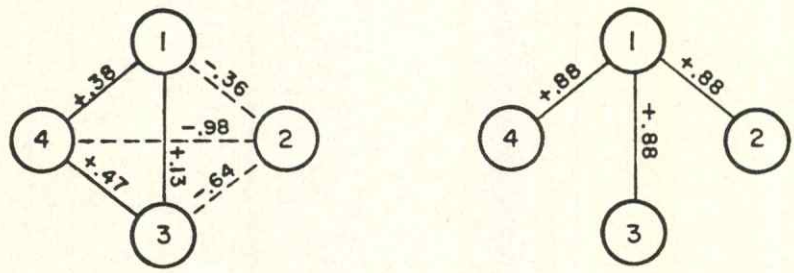
For the No. 9 samples, the R^2 value means 88.3% is accounted for by the equation which is a considerable improvement over the P samples.

The poor regression value for the P samples in contrast to the excellent one for the No. 9 samples suggests that for rocks of nearly uniform size (No. 9's) the variation is less than for the poorly sorted P samples. This may be due to the inherent differences in gradation be-



Simple Correlation Partial Correlation

IN-PROGRESS (P) SAMPLES



Simple Correlation Partial Correlation

NUMBER 9 SAMPLES

Legend:

1. Percent Loss, Los Angeles Abrasion.
2. Percent Harrodsburg Formation.
3. Percent Salem Formation.
4. Percent St. Louis Formation.

Figure 1. Cluster diagrams of correlation coefficients in aggregate processing study.

tween the two samples. Another possible explanation is that the Los Angeles abrasion values may not be representative of the P samples as a whole. This is a possibility, as P samples must be crushed to make the B gradation for the LA abrasion test and the crushed sample thus obtained may differ considerably from the original P sample. Preferred selection of certain aggregate types may occur during this crushing process. This problem was checked soon after it was suspected by the authors. A shift of as great as 10% in the percentages of formational constituents present between the total P sample and the LA sample obtained from it, was observed.

Another important conclusion reached after comparing the various abrasion values is that the average abrasion loss of the processed samples is lower than the average abrasion loss of the quarry ledge samples. Limited stock pile samples tested also had lower abrasion values on the average than did the quarry samples.

SUMMARY OF RESULTS

1. In the quarry studied, the change in abrasion value within a horizontal lithologic unit was insignificant as compared to the total variation.

2. The change in abrasion from unit to unit vertically was significant compared to the total variation. This in combination with result number one shows that a corresponding change in abrasion value is attendant with a change in lithology for this quarry.

3. The percentage of Harrodsburg fragments in the samples was reduced significantly during processing.

4. Harrodsburg, St. Louis, and Salem in decreasing abundance formed the P samples whereas the quarry as a whole contained Harrodsburg, Salem, and St. Louis in descending order of abundance.

5. St. Louis fragments become the most abundant constituents in the No. 9 samples but in the smaller-sized, No. 11 samples, the Harrodsburg retains its greater abundance.

6. Using a regression analysis, predicting equations were obtained for the abrasion loss based on the formational percentages. The equation for the P samples satisfies only about 1/3 of the variation whereas the equation for the No. 9 samples satisfies nearly 90% of the variation. This suggests that the behavior of the more uniform size (no. 9) is more easily predicted than the P samples with their great range of particle size.

7. The abrasion loss value is less for the in progress and stock pile samples than for the ledge samples in the quarry.

REFERENCES

American Society for Testing and Materials, Standards Part 10, Concrete and Mineral Aggregates, 1966, pp 85-90.

Krumbein, W. C. and Graybill, F. A., 1965, An Introduction to Statistical Models in Geology, McGraw-Hill, New York, pp 295-297.

APPENDIX A

Table A1

DESCRIPTION OF ROCK UNITS SAMPLED FOR PHYSICAL TESTING

Rock Unit	Description	Range of Thickness (feet)
Overburden	St. Louis Limestone and Pleistocene till	Not measured
St. Louis Limestone H	Tan lithographic limestone grading upward through unit to bluish gray dense limestone of coarser crystal size. Transition from lithographic to coarser limestone takes place within a bed. Locally contains minor chert.	3.0 to 3.8
G	Dark gray to tan, dense and brittle lithographic limestone that locally is faintly laminated and contains shaly streaks or thick lenses of shale. Gray dense limestone that weathers to tan. Grain size heterogeneous and grains consist of calcite crystals and fossil fragments. Locally rock contains chert or coarser replacement quartz, is laminated, and is capped by an inch or two of black shale. Rock similar to above, but lacks chert and laminations and is locally shaly at the base.	3.4 to 4.4
F	Rock is similar to matrix of breccia described below. Grayish-tan lithographic or slightly coarser limestone breccia fragments in a matrix of greenish-gray soft argillaceous limestone. Breccia is variable in thickness and lenses laterally into lithographic limestone. Tan, dense, and wavily laminated lithographic limestone topped by a shale parting.	2.2 to 2.3
	Range of thickness of quarried St. Louis	8.7 to 10.4
Salem Limestone E	Fossil Fragmental limestone of light tan to light tannish-gray color. Basically a single bed composed primarily of fragmented and fossilized remains of echinoderms and bryozoans, all bound together by small calcite crystals. Fragments range in size from 0.1 to 1.0 mm but chiefly are less than 0.5 mm. Unit is terminated at the base by thin shale and has	

Table A1 (cont)

Salem Limestone (cont)		
E	local and irregular hazy carbonaceous streaks	3.5 to 4.4
D	Fossil fragmental limestone of very light tannish-gray to light tan color. Beds of two-to-four-foot thickness are composed of the fossil Endothyra and fragmented and fossilized echinoderms and bryozoans bound together by calcite crystals. Fragments average about 0.5 mm, are in greater abundance than in rock above, and are found in laminations and other sedimentary structures. Rock is locally cherty (silicified limestone) in lower third and especially in lowest half a foot. Beds are separated by thin shales that pass laterally into stylolites.	6.3 to 7.5
	Range in thickness of Salem Limestone	10.4 to 11.3
Harrodsburg Limestone		
C	Gray dense limestone in beds of 0.4 to 0.8 foot thick. Rock is composed of fragmented and fossilized echinoderms and bryozoans averaging between 0.5 to 1.0 mm in size. Top half a foot is argillaceous and shaly and unit is slightly cherty (silicified limestone).	3.5 to 3.7
B	Dark gray limestone very similar to unit C above except for dispersed argillaceous material in wavy streaks and for wavy shale partings.	3.0 to 4.0
A	Very dark gray limestone very similar to Unit B above except for a few nodules of chert (silicified limestone) and is very shaly in the top half a foot.	3.7 to 4.4
	Range of thickness of quarried Harrodsburg	10.4 to 11.9
	Range of thickness of quarried rock	30.9 to 32.1

Table A2

Relationship between numbered samples collected for physical testing.

Rock Unit	Sample Number	Thickness Samples (ft.)	Sample Number	Thickness Samples (ft.)	Sample Number	Thickness Samples (ft.)	Sample Number	Thickness Samples (ft.)
St. Louis Limestone								
H	S65-RH1	3.0	S65-RH2	3.5	S65-RH3	3.0	S66-RH8	3.8
H			S65-RH5	3.5	S65-RH6	3.0		
G	S65-RG1	3.4	S65-RG2	4.4	S65-RG3	4.2	S66-R68	4.3
G	S65-RG4	3.4	S65-RG5	4.4	S65-RG6	4.2		
F	S65-RF1	2.3	S65-RF2	2.2	S65-RF3	2.3	S66-RF8	2.3
F	S65-RF4	2.3	S65-RF5	2.2	S65-RF3	2.3		
		8.7		10.1		9.5		10.4
Salem Limestone								
E	S65-RE1	4.1	S65-RE2	3.5	S65-RE3	3.5	S66-RE8	4.4
E	S65-RE4	4.1	S65-RE5	3.5	S65-RE6	3.5		
D	S65-RD1	6.3	S65-RD2	7.5	S65-RD3	7.0	S66-RD8	6.9
D	S65-RD4	6.3	S65-RD5	7.5	S65-RD6	7.0		
		10.4		11.0		10.5		11.3
Harrodsburg Limestone								
C	S65-RC1	3.5	S65-RC2	3.5	S65-RC3	3.6	S66-RC8	3.7
C	S65-RC4	3.5	S65-RC5	3.5	S65-RC6	3.6		
B	S65-RB1	4.0	S65-RB2	3.0	S65-RB3	3.0	S66-RB8	3.0
B	S65-RB4	4.0	S65-RB5	3.0	S65-RB6	2.0		
A	S65-RA1	4.4	S65-RA2	4.4	S65-RA3	4.3	S66-RA8	3.7
A	S65-RA4	4.4	S65-RA5	4.4	S65-RA6	4.3		
		11.9		10.9		10.9		10.4
		31.0		32.0		30.9		32.1

Key: Example S65-RH1
S - Sampled by Smith
65- 1965 Year Sampled
R - Quarry Designation
H - Rock Unit H
1 - First Sample Taken in Rock Unit

Table A3

ANALYSIS OF VARIANCE OF ABRASION LOSSES FOR QUARRY FACE SAMPLES

Units j		Locations i: 1 (K)	2 ($x_{.;.}$)	3	$x_{.j.}$	$\bar{x}_{.j.}$
St. L.	H	24.5 28.1* = 52.6	25.1 26.6 = 51.7	24.4 28.3 = 52.6	156.9	26.1
	G	27.4 28.1 = 55.5	28.2 28.8 = 57.0	25.3 27.2 = 52.5	165.0	27.5
	F	31.4 27.8 = 59.2	30.9 29.2 = 60.1	29.1 28.1 = 57.8	176.5	29.4
	E	36.3 37.0 = 73.3	35.5 32.0 = 67.5	33.0 36.9 = 69.9	210.7	35.1
Salem	D	24.7 24.0 = 48.7	22.5 25.3 = 47.8	25.9 26.0 = 51.9	148.4	24.7
	C	20.3 24.6 = 44.9	30.7 28.2 = 58.9	34.0 26.7 = 60.7	164.5	27.4
Harrods-burg	B	31.2 26.9 = 68.1	29.8 33.3 = 63.1	31.2 37.0 = 68.2	199.4	33.2
	A	36.2 37.7 = 73.9	37.6 33.2 = 70.8	33.9 34.5 = 68.4	213.1	35.5
		$x_{i..}$ 476.2	476.9	481.4	$x_{...}$ = 1434.5	

*Missing Sample

Table A3 (cont.)

	ss	df	ms	F	H:
col means (Sc)	$\frac{\Sigma x...^2}{rn} - \frac{x...^2}{rcn}$	c-1	$\frac{SC}{c-1}$	$F_{(1)(4)}=\frac{1}{4}$	$\sigma_c^2 = o$
row means (Sr)	$\frac{\Sigma x.j.^2}{rn} - \frac{x...^2}{rcn}$	r-1	$\frac{Sr}{r-1}$	$F_{2,4} = \frac{2}{4}$	$\sigma_r^2 = o$
Interaction	$S_s - S_c - S_r = S_i$	(c-1)(r-1)	$\frac{Si}{(c-1)(r-1)}$	$F_{3,4} = \frac{3}{4}$	$\sigma_i^2 = o$
Subtotal	$\Sigma\Sigma\frac{xij.^2}{n} - \frac{x...^2}{rcn}$	rc-1			
Within $S_t - S_s = S_w$		rc(n-1)	$\frac{Sx}{rc(n-1)}$		
Total (St)	$\Sigma\Sigma\Sigma xijh^2 - \frac{x...^2}{rcn}$	rcn-1			

Columns i: $\frac{\Sigma x..^2}{rn} - \frac{x...^2}{rcn} = \frac{685,946.01}{(8)(2)} - \frac{2,057,790.25}{(8)(3)(2)} = 42871.63 - 42870.63 = 1.00$

Rows: $\frac{\Sigma x.j.^2}{cn} - \frac{x...^2}{rcn} = \frac{261,644.13}{6} - 42870.63 = 42607.36 = 42,872.63 = 736.73$

Subtotal: $\frac{\Sigma x.j.^2}{n} - \frac{x...^2}{rcn} = \frac{87,438.27}{2} - 42870.63 = 42719.14 - 42870.63 = 848.51$

Interaction = 110.78

Within = 973.09 - 848.51 = 124.58

$\Sigma\Sigma\Sigma\frac{xijk^2}{} - \frac{x...^2}{rcn} = 43843.72 - 43870.63 = 973.09$

col means	1.00	2	0.5	0.5/5.19 = .096	3.40, $\sigma_c^2 = o$ true
row means	736.73	7	105.25	105.25/5.19= 20.28	2.42, $\sigma_r^2 = o$ false
Interaction	110.78	14	7.91	7.91/5.19 = 1.524	2.13, $\sigma_i^2 = o$ true
Subtotal	848.51	23			
Within (error)	124.58	24	5.19		
Total	973.09				

Table A4

ANALYSIS OF VARIANCE OF THE MILL SAMPLES FORMATION BY FORMATION

PART A

PERCENTAGE OF ST. LOUIS FORMATION IN THE MILL SAMPLES

P	9	11	
39.0	38.5	46.4	
32.3	30.9	22.8	
45.2	33.8	37.3	
33.3	32.0	28.3	
29.8	44.5	30.4	
31.4	46.8	31.0	
21.4	36.9	23.6	
34.0	63.6	34.5	
48.4	57.7	50.9	
31.0	35.8	36.5	
47.7			H: $\sigma_c^2 = o$
31.4			
$x_i. =$ 424.9	420.5	341.7	$x..=1187.1$
$x_i.^2 = \frac{180540.01}{12} =$ 15045.00	176820.25	116758.89	$x..^2=1409206.41$
			$\frac{x..^2}{N}=44037.70$

$\Sigma\Sigma xij^2 = 46980.89$

$\frac{\Sigma x_i.^2}{ni} = 44402.92$

	SS	df	MS	F_{calc}	F_{tab} (2.30)
44402.92 - 44037.70	= 365.22	2	182.61	1.80	3.32 at 95%
	=2577.97	29	101.49	not significant	
46980.89 - 44037.70	=2943.19			$\therefore \sigma_c^2 = o$	

PART B

25.1	28.5	37.5	
22.7	23.4	37.0	
19.8	23.4	31.3	
33.3	27.3	36.7	
24.6	23.9	27.6	
23.9	27.4	36.4	
25.4	28.2	29.1	
32.7	29.9	21.8	
30.2	32.1	28.8	
43.4			
29.5			
$x_i.=$ 319.9	265.5	314.5	
$x_i.^2 = \frac{102336.01}{12} =$ 8528.00	70490.25		$x.. = 899.9$ H:
		98910.25	$x..^2=809820.01$ $\sigma^2_c = o$
			$\frac{x..^2}{11}=25306.88$

Table A4 (cont.)

$\Sigma\Sigma x_{ij}^2 = 26364.57$

$\Sigma x_{i.}^2 = 25468.06$

	SS	DF	MS	F_{calc}	F_{tab} (2.30)
25468.06 - 25306.38 =	161.18	2	80.59	2.61 not	3.32 at
=	896.51	29	30.91	significant	95%
26364.57 - 25306.88 =	1057.69	31		$\sigma^2_c = o$	

PART C

PERCENTAGE OF HARRODSBURG FORMATION IN THE MILL SAMPLES

35.9	33.0	16.1
45.0	45.8	40.2
35.0	42.8	31.3
33.3	40.7	35.0
50.8	34.2	41.3
44.0	29.2	41.4
54.7	35.6	40.0
40.7	8.1	36.4
19.0	12.4	27.3
48.8	32.1	34.6
8.8		
39.1		
$x_{i.} =$ 455.8	313.9	343.6

$x_{i.}^2 = \frac{207753.64}{12} = 17312.80 \quad \frac{98533.21}{10} \quad \frac{118060.96}{10}$

H: σ^2_c o

$x.. = 1113.3$

$x..^2 = 1239436.89$

$\frac{x..^2}{N} = 35607.40$

$\Sigma\Sigma x_{ij}^2 = 42793.00$

$\Sigma x_{i.}^2 = 38972.22$

	SS	DF	MS	F_{calc}	F_{tab} (2.30)
389722.2 - 35607.30 =	3364.82	2	1682.41	12.9	3.32
42743.00 - 35607.40 =	7135.60	31		Significant	95%
	3770.78	29	130.03	$\therefore \sigma^2_c$ o	

Table A5

ANALYSIS OF VARIANCE OF MILL SAMPLES ACCORDING TO INDIVIDUAL SIZE GRADATION

PART A

IN-PROGRESS OR P SAMPLES

	St. L.	Salem	Harrodsburg
1-P	39.0	25.1	35.9
4-P	32.3	22.7	45.0
9-P	45.2	19.8	35.0
10-P	33.3	33.3	33.3
15-P	29.8	19.3	50.8
18-P	31.4	24.6	44.0
21-P	21.4	23.9	54.7
24-P	34.0	25.4	40.7
27-P	48.4	32.7	19.0
30-P	31.0	20.2	48.8
32-P	47.2	43.4	8.8
34-P	31.4	29.5	39.1
x_{ij}	424.9	319.9	455.1
x_{ij}^2	180540.01	1023360.01	207116.01

$x.. = 1199.9$

$x..^2 = 1439760.01$

$\Sigma\Sigma x_{ij}^2 = 44001.99$ $\quad \Sigma xij^2 = 48992.03$

$$\text{Col. } \frac{\Sigma x_{ij}^2}{r} - \frac{x..^2}{rc} = \frac{489992.03}{12} - \frac{1439760.01}{36} = 40832.6 - 39993.0$$

$$= 839.6$$

$H: \sigma^2 c = o$

Residue = St - Sc = Sr = 3169.4

Total $\Sigma\Sigma x_{ij}^2 - \frac{x..^2}{rc}$ = 44001.99 - 39993.0 = 4009.0

SS	df	MS	F	
839.6	2	419.8	4.37	$F_{95} = 3.32$ 95%
3169.4	33	96.04	Significant	
4009.0			$\therefore \sigma^2_c$ o	

PART B No. 9 SAMPLES

	St. L.	Salem	Harrodsburg
7-9	38.5	28.5	33.0
13-9	30.9	23.4	45.8
16-9	33.8	23.4	42.8
19-9	32.0	27.3	40.7
22-9	44.5	21.4	34.2
25-9	46.8	23.9	29.2
28-9	36.9	27.4	35.6

Table A5 (cont.)

PART B No. 9 SAMPLES

	St. L.	Salem	Harrodsburg
31-9	63.6	28.2	8.1
33-9	57.7	29.9	12.4
39-9	35.8	32.1	32.1
x_{ij}	420.6	265.5	313.9

$X.. = 1000.0$

$\frac{\Sigma x_{ij}^2}{r} - \frac{x..^2}{rc} = 34592.78 - 33333.33 = 1259.45$

H: $\sigma_c^2 = o$

Residue St - Sc = Sr = 2565.35

Total $\Sigma\Sigma x_{ij}^2 - \frac{x..^2}{rc} = 37158.13 - 33333.33 = 3824.80$

ss	df	ms	F		
1259.45	2	629.72	6.63	F = 3.32	95%
2565.35	27	95.01	Significant		
3824.80			$\therefore \sigma_c^2$ o		

PART C No. 11 SAMPLES

	St. L.	Salem	Harrodsburg
3-11	46.4	37.5	16.1
5-11	22.8	37.0	40.2
8-11	37.3	31.3	31.3
11-11	28.3	36.7	35.0
14-11	30.4	28.3	41.3
17-11	31.0	27.6	41.4
20-11	23.6	36.4	40.0
23-11	34.5	29.1	36.4
26-11	50.9	21.8	27.3
29-11	36.5	28.8	34.6
x.j	341.7	314.5	343.6

$X.. = 999.8$

$\frac{\Sigma x_{ij}^2}{r} - \frac{x..^2}{rc} = 33373.01 - 33320.00 = 53.01$

H: $\sigma_c^2 = o$

Residue St - Sc = Sr = 1555.33

Total $\Sigma\Sigma x_{ij}^2 - \frac{x..^2}{rc} = 34928.34 - 33320.00 = 1608.34$

ss	df	ms	F	
53.01	2	26.51	0.46	F = 3.32
1555.33	27	57.60	Not Significant	
			$\therefore \sigma_c^2 = o$	

Table A6

ABRASION RESISTANCE AND PROPORTIONS OF FORMATIONAL UNIT IN MILL AND STOCKPILE SAMPLES

Sample No.	Percent Loss Los Angeles Abrasion B Grading	Percent by Weight of Formations St. Louis	Salem	Harrodsburg
ML 1-P	25.4	39.0	25.1	35.9
ML 4-P	26.6	32.3	22.7	45.0
ML 9-P	26.8	45.2	19.8	35.0
ML 10-P	25.8	33.3	33.3	33.3
ML 15-P	27.3	29.8	19.3	50.8
ML 18-P	26.2	31.4	23.6	44.0
ML 21-P	28.0	21.4	24.6	44.0
ML 21-P	28.0	21.4	23.9	54.7
ML 24-P	27.4	34.0	25.4	40.7
ML 27-P	29.9	48.4	32.7	19.0
ML 30-P	22.6	31.0	20.2	48.8
ML 32-P	29.0	47.7	43.4	8.8
ML 34-P	27.5	31.4	29.5	39.1
ML 7-9	27.0	38.5	28.5	33.0
ML 13-9	26.5	30.9	23.4	45.8
ML 16-9	26.8	33.8	23.4	42.8
ML 19-9		32.0	27.3	40.7
ML 22-9	27.9	44.5	21.4	34.2
ML 25-9	25.3	46.8	23.9	29.2
ML 28-9	24.7	36.9	27.4	35.6
ML 31-9	26.8	63.6	28.2	8.1
ML 33-9	28.7	57.7	29.9	12.4
ML 29-9		35.8	32.1	32.1
ML 3-11		46.4	37.5	16.1
ML 5-11		22.8	37.0	40.2
ML 8-11		37.3	31.3	31.3
ML 11-11		28.3	36.7	35.0
ML 14-11		30.4	28.3	41.3
ML 17-11		31.0	27.6	41.4
ML 20-11		23.6	36.4	40.0
ML 23-11		34.5	29.1	36.4
ML 26-11		50.9	21.8	27.3
ML 29-11		36.5	28.8	34.6
ML 35-x		34.0	38.4	27.6
ML 36-x		29.1	67.9	3.0
ST1-53		21.7	51.1	27.2
ST 2-11		31.8	27.3	40.9
ST 2-11		28.3	32.6	39.1
ST 3-4		40.2	32.3	27.6
ST 4-5		39.0	39.0	22.0

LIGNITE--BLACK GOLD?

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ABSTRACT

World production of lignite is estimated at 760-800 million tons with East Germany, Russia, and West Germany the leading producers. Recoverable lignite reserves in the United States have been estimated at approximately 225 billion tons. Of the approximately 500 million tons of coal that are mined each year in the United States, only about three million tons are lignite. However, the potential use of lignite as a fuel to generate power and heat in addition to serving as a raw material for gasification and the production of fertilizers has renewed research, developmental and economic interest in this carbonaceous material.

Low-cost, long-range transportation of lignite or its energy presents the major hurdle to converting lignite to "black diamonds." Current efforts in this area, together with attempts to upgrade or convert lignite to a valuable high-dollar product for which transportation costs represent only a small fraction of the total costs, are being intensified. The future of lignite as a fertilizer may become an important economic factor in the future of the agricultural upper Midwest.

INTRODUCTION

Coal has been a basic source of fuel energy in the United States since early in the 19th century. Coal burned directly to produce steam generates about one half of our electricity. Coal converted to coke in modern ovens provides fuel for our blast furnaces and raw materials for a growing chemical industry. Coal is required to run our cement and aluminum plants and is still used extensively in some areas for heating of homes and commercial buildings. More tons of coal than of any other mineral are now mined in the United States except for petroleum. The coal produced in the United States each year has a greater dollar value than any other single mineral except petroleum and pretty close to the production of all the metals put together. Usually, the dollar value of the coal produced in any given year in this country has been more than twice that of the combined value of our gold, silver, copper, and iron ore.

The largest deposits of coal reserves in the United States are shown in Table 1. Although North Dakota has the largest estimated coal reserves, it is not a leading coal producer as shown in Table 2. One of the reasons that North Dakota isn't a leading coal producing state is that its coal is lignite.

Table 1. States listed in order of estimated reserves of all ranks of coal (tonnage basis)

1.	North Dakota	6.	West Virginia
2.	Montana	7.	Colorado
3.	Illinois	8.	Utah
4.	Wyoming	9.	Ohio
5.	Kentucky	10.	Missouri

Lignite is a low rank coal characterized by high moisture (30-40%) and ash (4-18%) contents as well as low thermal value (5000-7500 Btu./lb) as it is mined. Unfortunately, most lignite is found in areas of low population and far from water transportation. These two factors are the most important ones that have limited

its consumption to 2-3 million tons of the approximately 500 million tons of coal mined yearly in the United States.

Table 2. States producing coal (including lignite)

1.	West Virginia	6.	Virginia
2.	Pennsylvania	7.	Indiana
3.	Kentucky	8.	Alabama
4.	Illinois	9.	Tennessee
5.	Ohio	10.	Utah

There is little doubt that the future of lignite depends to a large extent, on the upgrading or conversion of lignite to valuable fuel or high value products for which transportation costs represent only a small fraction of the total costs. Presently, the cost of lignite is about $2.25 per ton at the mine but it costs about $13-14 to transport a ton of lignite from North Dakota to Houston, Texas. Another possibility for its widespread use is to find some relatively inexpensive way to transport lignite or the power derived from lignite to industrial areas where it can be utilized economically.

Some important possibilities for making lignite into an important economic factor are shown in Table 3. Only a few comments on each item are given.

Generation of Power and Heat

On a Btu. basis, almost 15% of the total energy reserves in the United States is in the form of lignite and most of this is in North Dakota. A country's gross national product usually parallels its power consumption and no doubt lignite will play a more important role in energy production in this country as our standard of living keeps increasing.

Lignite has been burned in North Dakota for domestic heating since the first settlers used it at fur-trading posts and forts as early as 1855. Since 1925, lignite has been used commercially as a fuel. However, because of lignite's high moisture content, low heating value, high ash, and lack of preferential transportation rates, lignite's use as a fuel has been largely restricted to industry-poor and low-population density North Dakota. Lignite remains one of the most economical fuels in the world when it is burned close to the mine from which it came.

Table 3. Possibilities for the utilization of lignite

Generation of power and heat
Long-range transportation of lignite or its energy
Gasification
Carbonization
Fertilizers
Miscellaneous products and processes

Long-Range Transportation of Lignite or Its Energy

The cost of transportation for lignite, as well as other coals, represents a major economic problem. Until recently, the cost of rail transportation has tended to increase. This increase tended to offset any reductions brought about by improved mining methods. However, in recent years, the Eastern railroads reduced the cost of transporting coal when they became threatened with the loss of their most important single source of freight revenue. Almost all lignite shipments and about 70% of all coal shipments are by rail.

The transportation situation may become greatly improved with the advent of the coal pipeline. In these pipelines, coal is moved as a water or petroleum slurry. A coal-water slurry pipeline was built in the Eastern United States but was shut down after railroad freight rates were drastically reduced to head off competition.

Electrical energy is costly to transport. Figure 1 shows a typical transmission cost vs. distance plot of AC power (Hochgesang, 1965).

Presently, about ninety million dollars worth of power generating plants are being built in North Dakota. It is the intent of these plants eventually to be able to transport electric power economically to sites up to 800 miles away, making use of modern transmission equipment and cables. The United Power Association plant is expecting to transmit power to Grand Island and Ft. Randell in Nebraska from North Dakota.

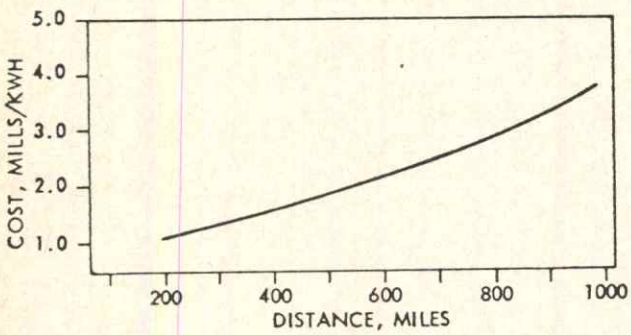

Figure 1. Typical Transmission Cost 700 KV - AC - 2000 MW (70% load factor)

Electrical energy is having its share of economic competition. Whereas, gas can be easily stored and transported, electrical energy is expensive to transport and difficult to store. Of course, electrical energy will always be a major factor in urban power requirements but great strides are being made by the gas industry to compete with electrical energy.

Gasification Processes

Natural gas is becoming increasingly important in the overall energy picture of the United States. Gas has increased its share of the total energy market from 18.0% in 1950 to 30.4% in 1965. However, during this time, despite federal regulation, prices of natural gas at the well have gone up sharply. Coal prices at the mine have remained fairly constant during this period. As the differential between coal and gas prices increases, as is likely, the conversion of coal to gas at the mine becomes increasingly attractive. The U. S. Bureau of Mines at Grand Forks, North Dakota, has an experimental gasifier in operation. Economically, the gasification of lignite offers a great potential.

Carbonization Processes

Carbonization is the heat treatment of organic materials in the absence of air to decompose the substances into a solid residue in the form of coke or char along with liquid and gaseous products. There is a plant in Dickinson, North Dakota, operated by the Husky Oil Co., that carbonizes lignite and uses the char to make briquets. Recently, there has been interest expressed in making a lignite char for the partial reduction of low grade iron ore from the iron range in Minnesota. The economic success of large scale carbonization appears doubtful unless the liquid (mostly tar) and the gaseous products can be converted to chemicals of high value.

Fertilizers

Although lignite contains only about 1% nitrogen, its chemical structure is such that increased amounts of nitrogen can be introduced in various forms thus providing continuous nutrition to the plant and thus possibly eliminating several costly fertilizer steps. Lignite samples containing 14.7% nitrogen have been produced. These samples, evaluated in greenhouse studies, appear to have great potential as slow-release nitrogen fertilizers (Schwartz, et. al., 1965).

The future of lignite as a fertilizer looks extremely promising and it may become an important economic factor in agriculture.

Miscellaneous Products and Processes

There are a great many other potential large scale uses of lignite. Some of the more important ones are listed in Table 4. A brief comment about each use is given here.

Hydrogenation processes - The production of synthetic liquid fuels, including gasoline, from coal is

scientifically plausible, although it will probably not be economically feasible in the United States for some time. The price of crude petroleum will have to become much higher than it is at present to justify the conversion of lignite or other coals to liquid fuels.

Table 4. Miscellaneous products and processes

Hydrogenation to fuels and oils
Synthesis of chemicals
Ammonia
Chemical grade carbon
Acetylene
Silicon carbide
Ion exchange material
Extraction of less-common elements

When and if crude oil does become more expensive, it is very likely that oil extracted from oil shales and tar sands can be converted to gasoline much more economically than it can be obtained from lignite or other coals. The deposits of oil shales in Colorado, Utah, and Wyoming are enormous and the oil industry, with all of its research money available, has shown considerable interest and is making great progress in the extraction of oil from shale.

It is important to note that when oil was very scarce in Europe, and Germany was trying to become independent of foreign sources of oil in the 1930's, considerable emphasis was placed on research in Germany on the production of synthetic fuels from coal. Two processes were developed by the Kaiser Wilhelm Coal Research Institute, namely the Bergius coal hydrogenation process and the Fischer-Tropsh process. Both processes quickly reached commercial production. These plants eventually produced most of the aviation gasoline and motor fuels used by the German armies during World War II and as a result became prime targets for Allied bombing raids. However, these operations could hardly be justified in a peace time economy, since without slave labor and huge subsidies the venture would have failed in Germany. A similar plant using the Bergius process also operated in England during World War II without slave labor. Presently, a government-subsidized plant is in operation in South Africa. The plant manufactures gasoline from coal.

Another use for the hydrogen produced in synthesis gas is for the hydrogenation of vegetable and animal oils and fats to produce vegetable shortening, margarine, and other substances. Other oils can be hydrogenated to inedible products used in soaps, lubricants, paints, and varnishes. This represents a large scale use of hydrogen.

Synthesis of Chemicals - Valuable chemicals can be obtained directly from lignite tar or from the synthesis gas which can be produced by passing steam over lignite at elevated temperatures. The following processes can be demonstrated successfully using lignite as the base raw material: a. Methanol synthesis - Hundreds of millions of gallons of methanol are used annually in the U. S. and it is estimated that this figure will increase rapidly in the near future. Originally, DuPont, Union Carbide, etc. made methanol from natural gas. Most of the plants were built where natural gas was readily available. However, in recent years many producers have converted their plants to the use of coal because of the high price of natural gas. b. Oxo process - Synthesis gas from lignite and olefinic hydrocarbons from lignite or from refinery streams can be combined to produce a mixture of aldehydes which can be reduced to alcohols by hydrogenation. These products may find use as solvents, plastics, plasticizers, etc. c. Other chemicals - Alcohols are the starting materials in many synthetic processes thus their production can give rise to the establishment of a small scale chemical industry in the area of lignite production.

Ammonia - Ammonia is synthesized directly from nitrogen and hydrogen. Nitrogen is readily available from the air and hydrogen can be obtained from the gasification of lignite. Synthetic ammonia has widespread use in the manufacture of fertilizer. In

agricultural communities, population is unimportant and transportation costs would be small for such products. There is an excellent chance that some ammonia plants may be built in the Upper Midwest in the next decade, the first ones probably being based on refinery streams from the petroleum industry but later based on lignite.

Chemical Grade Carbon - Activated carbon has been produced from Texas lignite for some time. Activated carbons are used for decolorizing sugar, syrups, solvents, chemicals, pharmaceuticals, etc. as well as in water filtering and purification plants to remove objectional odors, taste and colors. In the North Central States, it appears that enough activated charcoal can be used in sugar-beet processing and in water purification to merit a plant.

In addition to activated carbons, it may become economically feasible to convert lignite to carbon black, electrode carbon and graphites as the prices of natural gas and petroleum increase.

Acetylene - Since limestone is readily available in most areas, the establishment of calcium carbide-acetylene industries may develop. Lignitic char can be fused with limestone at high temperature to form calcium carbide which when reacted with water yields acetylene. Acetylene is very important as a starting material in synthetic chemistry and there are plants in operation producing acetylene from bituminous coal.

Silicon carbide - Silicon carbide is an important abrasive and high temperature refractory. It can be prepared by cheap electric power and a low-priced source of carbon. Since it is a relatively high value product, transportation costs will amount to only a small fraction of the total price.

Ion-exchangers - Ion-exchangers are a big volume business and may become very important in both the desalination of water and water softeners. It has already been demonstrated that treated lignite can serve as a very efficient water softener (Ind. and Eng. Chem., 1960).

Extraction of Less-Common Elements - Lignite ash contains various amounts of uranium, germanium, gallium, molybdenum, and many other less-common and valuable elements. Uranium and molybdenum are being recovered commercially from lignite by several companies. However, uranium is presently being purchased principally by the government and its economic future is questionable as it is in abundant supply. Research is needed in this area to economically develop methods for concentrating some elements other than uranium.

CONCLUSIONS

The large deposits of lignite in the United States are located in areas of low population density and at considerable distance from industrial areas. Therefore, many potential uses for lignite which are technically and scientifically feasible became economically marginal or questionable.

The generation of electrical power from lignite is likely to be its greatest use for some time to come. The possible long-range transportation of lignite-liquid slurries and lignite derived gases by pipeline and the extremely high voltage transmission of electrical power generated at the mines offer good possibilities for the future industrialization of the Upper Midwest.

The technology of carbonization processes is well understood. However, for such processes to be economically applicable to lignite, the liquid and gaseous by-products must be converted to relatively valuable chemical products. More research is needed in this area.

Metallurgical uses of lignite gasification products for the production of sponge iron and the reduction of non-magnetic to separable magnetic taconite show considerable promise for the future.

Extraction of some less-common elements from certain lignite deposits shows considerable promise, especially if it is combined with power generation. This area needs

more research. Other possible uses for lignite include the production of chemical grade carbons, electrode carbon, silicon carbide, ion-exchange material, drilling mud additives, fertilizers, and the like.

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SAND AND GRAVEL EXPLORATION BY THERMAL SENSING OF SOIL[1]

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ABSTRACT

The relationship of near-surface soil temperatures to underlying parent materials has been examined over a kame, esker, and valley-train terrace. These data, along with results from a study by the Indiana Geological Survey in 1965 and 1966 of an outwash plain, indicate that coarse parent materials, such as sand and gravel, can be differentiated from adjacent clays and silts by the relative magnitude of the diurnal soil temperature change.

Soil temperatures were measured at a depth of 30 cm by a thermistor probe with a sensitivity of 0.05°C. The diurnal temperature change was found to be greater in soils above sands and gravels of kame, esker, and valley-train terrace deposits than in soils above adjacent clay and silt areas. In the earlier study, however, the diurnal soil temperature range had been found to be smaller in soils above sand and gravel of an outwash plain deposit than in soils above an adjacent clay till area. The inverse relationship in diurnal temperature change appears to be controlled largely by variation in soil moisture due to the position of the ground-water table.

The use of the relative magnitude of the diurnal temperature changes in near-surface soils to prospect for unconsolidated sands and gravels is particularly attractive now that sensitive airborne infrared detectors can rapidly measure surface temperatures over large areas.

PREVIOUS WORK

In 1965 and 1966, the Indiana Geological Survey investigated the relationship of near-surface soil temperatures to underlying parent materials on an outwash plain. The object of the study was to determine whether coarse parent materials, such as sand and gravel, could be differentiated from adjacent clays and silts by variations of near-surface temperature. The results were reported at the Fourth Symposium on the Remote Sensing of Environment (Carr and Blakely, 1966, p. 203-214). This earlier study was then extended to include three other types of sand and gravel deposits: a kame, an esker, and a valley-train terrace. Because the study presented herein is an extension of the earlier study, it seems desirable to present a brief summary of the technique and results of the first investigation.

In the first study, an area in Johnson County, Ind., underlain by clay till and flanked by an area underlain by outwash sands and gravels (Fig. 1) was examined. The average ground-surface slope was less than 0.5° and the vegetation cover was fairly uniform. Soil temperature measurements were made each month during a year at 19 test stations located above parent materials of clay till and parent materials of sand and gravel. Temperatures were measured at a depth of 30 cm at these stations in the morning and the afternoon on clear days when there was little wind.

Temperatures were measured by means of 1000-ohm bead thermistor mounted in a probe attached to a wheatstone bridge. Equilibrium time was about 1 minute and sensitivity was 0.09°F (0.05°C). The probe was designed to avoid convection and conduction, and care was taken to

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keep the soil in place.

Temperatures measured at a depth of 30 cm in soils above clay till were not consistently higher or lower than temperatures measured in soils above sand and gravel, and the range in temperature above both materials was large. This overlapping

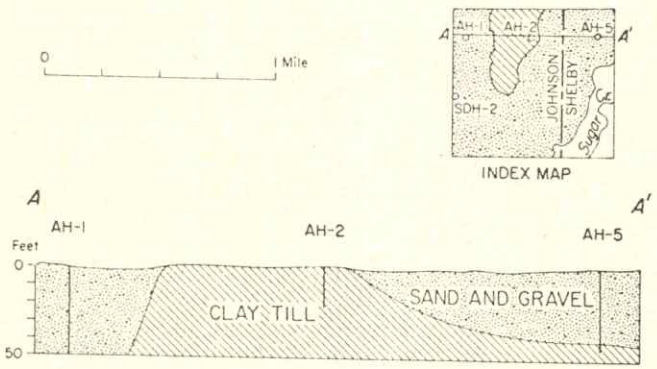

Figure 1. Diagrammatic cross section showing relationships of unconsolidated materials in Johnson County, Ind. From Carr and Blakely, 1966, fig. 5.

and lack of consistent temperature relationships were such as to make it impossible to distinguish one type of lithology from another by a single comparison of temperature at any particular time of day. However, because the clay till had a greater thermal diffusivity than sand and gravel, the diurnal temperature change was significantly different between these two types of unconsolidated sediments (Fig. 2). It was generally possible to distinguish between the clay till and the outwash sand and gravel by diurnal temperature change with more than 95 percent certainty, as shown by the 2 values of the standard deviation. A map of the average diurnal temperature change from May to September, 1965, correlates well with the geologic map of the area (Figs. 3 and 4).

PRESENT INVESTIGATION

In August 1966, we made a soil temperature traverse across a kame deposit, known as Money Hill, in Shelby County, Ind. (Figs. 5 and 6). The kame, consisting mostly of sand and gravel, has topographic relief of about 30 feet above the surrounding till plain where the temperature measurements were taken. The kame has been used as a source of sand and gravel but is not now being used.

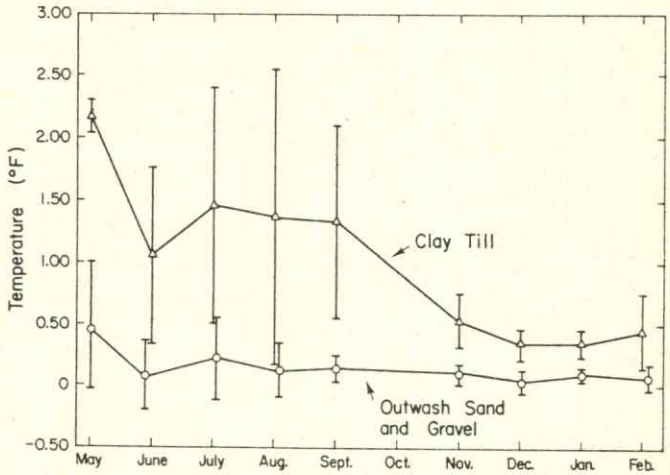

Figure 2. Graphs showing mean diurnal temperature changes at a depth of 30 cm in soils above clay till and outwash sand and gravel from May 1965 to February 1966. Standard deviations of 2 are shown. From Carr and Blakely, 1965, fig. 12.

The soil temperature traverse consisted of six stations located to include soils above both clay till and sand and gravel. Measurements were made in both the morning and the afternoon on a clear day when there was little wind. The diurnal temperature change at a depth of 30 cm ranged from 0.22°C to 0.58°C in soils above the clay till; it ranged from 1.48°C to 1.75°C in soils above the sand and gravel (Fig. 7). The average diurnal temperature change was about four times greater in the soils above sand and gravel than in the soils above clay till.

Also in August 1966, we made a soil temperature traverse across an esker deposit, known as the Malta Esker, in Putnam County, Ind. (Figs. 5 and 8). The esker consists principally of a ridge of sand and gravel about 300 feet wide and 3 miles long

that has a topographic relief of about 25 feet above the surrounding till plain. A few years ago, an augering program conducted by the Standard Materials Corp. indicated that the sand and gravel ranged from 25 to 30 feet in thickness and overlay clay till. Parts of the esker have been used as a source of sand and gravel, but no pits are active at the present time.

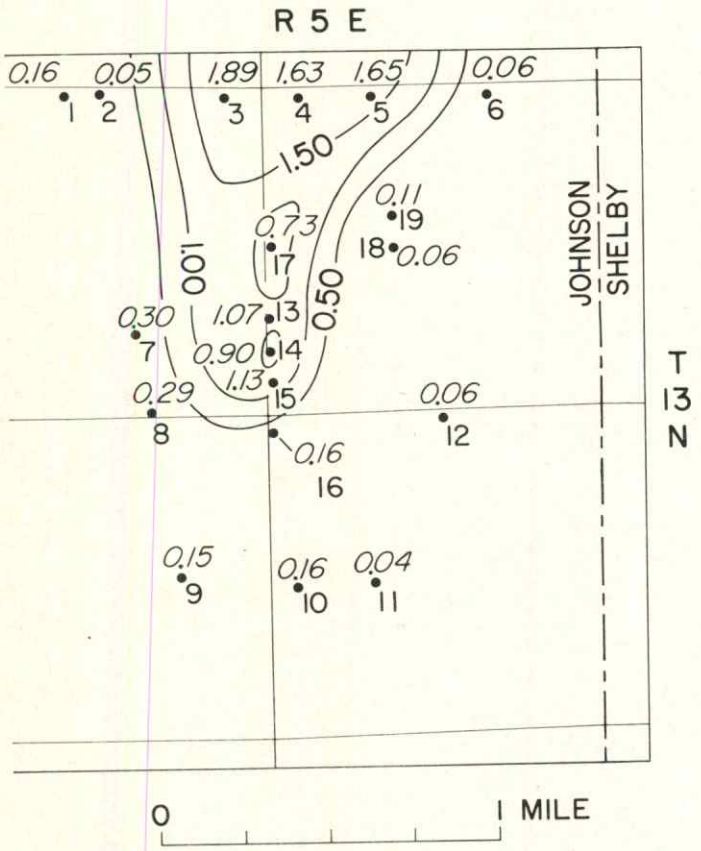

Figure 3. Contour map showing mean diurnal change of temperatures (^{o}F) from May to September 1965 at test site in Johnson County, Ind. From Carr and Blakely, 1965, fig. 14.

The soil temperature traverse consisted of seven stations located so that four were above parent materials of sand and gravel and three were above clay till. Measurements were made in both the morning and the afternoon on a clear day when there was little wind. The diurnal temperature change at a depth of 30 cm ranged from 0.75^{o}C to 0.80^{o}C in soils above the clay till; it ranged from 1.54^{o}C to 2.66^{o}C in soils above the sand and gravel (Fig. 9). The average diurnal temperature change was almost 2.5 times greater in soils above the sand and gravel than in soils above the clay till.

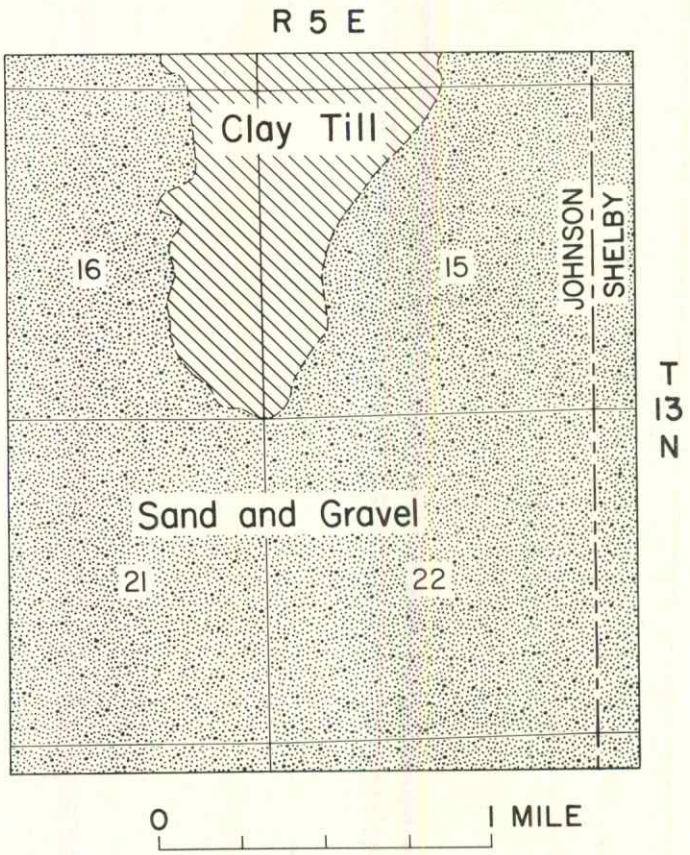

Figure 4. Geologic map of the test site in Johnson County, Ind. From Carr and Blakely, 1966, fig. 15.

During October 1966, we made a soil temperature traverse and drilled five auger holes on a terrace of Pleistocene age along the Ohio River just east of the town of Mauckport, Harrison County, Ind. (Figs. 5 and 10). The terrace is 70 feet above the normal pool elevation of the Ohio River and is separated from it by a modern flood plain that is 3200 feet wide along the line of traverse. The difference in elevation between the Pleistocene terrace and the modern

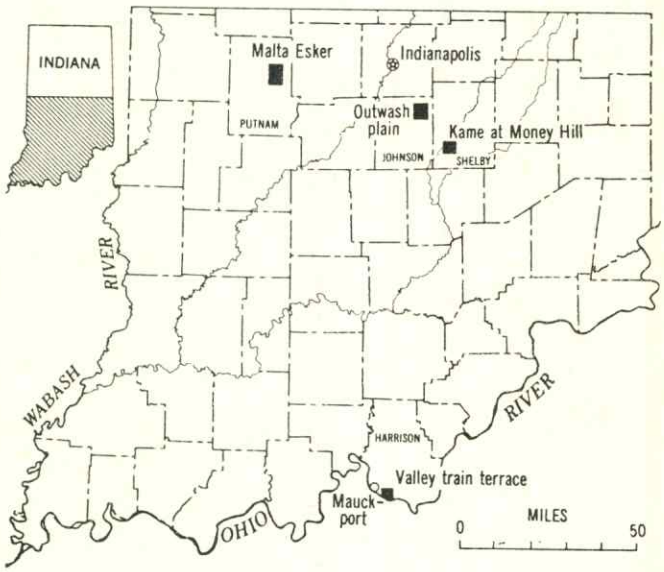

Figure 5. Index map of Indiana showing locations of soil temperature test areas.

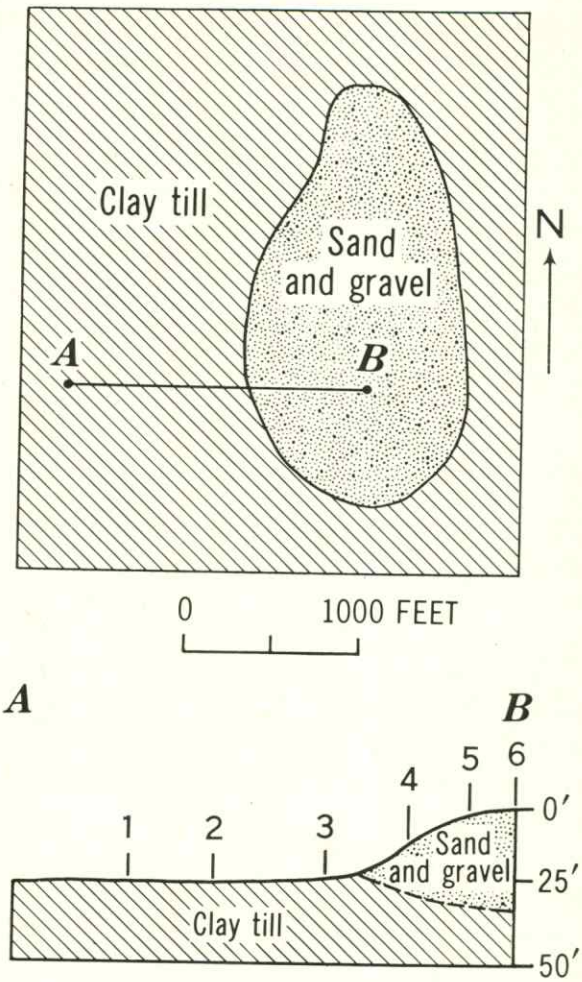

Figure 6. Geologic map and diagrammatic cross section showing relationships of unconsolidated deposits in kame at Money Hill.

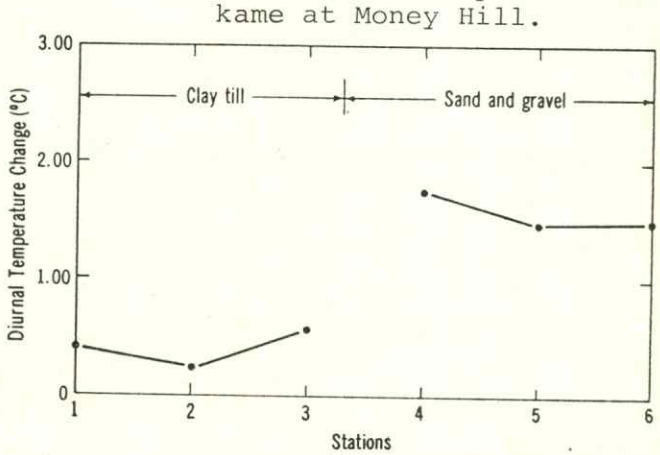

Figure 7. Graph showing diurnal temperature range at stations across kame at Money Hill.

flood plain is 30 feet. The terrace surface is relatively flat, and its relief is less than 20 feet. In this locality, sand and gravel are restricted to a zone about 2000 feet wide along the southern margin of the terrace. North of the sand and gravel zone, the terrace is underlain by lacustrine silt and clay. The modern flood plain south of the sand and gravel zone is composed mostly of silt and clay. Our augering and information from nearby drill holes showed that the ground-water table is lower in the sand and gravel area than in the adjacent silt and clay areas (Fig. 10). Two plants extract sand and gravel from this area.

The soil temperature traverse consisted of eight stations: three on the modern flood plain, three on that part of the terrace directly underlain by sand and gravel, and two on the terrace underlain by lacustrine clay and silt. Measurements were made both in the morning and the afternoon on a clear day when there was little wind. The diurnal temperature change at a depth of 30 cm ranged from 2.73° to 3.50°C in soils above the lacustrine silt and clay (Fig. 11). The diurnal temperature

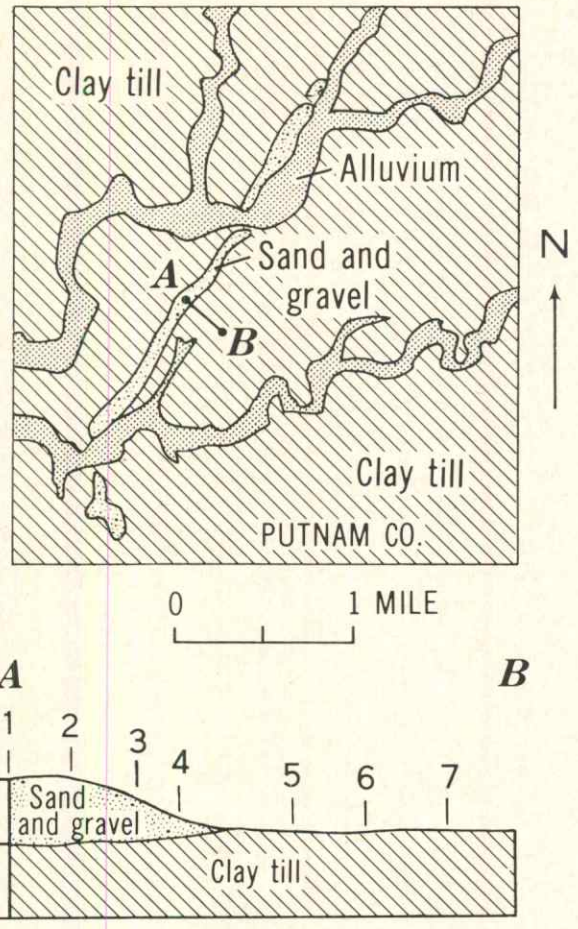

Figure 8. Geologic map and diagrammatic cross section showing relationships of unconsolidated deposits at Malta Esker.

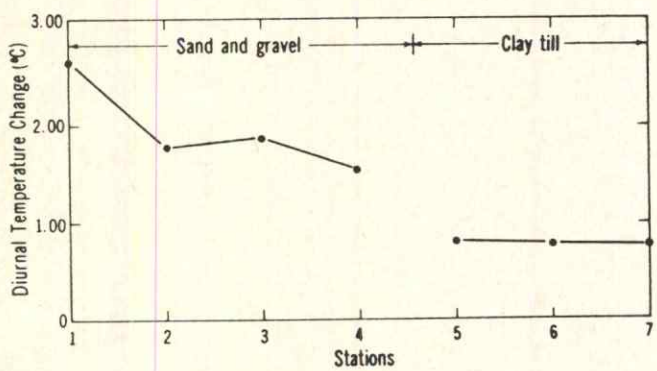

Figure 9. Graph showing diurnal temperature range at stations across Malta Esker.

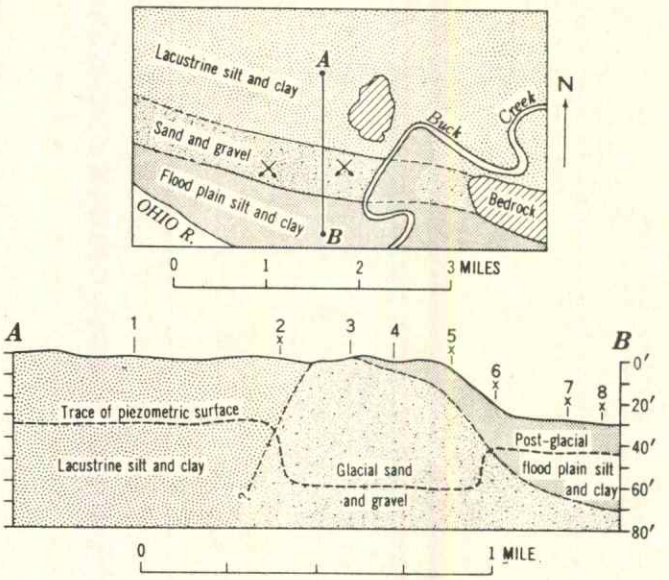

Figure 10. Geologic map and diagrammatic cross section showing relationships of unconsolidated deposits near Mauckport, Ind. Numbers refer to temperature measurement stations. X's refer to auger holes.

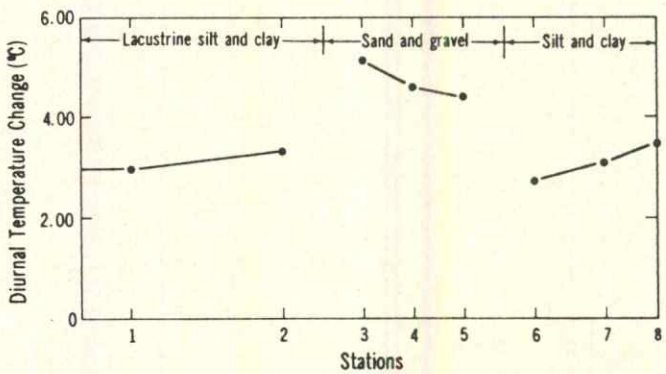

Figure 11. Graph showing diurnal temperature range at stations near Mauckport, Ind.

change was almost twice as great in soils over the sand and gravel facies as it was in soils over the silt and clay facies.

DISCUSSION AND CONCLUSION

The relative magnitude of the diurnal soil temperature change can be used to interpret underlying unconsolidated parent materials. In the areas studied, it was found that diurnal temperature change was less in near-surface soils over sand and gravel of an outwash plain than in near-surface soils over an adjacent clay till area. The diurnal temperature change was greater, however, in soils above sands and gravels of kame, esker, and valley-train terrace deposits than in soils above adjacent clay and silt areas (Fig. 12).

		TYPES OF DEPOSITS			
		OUTWASH PLAIN	VALLEY TRAIN TERRACE	KAME	ESKER
RELATIVE DIURNAL SOIL TEMPERATURE RANGE AT DEPTH OF 30 CM	SAND AND GRAVEL	Low	High	High	High
	ADJACENT CLAY AND SILT	High	Low	Low	Low

Figure 12. Comparison of relative diurnal temperature range at a depth of 30 cm in soils above unconsolidated materials associated with outwash plain, valley-train terrace, and kame and esker deposits.

It is generally agreed that the major fluctuation in temperature of the soil layer is due to variations in the radiation of the sun. The diurnal change in near-surface soil temperature is also affected by other factors, particularly moisture content, ground surface cover, ground surface color, and topographic position. To minimize the effect of variations in the radiation of the sun, the measurements were made on clear days when there was little wind. Also we selected areas with similar vegetation cover, ground surface color, and topographic position. Moisture content of the soils is believed to be largely the cause for the differences in diurnal change that we observed. Near-surface soil moisture is greatly influenced by the position of the ground-water table and the texture of the soils and parent material.

Relief on the outwash plain studied by Carr and Blakely is low in both the area of clay till and the area of sand and gravel. The ground-water table is relatively high in the entire area, but the coarser textured soils over the sands and gravels contain more moisture than the soils over the clay till. The greater moisture content in the soils over the unconsolidated sands and gravels appears to have reduced the relative magnitude of the diurnal soil temperature change.

Relief over the kame and esker deposits is greater than over the outwash plain deposits, and the soils over the areas of sand and gravel generally contained less moisture than the soils over the adjacent silt and clay areas. The configuration of the ground water table in the area of the valley-train terrace (Fig. 10) was such that the sand and gravel contained relatively less moisture than the adjacent clay and silt. The lower moisture content in soils over parent material of sand and gravel resulted in a higher diurnal temperature change than in soils over parent material of clay and silt.

SUMMARY

The use of the relative magnitude of diurnal temperature changes in near-surface soils may be a useful way to prospect for unconsolidated sands and gravels. The technique seems particularly attractive now that sensitive airborne infrared detectors can rapidly measure surface temperatures over large areas. Additional study needs to be made, however, since infrared detectors essentially measure surface temperatures and our measurements were made

at a depth of 30 cm. Such methods may be most successful in outwash-plain areas where changes in near-surface soil temperature reflect mainly the underlying parent material. In other areas of moderate to high topographic relief, geomorphology and the influence of the ground-water table must be considered in interpreting the underlying parent materials.

REFERENCES

Carr, D.D. and Blakely, R.F., 1966, Temperature variation at a depth of 30 cm in clay till and outwash sand and gravel: Proceedings of the Fourth Symposium on Remote Sensing of Environment, The Univ. of Michigan, Ann Arbor, p. 203-214.

EVALUATION OF COARSE AGGREGATE FOR ARCHITECTURAL CONCRETE

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ABSTRACT

The accelerated use of exposed aggregate for architectural concrete demands new concepts of stone evaluation. Variations of color and texture are critical and therefore the quarrying procedures must be integrated with rock variations so as to produce the desired color affects in the product. Because exposed aggregate may undergo rapid freezing and thawing, cyclical lesser temperature extremes, and wetting and drying, evaluation by accepted standard procedure is not adequate to assure high quality. A highway service record of a material does not necessarily indicate the potential quality of exposed aggregate.

Extremely high quality aggregate is required because of the uniqueness of architectural concrete. It is distinct for a number of reasons: 1) three sides of the aggregate are often exposed to the natural elements; 2) the aggregate must maintain its color and soundness over the lifetime of the structure (generally in excess of 60 years); and 3) the extremely high cost of maintenance and repair of failures. To approve an economical source that will meet the rigorous requirements, and not to waste money by over-specification puts a large responsibility on the geologists.

The soundness tests used to establish structural strength, wet-dry and/or frost sensitivity are the New York State Department of Public Works 25-cycle freeze-thaw, the 10 per cent sodium chloride solution, the New York State Department of Public Works 10-cycle $MgSO_4$ solution, and the ASTM Los Angeles Abrasion test.

All tests are run on relatively homogeneous lithologic thicknesses (layers). Heavy emphasis is placed on the 25-cycle freeze-thaw test results because of its known reliability in eliminating both wet-dry and frost-sensitive rocks.

Field criteria are presented to establish quality, stratigraphic continuity, color control, and rock symptoms which might "telegraph" potential problems.

INTRODUCTION

The use of aggregate on buildings for special color and textural effects has many pitfalls because of the need for tight control of both color and soundness. The application of geologic and engineering knowledge in controlling quarrying operations will solve many of the problems provided the geologist is well aware of the nature of the shortcomings of standard evaluation techniques. The geologist, in order to be effective, should not be misled by service records, the results of standard acceptance tests or official government stone ratings. Most states do not employ tests which are capable of evaluating aggregate for architectural use, but even those which do, may have sampling techniques which allow bad aggregate to slip through.

Concrete in which special texture or colors are created is called architectural concrete. Frequently this involves exposed aggregate. Aggregate may be exposed by sand blasting, bush

hammering, wire brushing, or acid washing concrete walls which contain the special aggregate throughout. The quantity of special aggregate employed under such conditions may be many thousand tons. Exposed aggregate may also be a veneer, particularly when prefabricated panels are used.

Definition of Special Conditions

Soundness - At first thought one might conclude that concrete used in buildings does not require the high quality aggregate which is needed for highways, because weathering conditions are generally less severe and buildings are not treated with salt during the winter. However, the reverse is true for four reasons: (1) the cost of the aggregate used in a building is a relatively small part of the total cost. Therefore, to save a few dollars by using a questionable aggregate is not justifiable. Conversely, because the cost of the aggregate is a large part of highway construction cost, it is frequently cheaper to use an inexpensive local and possibly questionable aggregate in concrete and later cover it with asphaltic mixes if it starts to deteriorate. (2) If a mistake is made in the type of aggregate used in a building, it is difficult or impossible to correct the error, short of tearing down the building (3) Aggregate which is exposed on a concrete wall is not protected by a mortar shell as it is on highways. Therefore, minor disruptive pressure within the aggregate can cause splitting or other deterioration of a type which may never be a problem in a highway. (4) The structural strength of concrete used in buildings is more critical than that of concrete used in highways.

Aggregate in buildings must be superior in its resistance to frost action (freezing and thawing) or warm-cool cycling in the presence of water or high humidity. It must also be resistant to wet-dry deterioration, especially where the aggregate is exposed to weathering. It is particularly important to recognize and understand this sort of deterioration. Many aggregates in New York which are acceptable for use in highways and have never been known to deteriorate in concrete are wet-dry sensitive. Such a rock exposed on the side of a building would ultimately spall off. Rocks which are sensitive to warm-cool cycling in the presence of water or which are wet-dry sensitive are herein categorized as sorption sensitive.

The potential chemical reactivity of aggregates in buildings is largely a less severe problem than in highways. However, it would be taking needless risks to use alkali reactive siliceous aggregate or alkali reactive dolomite or deleteriously reactive limestone without taking effective countermeasures. In addition, certain materials react chemically with air and moisture and these should be avoided. Particularly objectionable are the iron sulfides which could cause rusty streaks on the side of a building.

Color - Most quarry operators and high departments have no apparent need to be sensitive to the color of aggregate, and therefore color control is rarely, if ever, considered. However, when the aggregate is to be exposed, slight changes in rock type due to varying quarrying procedures, segregation by the way the rock is thrown when blasted, weathering or lithologic variations can become a major problem relative to its aesthetic appearance. Carelessness in the blending procedure in batching concrete can also cause color variations.

It is important for exposed aggregate to be approximately the same color both weathered and fresh. Failure to note carefully such variations could lead to different colors on the sides of a building (because of variation in exposure) and to a loss of the originally intended effect. As an example, many diabases and dolomites weather to a buff color.

Abrasion and Impact Resistance, Strength: - Compressive strength of concrete is more important in buildings than in highways and is generally checked by fabricating test cylinders in advance of stone use and by testing cylinders cut from walls in place. The geologist is generally most important here for gathering significant samples, and for assisting in evaluating the significance of test results.

Abrasion resistance is far less important in building structures, than in highways. However, a soft aggregate or an aggregate which is brittle may degrade during mixing and cause an increase in the ratio of fine aggregate to coarse aggregate, potentially resulting in a decrease of concrete strength.

The Control of the Quality of Aggregate for Architectural Use

Introductory Statement: - The control of stone quality for architectural use falls into several categories. The initial evaluation of stone on the basis of availability, physio-chemical quality and color is done best by a geologist in the field. Logging of the rock and layer by layer sampling, preferably of diamond drill cores, is followed by laboratory soundness testing. Once an aggregate is selected there should be continuous supervision to assure quality.

Field Examination - Usually the most critical single aspect of evaluation of a site is the initial field examination. The probability of a rock being high quality is generally established at this time. The procedures for petrographic examination are detailed in writing of Mielenz, R. C. and Rhoades, R. "Petrography of Concrete Aggregate", A.C.I., Vol. 42, 1946, p. 581 and in ASTM C-33 procedures. For exposed aggregate the following observations are particularly critical: (1) the layers which naturally outcrop and those which do not outcrop. (2) The physical change of a rock on weathering, i.e. does it deteriorate rapidly on short exposure? (3) The weathered color relative to the fresh color of the rock. The geologist should have a strong suspicion of the layer he does not see in a natural exposure. Those he cannot see are most likely to be the problem rocks.

A careful field examination of outcropping rocks or of a quarry is more critical than tests in most cases. Tests are notoriously unreliable indicators of rock quality if applied without sound judgment. As examples: (1) Shale of the Mauch Chunk formation in Pennsylvania nearly passes the N.Y.S.D.P.W. freeze-thaw test and passes the magnesium sulfate and sodium sulfate soundness tests run according to N.Y. or ASTM procedures. Yet in a single summer season it deteriorates on the stone piles or on the quarry floor because of its wet-dry or sorption sensitivity. A few cycles of wetting and drying in the laboratory are sufficient to cause deterioration. Incidentally, the same shale has very low Los Angeles abrasion losses, yet it tends to grind up on mixing for concrete.

A field examination indicating that shale is present would eliminate this rock simply because it is shale. (2) Most quarries in limestones and dolomites in New York State have weak layers which are frost and/or sorption sensitive. This shows up as a tendency to deteriorate rapidly on a quarry floor. Carbonate rocks of this type will generally fail the N.Y.S.D.P.W. freeze-thaw test but generally pass the ASTM-C-33 sulfate soundness tests. Such rocks often do not deteriorate in concrete in a highway but would if exposed on the side of a building. Often such rocks may be concentrated on one lift of a state accepted quarry and care must be taken to note such layers and be sure they are not quarried in any quantity for architectural concrete. (3) Conversely, many graywackes of the Catskill area outcrop extensively in cliffs which have been exposed for thousands of years and yet deteriorate badly in the unnatural conditions of simulated soundness tests. Such rocks have high natural soundness but little resistance to tests. Because of the lack of specification rock in the Catskills, Catskill graywackes have been used in concrete highways - a decision based on economic judgment and natural weathering observations. To date not a single highway made from such rock has deteriorated, even though some are nearly two decades old.

Clearly acceptance tests are not always reliable indicators of rock quality, and it is also clear that what may be a good test for one rock type may not be satisfactory for another.

Therefore, the best indicator of what a rock will do in concrete is its service record in concrete. But even the service record, as previously

implied is not necessarily infallible. A quarry's service record may be based on rock layers not currently quarried. For instance, if a quarry is deepened to intersect new layers, or if dipping beds are quarried across the strike, the service record may not indicate the quality of the rock currently being quarried. The appearance of a coral reef in a limestone face may also suddenly change the quality of the stone produced from a quarry. In addition, because of the distinct demands made on the aggregate, a highway service record is not necessarily directly applicable to an aggregate's use in architectural concrete.

The field examination of color is also critical. Color heterogeneity of a quarry face is likely to be objectionable even if the average mixture of colors is considered satisfactory by an architect. The reason for being careful of heterogeneity is that rocks are frequently segregated by blasting and this may persist to the final product. If heterogeneity of lithologies exists and an architect insists on using such a rock, care must be taken in blasting, shoveling, stockpiling and loading to assure maximum mixing.

Minimal change of rock color on weathering is also very important. Each lithology exposed at a site should be looked at and evaluated separately. Siderite, ankerite or iron sulfides are obvious causes of color change on weathering and may be objectionable even in small quantity. Dark gray to black limestones tend to weather to lighter colors of gray which may be aesthetically objectionable. Many such examples can be given.

In many cases, particularly in th the Midwest, little rock is exposed at a new site and judgments about aggregate quality have to be made without naturally weathered surfaces. For architectural concrete, such situations should be avoided because both weathered color and soundness may be difficult to evaluate.

Because the nature and distribution of each variation of lithology is critical, existing quarries and new sites should be examined on a layer by layer basis. This means detailed logging of faces, when available, and cores when rocks are not fully exposed. Even when the developed quarry faces expose all units, NX (2-1/8") core should be drilled, because core samples are believed to be the best for testing. This is not because of the shape of the cores, but because by using cores it is possible to test the whole of each lithology intersected. Conversely, sampling of single stone blocks requires the omniscience of knowing what is a typical block of a particular lithology; and sampling a pile of crushed stone is likely to be valid only if a quarry operates one lift in a homogeneous rock. Multiple lifts and heterogeneity of stone lead to heterogeneous stone piles.

When rocks are horizontal or nearly so or when the structure is simple, usually little or no geologic mapping is needed to assure continuity and homogeneity of product. However, when working with undeveloped sites in structurally simple rocks, the zones of non-outcropping units should be observed and described. In some cases, the outcrop tendency of a unit is a faithful indication of its soundness. A good example is in the Pamelia-Lowville formation transition quarry at LaFargeville, New York, where the sound carbonate rocks do not.

Even in areas of seemingly homogeneous lithologies, problems can come up if a site is not studied quite carefully. Two quarries opened up recently in pink granites in the Grenville lowlands near the St. Lawrence River illustrate what can happen. Every outcrop was granite, and it might seem logical therefore, to connect the outcrops. But we asked: why should some of the granite occupy topographic lows? Further investigation revealed that the lows were not underlain by granite but by friable, silicated marble unsuitable for most aggregate uses.

The basic rule is: What you don't see can hurt/kill you. The structure and the lithologic variations determine the sample intervals. As noted before, the best samples for most testing are split NX cores. Sampling should be done by lithologies with all of each distinct lithology tested.

A basic rule is: In heterogene-

ous lithologies never sample at regular core interval lengths. Sample according to lithologic types.

Performance Criteria

Performance criteria are imperfect indicators of the quality of rock materials. However, in the absence of a service record they are often the best available indicators of stone quality. From a practical viewpoint it would require a brave man to recommend the use of aggregate for a major structure which did not pass standard tests.

As a rule, minimum performance criteria are conservative, or are intended to be conservative. Engineers specifying quality often tend to be more conservative than the optimum limits specified. There may be a thin and barely definable line between being conservative - as they should be - and refusing to take responsibility for something new. The geologist is essential in helping to make decisions about new materials because rocks which geologists observe to weather well in nature are usually sound aggregates in concrete.

Soundness

Soundness is determined basically by the loss in the N.Y.S.D.P.W. freeze thaw test, which is 25 cycles of freezing and thawing of unconfined aggregate in a 10% NaCl solution, the loss determined by weighing before and after back-screening. As mentioned before, the test has shortcomings in that it does not react strongly on shales (which have to be eliminated by petrographic means) and it causes intense disintegration of some sandstones which seem to weather very well. However, it seems to be 100% accurate as a means of detecting carbonate rocks which weather badly. For instance, the DeCew member and part of the Gasport members of the Lockport formation, most of the dolomitic layers of the Pamelia and the Pamelia-Lowville transition, the Nedrow of the Onondaga formation and certain dolomitic layers of the Manlius. The test apparently does not distinguish between sorption sensitive and frost sensitive carbonate rocks, but as far as exposed aggregates are concerned, this point is irrelevant since neither type of deterioration can be tolerated.

When rocks are layered the freeze-thaw loss is determined on the basis of the following equation:

$$\% \text{ Loss} = \frac{T_1 x \%L_1 + T_2 x \%L_2 + \ldots, T_n \times \%L_n}{\text{Total T}}$$

Where T = Thickness and L = Loss. Subscripts refer to the separate described layers whose combined thickness is the total thickness. Per cent freeze-thaw loss calculated in this way shall not exceed 3%.

Soundness is also checked for individual layers by the 10 Cycle Magnesium Sulfate Soundness Test, run according to ASTM C-33. The maximum allowable limit is 10% for architectural concrete.

Abrasion Resistance:

The Los Angeles Abrasion Test is used to determine abrasion resistance. The maximum allowable loss of 50% is somewhat higher than the usual acceptable limits. This limit was set because: (1) abrasion is a major factor only in mixing the concrete and (2) many very attractive and highly acceptable and desirable granites would be eliminated if the losses were set lower.

Omnibus Rejection:

Rejection of an aggregate is possible if it has any other unsatisfactory qualities. For instance, any deleterious materials occurring in excess of allowable per cent may reject the aggregate, following procedures outlined in ASTM C-33. Excessive shale or discoloring substance or dirt, clay, wood particles, coal, or any deleterious substance occurring over 1% is enough to reject the stone. An excessive per cent of flat or elongated pieces could also make an aggregate unsatisfactory.

Color Evaluation:

The evaluation of the color of an aggregate is made generally by an

architect who works with samples of typical aggregate supplied by the geologist. When a satisfactory arrangement is reached a record sample color panel generally is constructed according to design mix for the purpose of color comparison during production.

Source Approval:

If an aggregate passes all tests conducted on the split core samples and no other extenuating circumstances have developed, the source can be tentatively approved for use as aggregate for architectural concrete. Final approval is reserved for evaluation of the operator's finished product.

Samples of the finished product which have been subjected to the various tests of the performance criteria renders final approval. One or more of the lithologic units of a mixed lithology will have test results which will fall outside the recommended limits. This can be tolerated if the average material is still satisfactory, and if the quarrying and processing procedures are such that the inferior materials do not segregate. If an inferior lithology cannot be averaged in satisfactorily, operating in another portion of the quarry, or stripping, or stepping up may solve the problem. Most producers will cooperate if the request is within reason.

Geologic Quality Control During Production:

In addition to mapping, logging, sample selection, test evaluation, and selection of the area to be quarried, the geologist should also be involved with maintenance of quality control. For many reasons unexpected changes can occur which may adversely influence the quality of stone. For instance, a pod of marcasite, a small reef or a clay seam in a carbonate rock could create problems. Unannounced changes in quarrying procedures, done for operational reasons, could adversely influence stone quality or color. The least expensive method of maintaining quality control is to have periodic samples of the crushed stone sent directly to the geologist from the quarry before shipment to the point of use. The frequency of samples to be sent, the nature of sampling, and who samples are determined by the size of a job, the nature of the lithologies and the type of quarry operation. Particular care should be taken when a quarry operates with several lifts and the stone desired occurs on only one lift. Mixing of stone types is very common and for architectural concrete could cause a real problem if inadvertently used in the structure.

Cost of Geologic Control:

The cost of geologic work is highly variable, depending mostly upon the manner and rate of charging, the size of the job, and the complexity of problems encountered. For the selection, evaluation and quality control of relatively homogeneous rock from an operating quarry, the total charge could be a few hundred dollars. Charges may run to several thousand dollars in complex cases. But the cost of geologic work must be balanced against the cost of errors. The geologic cost is small indeed, relative to the remedial costs if a wall had to be torn down.

Geologic work can save large sums by showing how less expensive local aggregate may be entirely adequate for a particular job. In our experience, the saving in the cost of colored aggregates may range from $5 to $45 a ton. Even in a small structure involving 1,000 tons of aggregate, this is a sizeable item. For major construction, as at the Fredonia Campus, 40,000 tons or more may be used. The value of sound economic geology is very clear.

GEOMETRY OF DEPOSITS OF THE SEDIMENTARY NONMETALLICS

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ABSTRACT

Nonmetallic deposits of sedimentary origin are found to occur mainly as sheets and lenses, and to a minor degree in other forms. Sheets are of wide lateral and limited vertical extent, and present relatively few geologic complexities. Small lenses are of quarry width and the largest grade into sheet deposits. All major lens deposits are buried, and all have been found by accident, in drilling for oil or water. Lenses present numerous problems of origin and detection. Minor sedimentary forms include a sedimentary pinch-out, deposits in the zone of weathering of outcropping flat strata, and erosional remnants.

Examples of all these geometric types are described.

INTRODUCTION

It is the purpose of this paper to consider a group of familiar objects the sedimentary nonmetallics, from an unfamiliar point of view, namely that of geometrical form. Like crossing one's home city by unfrequented streets, this exercise may provide some new perspectives. Deposits are considered in terms of physical configuration, without reference to scale. Only relatively undeformed deposits are included.

SHEET DEPOSITS

Geometrically the simplest variety sheet deposits (Fig. 1) are so extensive that their lateral boundaries are of no significance in a quarrying or mining district. Extraction from a given rock unit may take place at localities that are scores or even hundreds of miles apart. Vertical boundaries, on the other hand, are controlling factors. They govern not only the minable thickness but also the roof and floor conditions. Factors that limit sheet deposits in the vertical dimension include change in rock purity or other desired property, change in strength or stability, depth of weathering, and position of the water table.

Of the scores of well-known examples, we may mention the St. Peter sandstone, which averages 75 feet in thickness over an area of more than 200,000 square miles. This sheet deposit par excellence is utilized for its high silica content as far as Illinois, Missouri, and Oklahoma. Sheets of carbonate rock such as the Middle Silurian dolomites of Ohio-Indiana-Illinois, and such evaporites as the Salina salt of New York-Ohio-Ontario and the Blaine gypsum of Kansas, are other examples. Some deposits of outwash underlying several hundred square miles are reasonably considered sheet deposits.

Problems that arise in exploiting sheet deposits are less likely to be geologic than political or economic. The escalating conflict between urbanization and the mineral industries is especially serious for producers of construction materials and other low-cost large-volume nonmetallics commonly derived from sheet deposits.

LENSES

The most interesting form taken by sedimentary deposits of value is the lens (Figs. 2 and 3). Lenses differ greatly in size, the smallest being perhaps a few hundred yards across and the most extensive ones grading into sheet deposits. Some lenses consist of material entirely

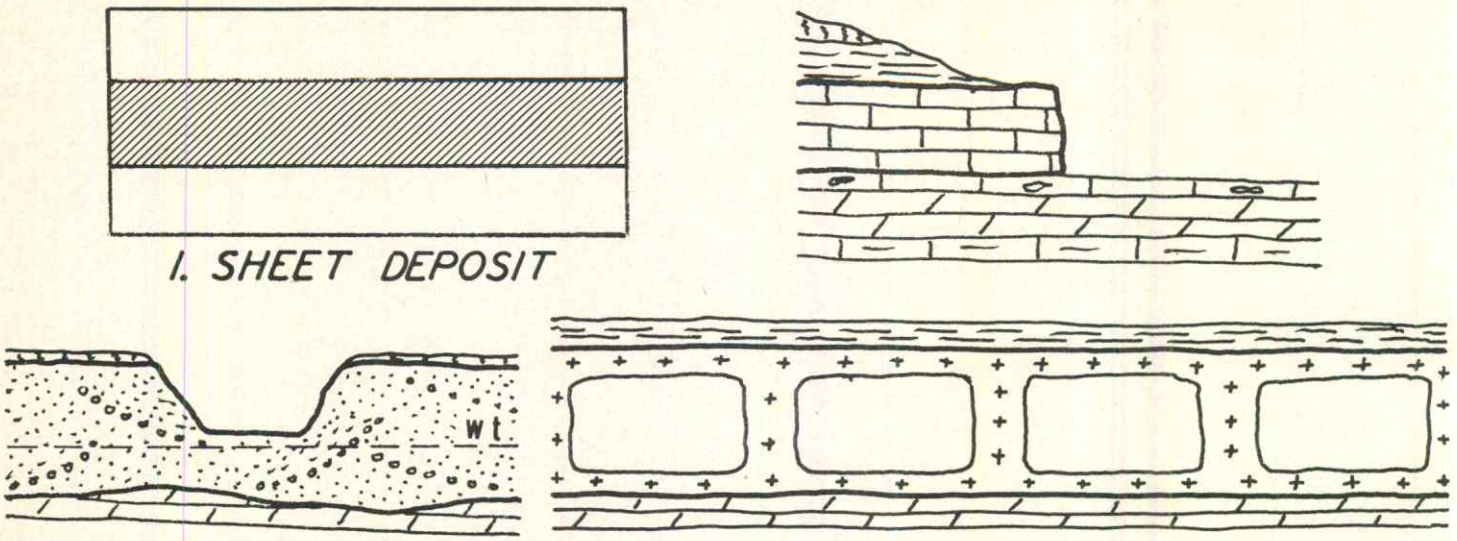
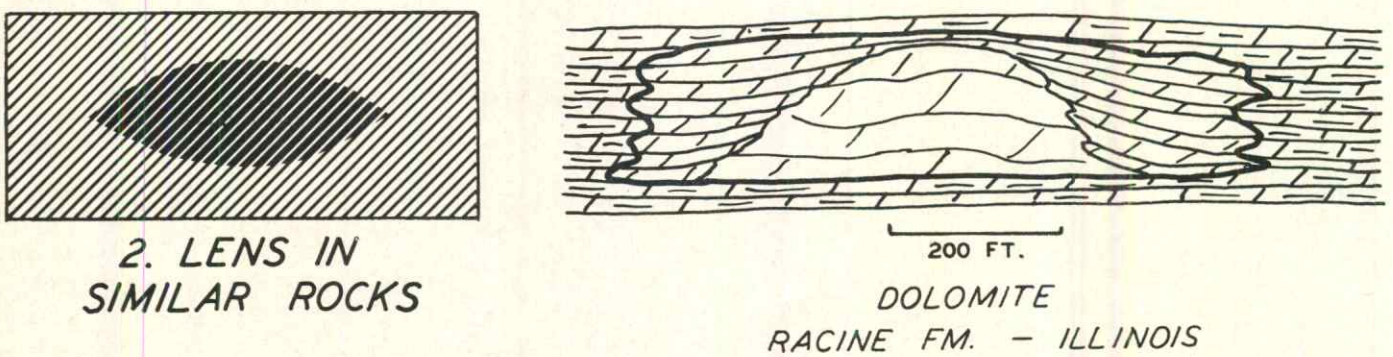


Figure 1. Sheet deposits wt = water table.



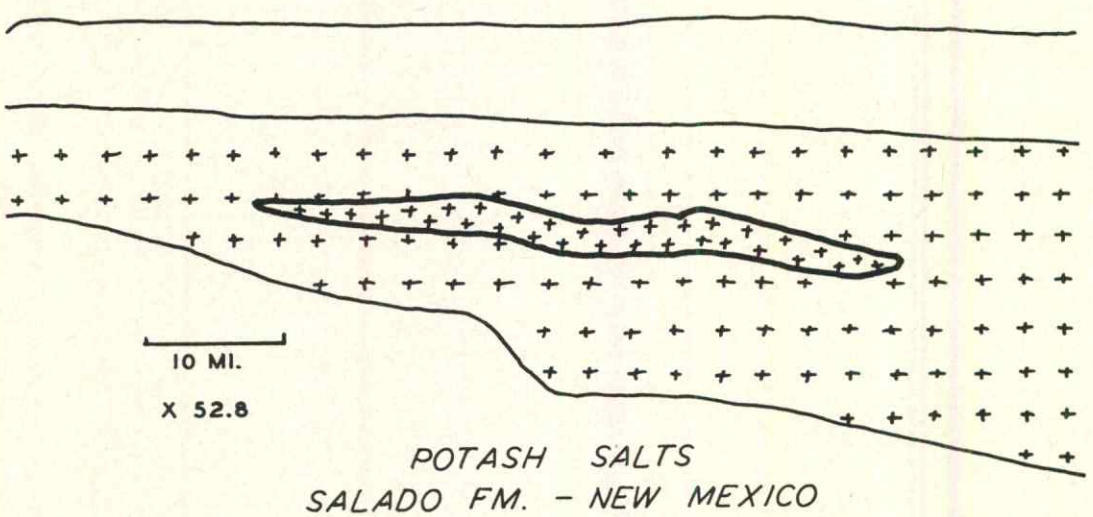


Figure 2. Lens deposit.

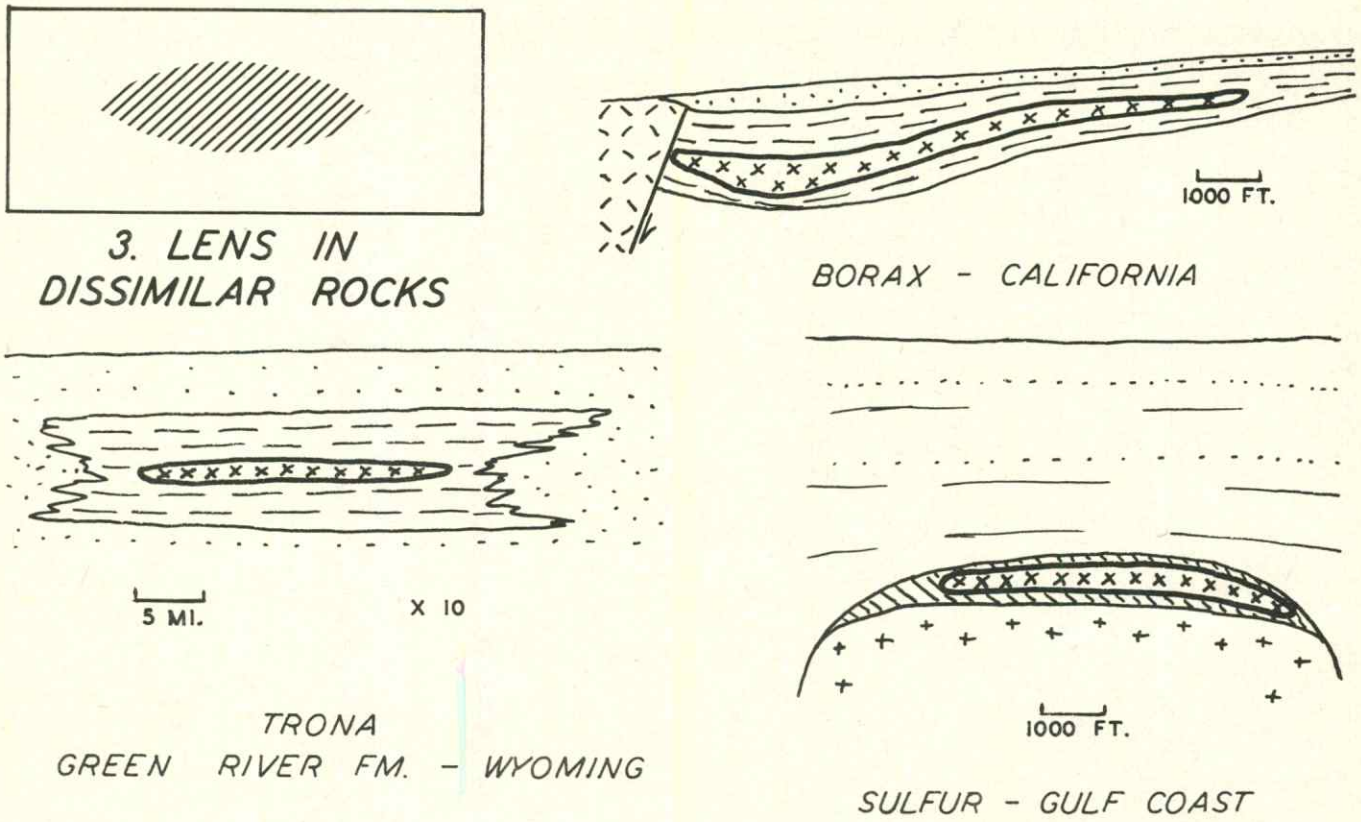


Figure 3. Lens deposit.

different from the surrounding rock, whereas the substance of others is merely a variant of the enclosing formation.

Two of the latter type are shown in Figure 2. Lenses of high-purity dolomite in the Racine formation (Middle Silurian) of northern Illinois include reef-core and flanking strata, but not the interreef beds, which are argillaceous and silty. The great lens of potash-bearing beds east of Carlsbad, New Mexico, is enclosed in the Salado formation (Upper Permian), 1,400 to 2,000 feet thick, which is dominantly rock salt. The beds of potassium salts, together with the intervening barren strata, form a lens about 250 feet in thickness and 1,000 square miles in area. Eleven active mines are located in this lens.

Each of the lenticular deposits shown in Figure 3 consists of material quite unlike the enclosing rock. The native sulfur of the Gulf Coast occurs as granular masses and crystalline aggregates in the gypsum and calcite portions of the caprock of salt domes. In the strict sense, the sulfur is not sedimentary, as apparently it is the product of bacterial action in the caprock; but its associations are with sedimentary rocks, and the geometry of deposits is that of the lens.

Whereas there are a number of sulfur-bearing salt domes, each of the other deposits illustrated in Figure 3 is unique. The deposit of borax and kernite at Boron, California, is a buried playa of Pliocene(?) age. Its minuscule size --- less than 2 square miles, or 0.001 percent of California's land surface --- is far out of proportion to its value, which at 1965 prices was in excess of $7 billion. The boron salts form a lens with a maximum thickness of 250 feet, enclosed in lake-deposited clay. The salt beds terminate in the surrounding sediments as though lapping against a former shore line. The Wyoming deposit of trona (sodium carbonate) is much larger, underlying some 1,400

square miles. A recent estimate is that it contains 67 billion tons of trona in beds more than 3 feet thick. The deposit is well described as "a lens within a lens." The bedded salt body, which in addition to trona contains halite and several rare salts, occurs in the Green River formation (Eocene), which is a lake deposit; and this formation in turn is enclosed within streamlaid deposits of the Wasatch and Bridger formations. The Eocene lake fluctuated in size, and the trona and other salts were apparently formed through evaporation at low stages.

Variable as they are in size and relations, deposits with lenticular geometry present two sets of problems in common. First, there are serious deficiencies in our understanding of the origin of every one of them. How and when did the Racine formation, including its reefs, become dolomitized? What is the significance of mineral paragenesis in the Carlsbad potash deposits? Exactly how did salt-dome sulfur become separated from its parent H_2S? What were the conditions that allowed precipitation of 100 million tons of borax-kernite, to the exclusion of other salts, in one place at one time, and 67 billion tons of trona in another place at another time? More or less educated guesswork is the best we can provide in the way of answers.

The second set of problems, which is of more interest to industry, has to do with discovery. Here we must proceed from two basic facts: all the lenticular deposits of high valu are buried, and not one was discovered as a result of applying geological reasoning. Geophysics can find salt domes, but the only way to test for sulfur is to drill holes. The New Mexico potash and the Wyoming trona were found in drilling for oil; the California borax, in drilling for water. Suppose that we urgently needed an additional supply of a mineral that occurs in hidden lens deposits, could we put geological theory to work to find this supply?

Just such a situation arose early in the 1950's, when it appeared that the large-scale use of boron compounds as rocket fuel was imminent and that new supplies might shortly be needed. The U.S. Geological Survey was handed the job of finding these supplies. More than 5 years of intensive search followed, in which theoretical and empirical geology was applied, every known occurrence was visited, and all possible clues were investigated. This thorough and geologically sophisticated search failed to turn up a deposit at all comparable to the buried playa at Boron. (Fortunately the increased demand failed to materialize). Hard as it is to believe, the Boron lens is apparently the single major borax deposit on the North American continent (aside from the brines of Searles Lake, a minor source). The only countries other than the United States with borax reserves of any consequence turn out to be Argentina and Turkey.

Although the results of the borax search were disappointing, its lack of success seems not to have been due to shortcomings of geological science but simply to lack of material to be discovered. (One suspects that the same factor might doom an attempt, no matter how sophisticated, to locate another large trona deposit). Geology cannot be blamed for failing to find what is not there. Besides, the information that additional reserves are not available is itself of much value.

If the desired material were potash, and if undiscovered deposits existed, there is evidence that we could find them by applying bromine geochemistry. The element bromine can replace chlorine in the crystal lattice of halite, and the bromine content of rock salt is an index of the salinity of the brine from which the salt formed. It has been found that the content of bromine in rock salt increases upward and inward in an evaporite basin, and thus it may be used as an indicator of the late-crystallizing potash salts. Since the area in which the rock salt contains more than 0.02 percent (220 ppm) of bromine forms a halo around a potash deposit, a small number of drill holes can effectively indicate the direction in which to explore.

The major basins on the North American continent have been "punched full of holes" by the oil drill, how-

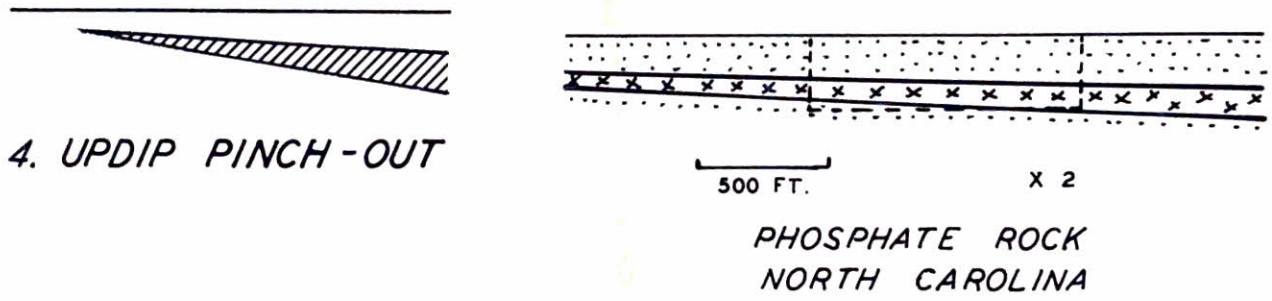


Figure 4. Pinch Outs Dashed line, approximate outline of open pit.

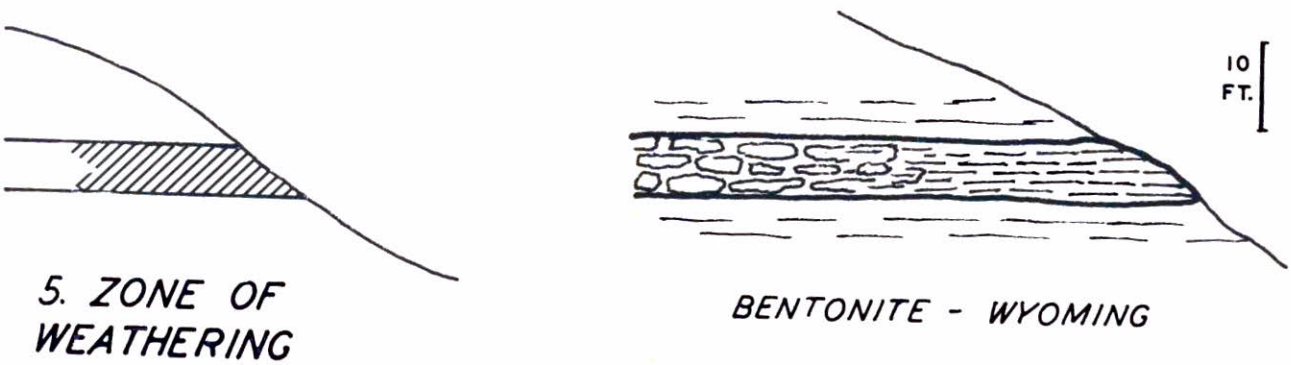


Figure 5. Weathering Zones, shale pattern, shows swelling bentonite of commercial value.

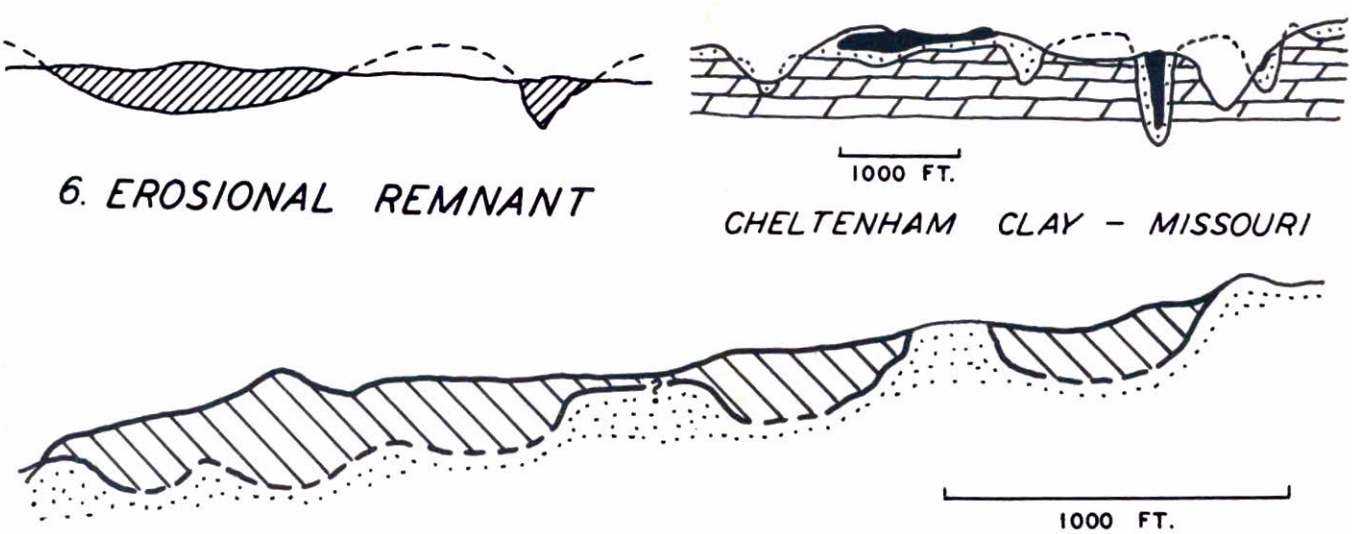


Figure 6. Erosional Remnants

ever, and the method just outlined may have been developed too late to be of much use. It has been applied in the Paradox Basin, but we already knew there was potash there. No doubt it could be shown to work in the great sedimentary basin of western Canada, but the oil drill got there first and discovered enough potash to last for generations. The bromine technique may be of great value in little-prospected regions of the world. The Russions are reported to be utilizing it in exploring for potash in the Angara-Lena salt basin.

OTHER FORMS

A large deposit of phosphate rock was developed in the early 1960's at Lee Creek, on Pamlico Sound, coastal North Carolina. It is near the updip edge of a Miocene bed that is inclined gently seaward and becomes thicker and more deeply buried in that direction (Fig. 4). Although a cross section makes this appear to be simply the margin of a sheet deposit, the phosphate bed changes facies both ways along the strike, so that in reality the deposit has definite known limits in all directions except down the dip. The top of the bed is 90 feet below the surface, and the bed itself is 40 feet thick. First reported by the U.S. Geological Survey, the deposit was explored and is now being mined by Texas Gulf Sulphur Company. The phosphate rock has a measurable uranium content, and this fact was utilized in exploration. The records from gamma-ray probes in farm water wells, and in some 95 core holes, allowed the company to block out the most favorable area. A serious problem in exploitation has been dewatering. The entire deposit is below sea level, and heavy pumping is necessary to keep the open pit dry. This has produced a cone of depression in the water table, has raised the specter of salt-water contamination, and has stirred demand for a state policy on ground-water management.

In Figure 5 is shown a section through an exposure of the Clay Spur bentonite, a unit at the top of the Mowry formation (Cretaceous), in the northwestern Black Hills, Wyoming. Under more than 20 or 25 feet of overburden, the fresh bentonite is bluish and without value because deficient in colloidal and swelling properties. Along the belt of outcrop, however, the bentonite has weathered to a pale yellow swelling clay of high quality. The Clay Spur is a widespread unit and its weathered outcrop is continuous for many miles.

Another example of the zone-of-weathering form is provided by the "rim" or "hatband" deposits of Tennessee brown-rock phosphate. These are concentrations along the edges of phosphatic layers in Ordovician limestones that crop out around the Highland Rim.

A final and highly variable geometric category is the erosional remnant, two examples of which are shown in Figure 6. The Cheltenham fire clay of central Missouri, Pennsylvanian image, rests with marked unconformity on carbonate rocks that range in age from Ordovician to Mississippian. The clay, with its underlying sands, was deposited in solution depressions in limestone or dolomite, underwent weathering and leaching, was buried by younger strata, and has since been exposed and partly dissected during several periods of erosion. Since the deposits are patchy and are covered by soil and vegetation, prospecting is difficult.

The gypsum that occurs in the Fish Creek Mountains, some 70 miles east of San Diego, California, is pure, massive, nearly 100 feet thick, and without overburden. Of Miocene age, it has been preserved from erosion in a shallow synclinal basin. The gypsum is extracted in a large bench quarry.

CONCLUSION

In this geometrical exercise we have reviewed the several forms taken by the chief industrial rocks and minerals of sedimentary origin. Of the forms considered, the lens commands the most attention because of its economic and scientific significance. There are enough interesting problems connected with this seemingly simple form to challenge the geologic disciplines for a long time to come.

SECTION TWO

APPLICATION OF GEOCHEMISTRY TO INDUSTRIAL MINERAL EVALUATION

STRATIGRAPHY AND GENESIS OF DOLOMITE, EDWARDS FORMATION (LOWER CRETACEOUS) OF TEXAS[1]

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ABSTRACT

The Edwards Formation (Lower Cretaceous) of Texas is characterized by lime grainstones and rudist bioherms which were deposited or grew upon an extensive, very shallow-water, marine platform (Comanche Platform). This platform was bounded by deeper water basins in which chiefly lime muds were deposited (Ancestral Gulf of Mexico to the east and south, North Texas-Tyler Basin to the north and west). Evaporites were deposited periodically in two areas on the Platform--Kirschberg Lagoon, chiefly in outcrop of Central Texas, and McKnight Lagoon, chiefly in subsurface of southwestern Texas and northern Mexico. Rudist bioherms were constructed principally along platform edges and peripheral to the platform lagoons. Main outcrop deposits of dolomite are in a concentric belt marginal to the Kirschberg lagoonal-evaporitic facies.

Two main types of dolomite occur in the Edwards Formation. I. Stratal dolomite: very fine grained (10 microns or less), tightly knit and intergrown mosaic of crystals, laminated to thin bedded, rarely fossiliferous, only slightly porous and permeable, and associated with thin-bedded, locally mud-cracked, locally stromatolitic lime mudstones, thin-bedded, cross-laminated, ripple-marked lime grainstones, and very thin evaporite-collapse layers; dolomite units are generally less than 2 feet thick; magnesium carbonate content among several dolomite and dolomitic limestone samples varies irregularly from low to high. II. Massive dolomite: fine to coarse grained (generally greater than 30 microns), loosely knit mass of euhedral crystals, moderately to highly porous and permeable, typically replacing thick-bedded, fossiliferous, lime grainstones, and displaying relict structures of the host rock. Dolomite units are thick, commonly about 10 feet, but locally up to 80 feet thick, and generally underlie or are associated with prominent evaporite-solution units; content of magnesium carbonate among several massive dolomite and dolomitic limestone samples is either low or high with few intermediate values.

Both stratal and massive dolomites are judged products of metasomatic replacement of calcium carbonate under conditions of elevated pH and salinity resulting from contact with magnesium-enriched brine waters. Features of stratal dolomite indicate very early replacement of nonlithified lime muds and grains in the marginal, supratidal zone of the central lagoon; replacement was chiefly at the depositional surface, though some occurred in nonlithified sediments below this surface by downward and outward seepage of brines. Features of massive dolomite indicate post-lithification replacement by means of seepage refluxion of brines from the evaporitic Kirschberg Lagoon. Generally, only permeable grainstones along the margin of the Lagoon are dolomitized in this manner; associated, less permeable lime mudstones were unaffected and locally effectively shielded underlying permeable grainstones. Stratal dolomite occurs chiefly within the lagoonal facies and along its southern margin where the Platform-Lagoon boundary was marked at times by an extensive, low-relief, low-energy tidal flat. Massive dolomite occurs mainly along the northern margin of the lagoonal facies, largely coincident with areas of numerous rudist bioherms and associated grainstone facies. The two types of dolomite are not entirely mutually exclusive, though massive dolomite is more common in the southern facies than is stratal dolomite in the northern facies.

Nodular chert is chiefly coextensive with dolomite, though chert does not occur in the reef-core or reef-flank deposits within the dolomite facies.

[1] Publication authorized by the Director, Bureau of Economic Geology

Dense hard limestones of the reef core are only rarely dolomitized, but grainstones of the reef-flank deposits within the dolomite belt are thoroughly dolomitized. Reef-flank deposits are the only dolomitized depositional unit consistently free of chert.

Dolomitization in the Edwards Formation was secondary, ranging from pre- to post-lithification; however, it was contemporaneous with and directly associated with the central evaporitic facies. Significantly, dolomites in the Edwards Formation were a part of the regional depositional system of that formation and, in terms of the regional quality, variation, and occurrence of an industrial mineral, can be studied and evaluated within the depositional framework.

INTRODUCTION

Within the past six or seven years there have been three significant observations concerning the formation of dolomite. These include: (1) field evidence of dolomite or protodolomite formed on modern carbonate tidal flats by metasomatic replacement of lime muds, from such diverse, low-latitude places as Florida and the Great Bahamas (Shinn et al., 1965), the Persian Gulf (Illing et al., 1965), the Netherlands Antilles (Deffeyes et al., 1965), and South Australia (Skinner, 1963 and others); (2) laboratory precipitation of protodolomite under conditions of normal pressure and temperature (Siegel, 1961); and (3) development of the seepage refluxion model (Adams and Rhodes, 1960), based on regional distribution of dolomite and related carbonate-evaporite facies. Models developed from these studies applied within the framework of regional stratigraphy aid in recognition and genetic interpretation of at least certain types of dolomite as well as time of dolomitization. This approach demonstrates that dolomitization commonly is a basic element of the original depositional system. The purpose of this report is to present results obtained from applying current models of dolomitization to the Edwards Formation of Texas, a widespread, Lower Cretaceous carbonate unit which includes a prominent dolomite facies.

Regional Stratigraphy

The Edwards Formation is characterized by lime grainstones and rudist bioherms and biostromes which were deposited or grew upon an extensive, shallow-water, medium- to high-energy, marine platform. This feature, here designated the Comanche Platform, was constructed on the tectonically positive Llano and Devils River Uplifts in Texas, the Coahuila Peninsula of northern Mexico, and associated smaller positive areas (Fig. 1). This regional platform includes smaller scale units--the San Marcos Platform, the Devils River Platform, and the Coahuila Platform. The Comanche Platform was bounded on the east and south by a relatively deep-water, oceanic basin--the Ancestral Gulf of Mexico--and on the north and west by an extensive shallow-water, oceanic basin--the North Texas-Tyler Basin. Contemporaneous with grainstone deposition on the Comanche Platform, basinal deposits to the north and west were chiefly low-energy lime muds and clays; these include shelly and marly clays of the Walnut Formation and nodular lime mudstones and wackestones of the Goodland and Comanche Peak Formations. Deposition in the Ancestral Gulf of Mexico, based on outcrops in northern Mexico (Smith, 1966) and the subsurface of South Texas, was mainly dark lime muds and clays.

Two areas of periodically restricted deposition developed on the Comanche Platform--the Kirschberg Lagoon (here designated, after Kirschberg Evaporite, Barnes, 1944), a broad, very shallow, shelf-type lagoon in Central Texas, and the McKnight Lagoon (here designated, after the McKnight Formation of Winter, 1962), known generally from the subsurface of South Texas and outcrop of northern Mexico. Alternating evaporites and shallow-water, lime mudstone and

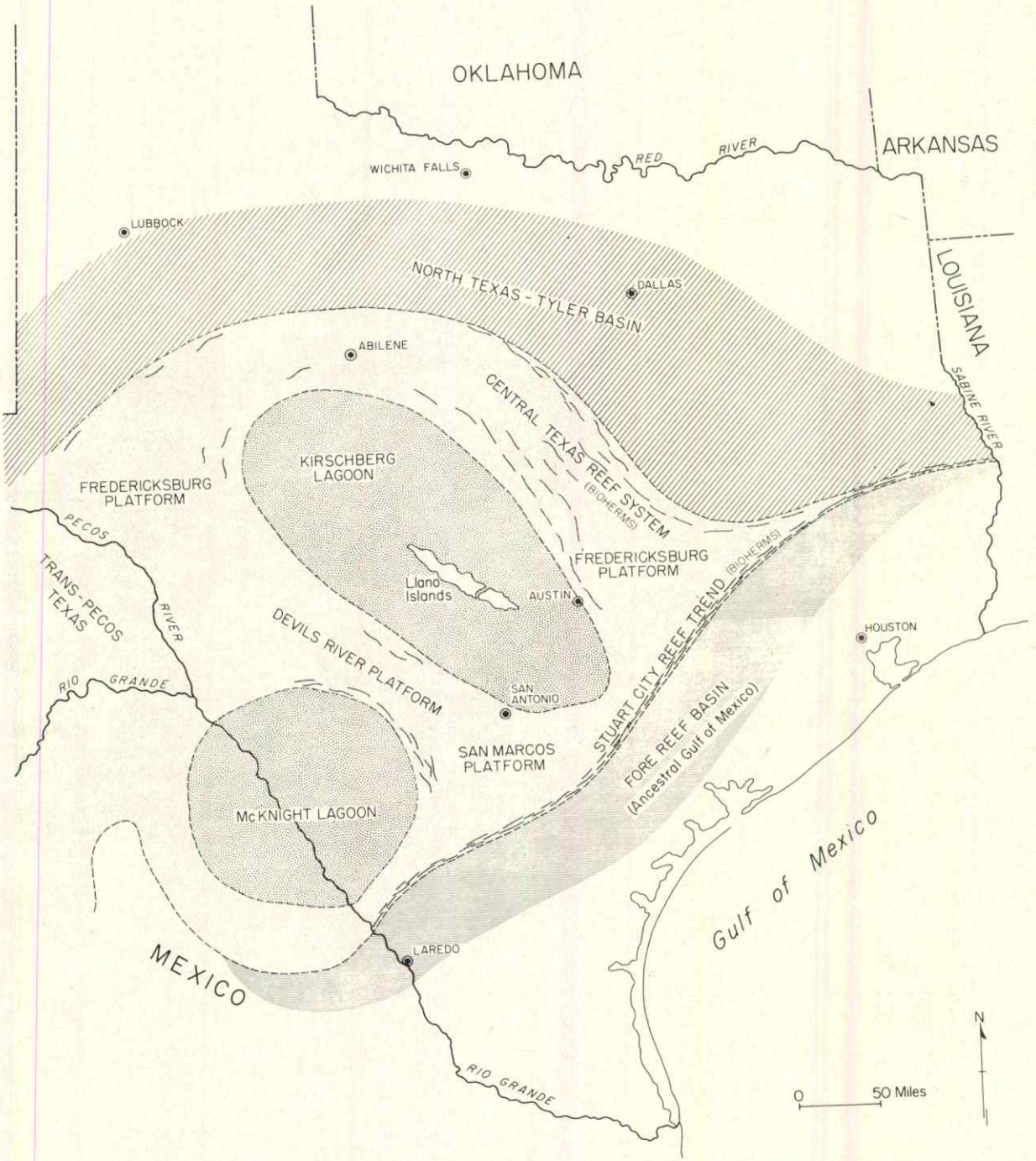

Figure 1. Paleogeography of Edwards Formation.

grainstone were deposited in the Kirschberg Lagoon; thin-bedded, ammonite-bearing black shale, lime mudstone, and evaporites were deposited in the McKnight Lagoon (Lozo and Smith, 1964; Smith, 1966).

For purposes of this report, facies within the Edwards, and certain associated facies, are treated as a time-stratigraphic unit; the several facies are arranged as a depositional model against which dolomite distribution can be better understood. Precise stratigraphic relationships of the several facies of the Edwards of North-central Texas, the Edwards of the Edwards Plateau region, and the Edwards of the South Texas subsurface are not firmly established. Work in progress, by us and others, should demonstrate more exactly the relationships of these units.

The Edwards Formation used herein includes rocks known as Edwards north of the Colorado, rocks commonly designated as "lower Edwards," or "Edwards B," in outcrop and subsurface south of the Colorado River, and the "unnamed lower unit" of Lozo and Smith (1964). It is the approximate stratigraphic equivalent of the West Nueces, McKnight, and lower part of the Devils River Formations of southwestern Texas and northern Mexico (Lozo and Smith, 1964), the lower part of the Stuart City Reef (Winter, 1962), and the Del Carmen Formation of Trans-Pecos Texas and northern Mexico (Maxwell and Dietrich, 1965; Maxwell, et al., 1967).

Outcrop of the Edwards Formation generally parallels the Balcones Escarpment and extends from the Parker-Hood County line in the north to northeastern Medina County in the southwest. It forms extensive outliers along the divide of the Colorado and Brazos Rivers in North-central and West-central Texas and is a prominent outcrop unit in the northeastern part of the Edwards Plateau and locally as outliers on the Llano Uplift.

The Edwards is a feather edge along the northern margin of the Comanche Platform, increasing in thickness southeastward; thickest sections (up to 450 feet) occur in the subsurface of South Texas a few miles west of the eastern Platform edge. Equivalent units farther south in South Texas and northern Mexico (lower Devils River, West Nueces, McKnight, and Del Carmen) are up to 600 feet thick.

Throughout its extent the Edwards Formation (as here defined) is overlain by approximately time equivalent, open marine marls and nodular lime mudstones containing oxytropidoceroid ammonites. This facies, characteristically a basinal one, is best developed in the North Texas-Tyler Basin, where it constitutes the Kiamichi Formation. In the Edwards Plateau a similar facies has been designated informally as the "Dr. Burt Beds" (Lozo and Smith, 1964; Young, 1966). In the subsurface of South Texas, an equivalent rock unit has been called "middle Edwards" by Tucker (1962), and "regional dense marker" by oil industry geologists. Along the northern and northwestern margin of the Comanche Platform the Edwards overlies nodular lime mudstones of the Comanche Peak Formation and marls and clays of the Walnut Formation; a nodular mudstone (Goodland Formation) is the basinal equivalent of the Edwards. Southwestward, toward the Colorado River, these underlying rocks interfinger with and are gradually replaced by the Edwards Formation. South of the Colorado the Edwards generally overlies limestones and marls of the Glen Rose Formation. The southern limit of the Edwards Formation is defined arbitrarily by lateral termination of the overlying oxytropidoceroid beds; rocks equivalent to the Edwards are included with overlying units and form an undifferentiated platform sequence designated the Devils River Formation. This platform sequence (Lozo and Smith, 1964, and Smith, 1966) separates the Kirschberg and McKnight lagoonal facies.

Outcrop Facies

Three primary depositional facies and one diagenetic facies are recognized in the outcrop and subcrop of the Edwards Formation. Primary facies include: (1) rudist biohermal-biostromal facies; (2) platform grainstone facies, and (3) lagoonal facies. A diagenetic dolomitic facies is super-

imposed on parts of the primary facies.

Rudist biohermal-biostromal facies. --Biohermal and biostromal reefs are well developed at numerous places in the Edwards Formation, chiefly along the edge of the Comanche Platform and partly around platform lagoons (Fig. 1, 2). In outcrop, reefs are especially numerous in North-Central Texas (Nelson, 1959; Young, 1959; Rodda et al., 1966; Frost, in press) where they formed the north edge of the Comanche Platform and fringed the northern side of the Kirschberg Lagoon; only local bioherms grew along the southern margin of the Lagoon. Individual bioherms are relatively small-scale features with average relief of 10 to 20 feet but locally as great as 50 feet; they consist of a core made up of whole rudist pelecypod shells (in growth position) enclosed in a dense, generally nonalgal, lime mudstone matrix. Flank deposits of coarse, angular, poorly sorted shell fragments dip radially from the core at inclinations up to 35°. Several types of rudists occur in the reef, though the chief building forms are caprinids and radiolitids (Fig. 3). Generally, well-bedded lime grainstones and locally lime mudstones constitute the inter-reef areas. Sediments are well sorted, except adjacent to reefs; nodular to locally bedded chert is a characteristic adjunct. Bioherms along the Platform edge bordering the Ancestral Gulf of Mexico (commonly designated the Stuart City reef trend) are constructed of corals and stromatoporoids in addition to a variety of rudists. Biohermal and biostromal reefs also fringed parts of the McKnight Lagoon in South Texas and northern Mexico and locally developed randomly on the Comanche Platform. Oolitic shoal units (e.g., Whitestone lentil, Moffat lentil, Sweetwater lentil) locally

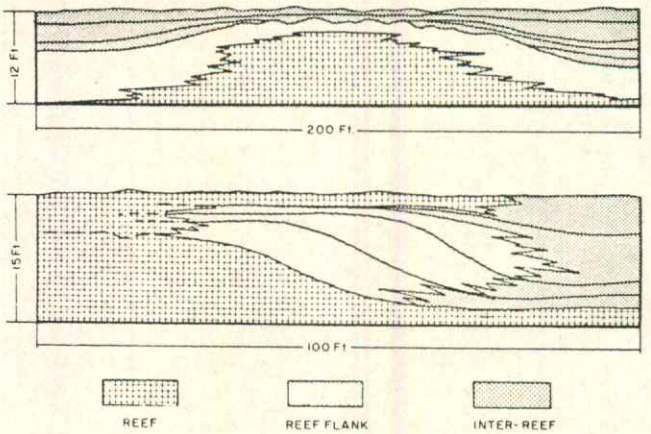

Figure 2. Diagrammatic cross sections, rudist bioherms, Edwards Formation (adapted from Nelson, 1959).

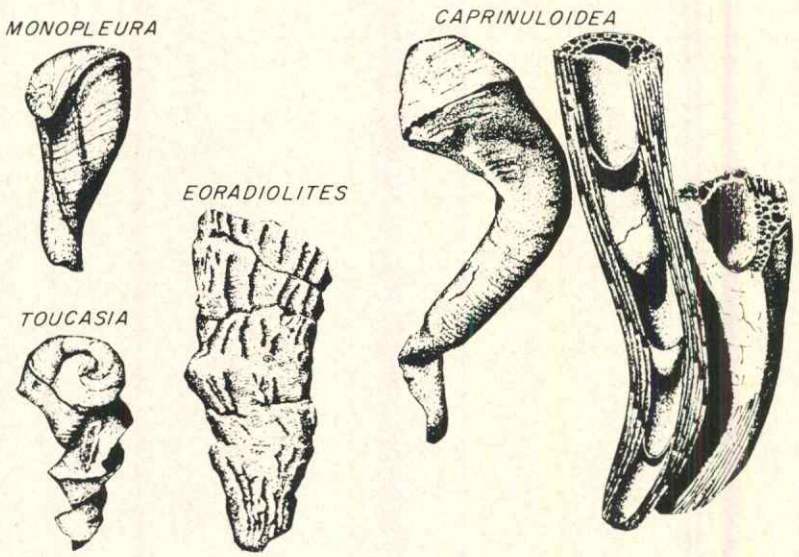

Figure 3. Typical rudist pelecypods, Edwards Formation (adapted from Young, 1959).

developed along the northern margin of the Comanche Platform, possibly along and at the heads of local embayments of the Platform, in areas of relatively high tidal velocities

Platform facies.--The platform (or nonbiohermal) facies consists chiefly of bedded, well-sorted, lime grainstone similar to interreef deposits, interbedded with lime mudstone and rudist lime wackestone. Grainstones commonly are cross bedded and contain abundant miliolid foraminifers; mudstones are thin bedded or massive. Nodular to locally bedded chert occurs throughout much of this facies in outcrop.

Lagoonal facies.--The lagoonal facies, as judged from preserved marginal sections, consists chiefly of thin-bedded to nodular, lime mudstone and thoroughly burrowed lime mudstone; lime grainstones are less common. Gypsum is preserved locally. Evaporite-solution units composed of brecciated and randomly dipping beds are numerous and indicate original wide extent of several evaporite deposits. Four principal evaporite or evaporite-solution units can be mapped in the most centrally preserved parts of the Kirschberg Lagoon (vicinity of Menard), but along the periphery of the Lagoon only one or two evaporite-solution units are prominent. Lagoonal deposits occur stratigraphically in the middle and upper parts of the Edwards Formation and make up about two-thirds of the formation where the lagoonal facies is best developed. The lagoonal facies expanded through time; successively younger evaporite deposits were more widespread and onlapped the surrounding, underlying platform and biohermal facies. This expansion coincided with northward progradation of bioherms fringing the north side of the Kirschberg Lagoon. Evaporite deposits comparable in lithology and stratigraphic position to those of the Kirschberg Lagoon characterize the McKnight Lagoon of South Texas and northern Mexico.

Much of the original evaporite of the Kirschberg Lagoon, and indeed most of the central part of the lagoonal facies, is no longer preserved. Reconstruction of the original lagoon is based on recognition in preserved sections of various evaporite-solution units marking the original extent of evaporite deposits. The nature of these evaporite-solution units depends chiefly on the original thickness of underlying evaporites, amount of evaporite removed, and subsequent groundwater solution and alteration. Lateral variation of these evaporite solution units reflects position relative to the original evaporite lagoon (Fig. 4). The lagoon center zone is marked commonly by at least partial preservation of the underlying evaporite (gypsum) unit so that overlying beds are not extensively disturbed; this zone also is marked by the thickest original accumulation of evaporites. Marginal to the lagoon center zone is the collapse-breccia zone where the original underlying evaporite unit has been completely removed by subsequent solution; this zone is characterized by a lower unit of highly brecciated or conglomeratic rocks succeeded by a sequence with beds dipping in random directions and commonly at relatively steep angles. These brecciated and contorted rocks are especially permeable and as a result they are typically altered; secondary coarsely crystalline calcite is common. Collapse-breccia units generally are 5 to 10 feet thick; overlying strata commonly are undisturbed, indicating that deposition and subsequent solution removal of evaporites within the Edwards Formation (Kirschberg facies) was episodic. Marginal to the collapse-breccia zone and representing the maximum extent of primary evaporite deposition is an evaporite-solution unit characterized by a thin, finely honeycombed rock displaying cuneiform or gash texture resulting from solution of relatively minor amounts of primary evaporite. Similar structures are common in Silurian rocks associated with evaporites in northeastern United States and southeastern Canada (Summerson, 1966). Overlying beds are only slightly disturbed. Evaporite-solution units generally are poorly exposed and difficult to see on the ground except in artificial exposures, but in the preserved parts of the lagoon proper they form distinct patterns on aerial photographs. In outcrops of the marginal facies of

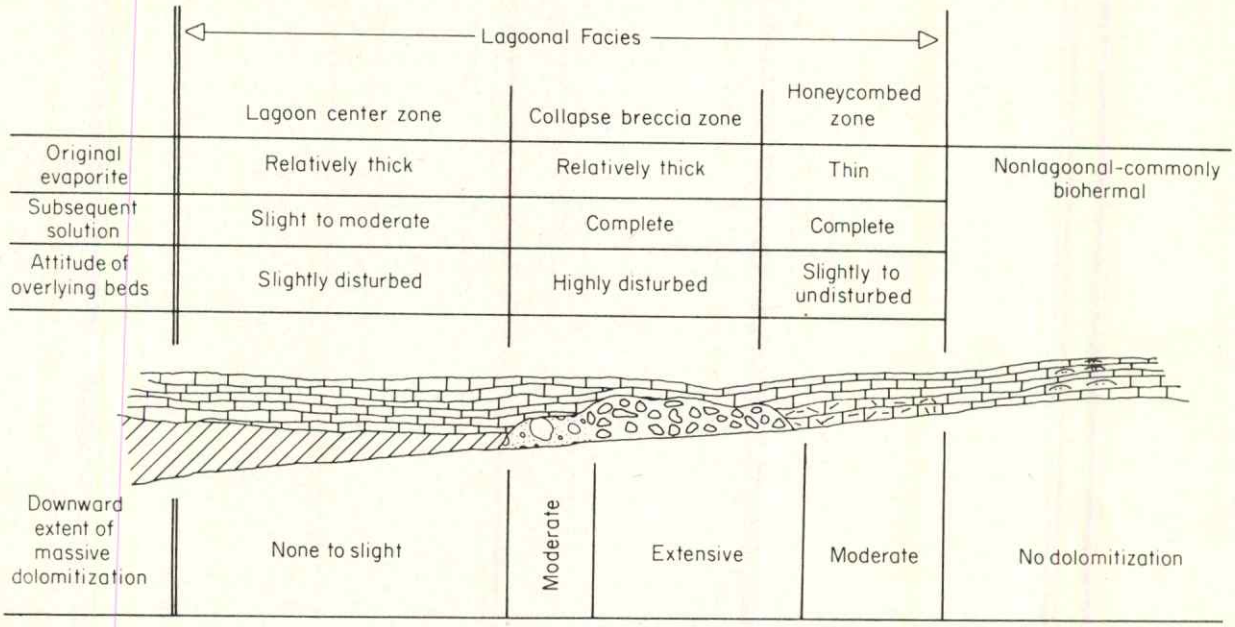

Figure 4. Lateral relationship of evaporite and evaporite-solution units, Edwards Formation.

the lagoon, only the upper one or two solution units, representing the maximum extent of the lagoon, are prominent.

Dolomite facies.--Regional geologic mapping coupled with chemical analyses of approximately 1,200 samples from 250 localities throughout the outcrop area of the Edwards Formation (Rodda et al., 1966) permit reasonably detailed delineation of the dolomite facies (Fig. 5). Dolomite in the Edwards Formation is in part coincident with, but chiefly marginal to, the Kirschberg lagoonal facies. Association of Edwards dolomites and evaporites is similar to that observed on carbonate shelves and platforms throughout the geologic column.

Two main types of dolomite occur in the Edwards Formation, here designated stratal dolomite and massive dolomite (Fig. 6; Table 1). Stratal dolomite is a tightly knit and intergrown mosaic of dolomite crystals. Individual crystals are very small, generally less than 10 microns in diameter; rhombs are poorly developed due chiefly to the crowded or intergrown fabric. Porosity is slight and permeability is practically nil. Stratal dolomite is regularly to irregularly laminated or thin bedded and generally associated with thin-bedded lime mudstones. Locally, thin beds of ripple-marked, cross-laminated lime grainstone containing lime mudstone clasts are interbedded with laminated dolomite; the dolomitic mudstones fill troughs of grainstone ripples (Fig. 7). Fossils are rare except for associated stromatolitic lime mudstones. Mudcracks and rip-up mud clasts are common in stratal dolomites and associated lime mudstones. Individual dolomite units generally are less than 2 feet thick. Evaporite-solution units are rare to common, thin (< 1 inch), inconspicuous, and crust-like (Fig. 7). Magnesium carbonate content of stratal dolomites and associated lime mudstones and dolomitic mudstones vary irregularly from low to high (Fig. 8). Iron oxide content is relatively high. In addition to dolomite mudstone beds, dolomite of similar grain size and fabric locally occurs as matrix in lime grainstones, as fill of animal burrows (Fig. 7), or as shell replacement.

Massive dolomite varies in grain size from fine to coarse, though most crystals are greater than 30μ in diameter. Fabric is a loosely knit mass of euhedral crystals, resulting

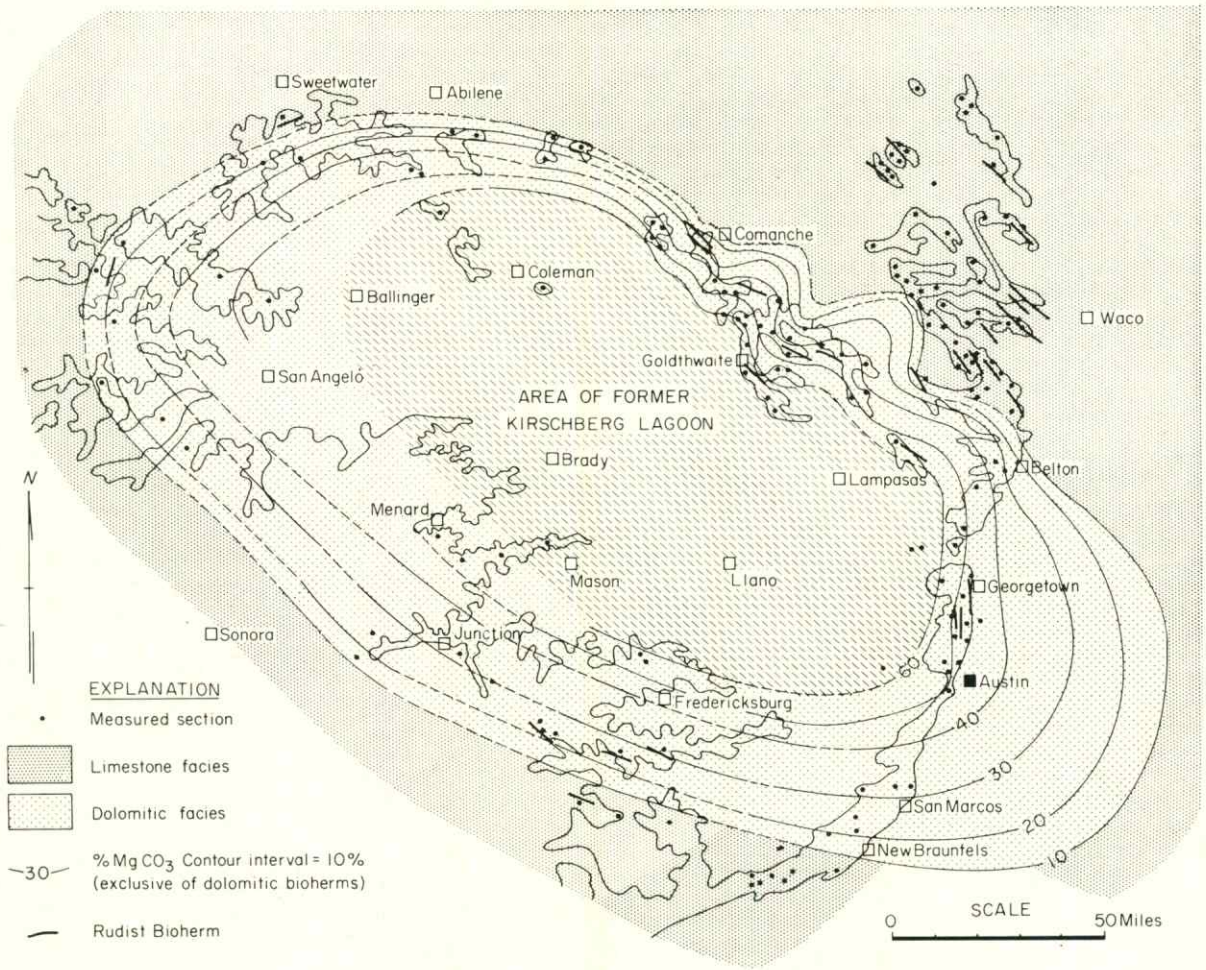

Figure 5. Dolomite distribution and generalized outcrop area, Edwards Formation.

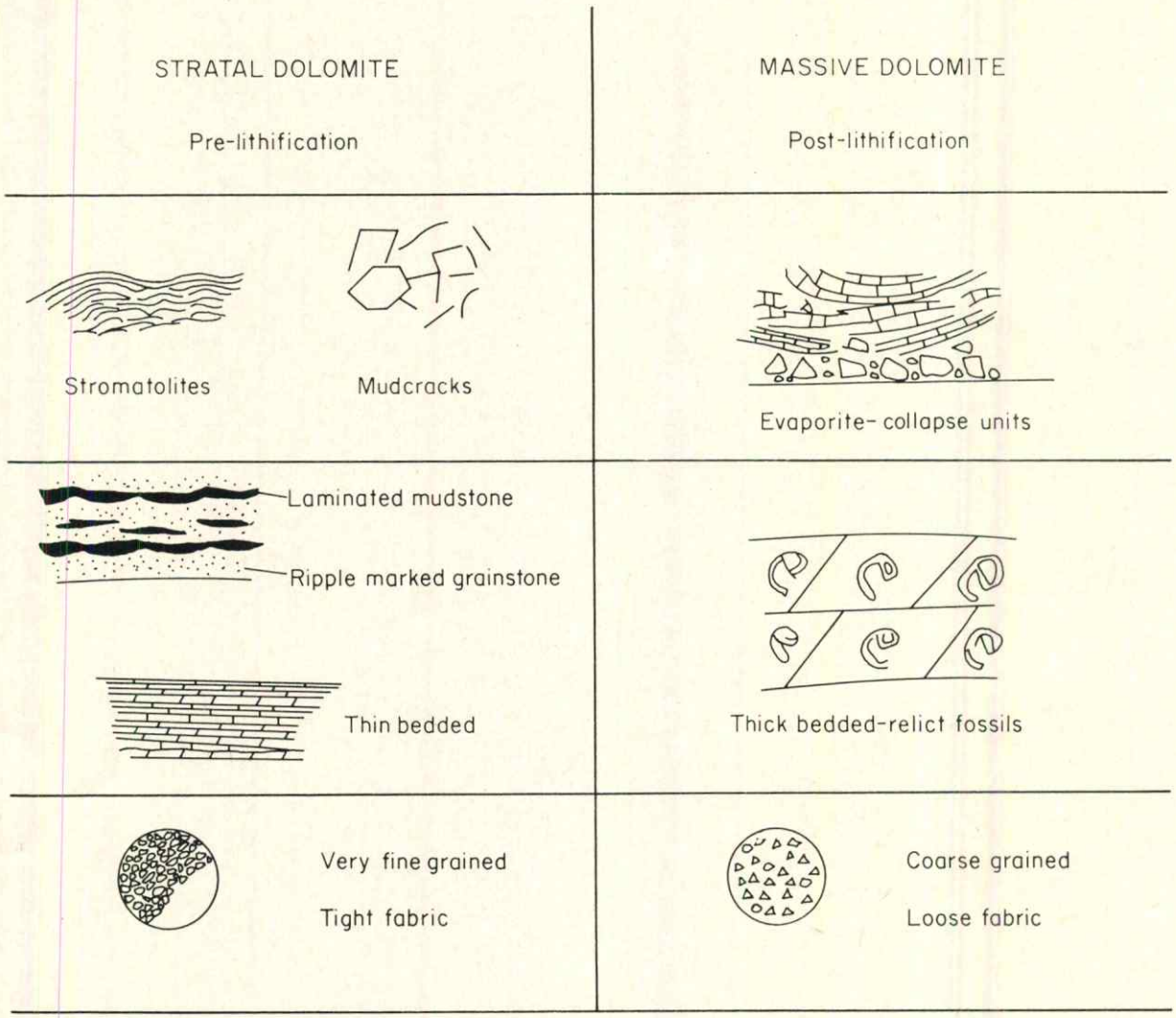

Figure 6. Features of stratal and massive dolomite.

Table 1. Characteristics of principal dolomite types, Edwards Formation, Texas.

	Stratal Dolomite	Massive Dolomite
Grain size	Very fine, average 10 microns	Very fine to coarse, 10 to 150 microns, generally more than 30 microns
Fabric	Tightly knit and intergrown mosaic	Loosely knit mass of euhedral crystals
Porosity	Very low	Moderate to high; pinpoint to vuggy
Crystal shape	Poorly developed rhombs, due to crowding and packing	Well-developed rhombs
Structural occurrence	As specific mudstone beds, selectively in burrow fill and as fossil replacement, and as matrix of lime grainstone	Replaces variety of original rock and textural types but generally other than mudstones
Fossils	Rare	Common to abundant, as typical of Edwards grainstone facies
$MgCO_3$ content among representative samples	Low to high, irregular	Low to very high, but with strongly bimodal frequency; few intermediate values
Fe_2O_3 content	Relatively high	Relatively low
Thickness of individual dolomite units	Thin, generally less than 2 feet	Thick, generally greater than 2 feet, commonly 10 feet, up to 80 feet
Bedding	Generally laminated to thin bedded	Variable, that of host limestone
Sedimentary structures	Mudcracks, stromatolites, mud clasts	Variable, that of host limestone

Table 1 (continued)

Evaporite or evaporite-solution units	Very thin (less than 1 inch) to absent, commonly crust-like	Generally predominant, collapse-breccia or honeycombed solution units overlie dolomite unit
Geographic occurrence	Best developed along southern margin of lagoonal facies and within lagoon	Best developed along northern reef margin of lagoonal facies
Time of formation	Pre-lithification, early diagenetic	Post-lithification, early secondary
Mode of formation	Metasomatic replacement of lime muds in supratidal zone	Metasomatic replacement of permeable grainstones by seepage refluxion of lagoonal brine

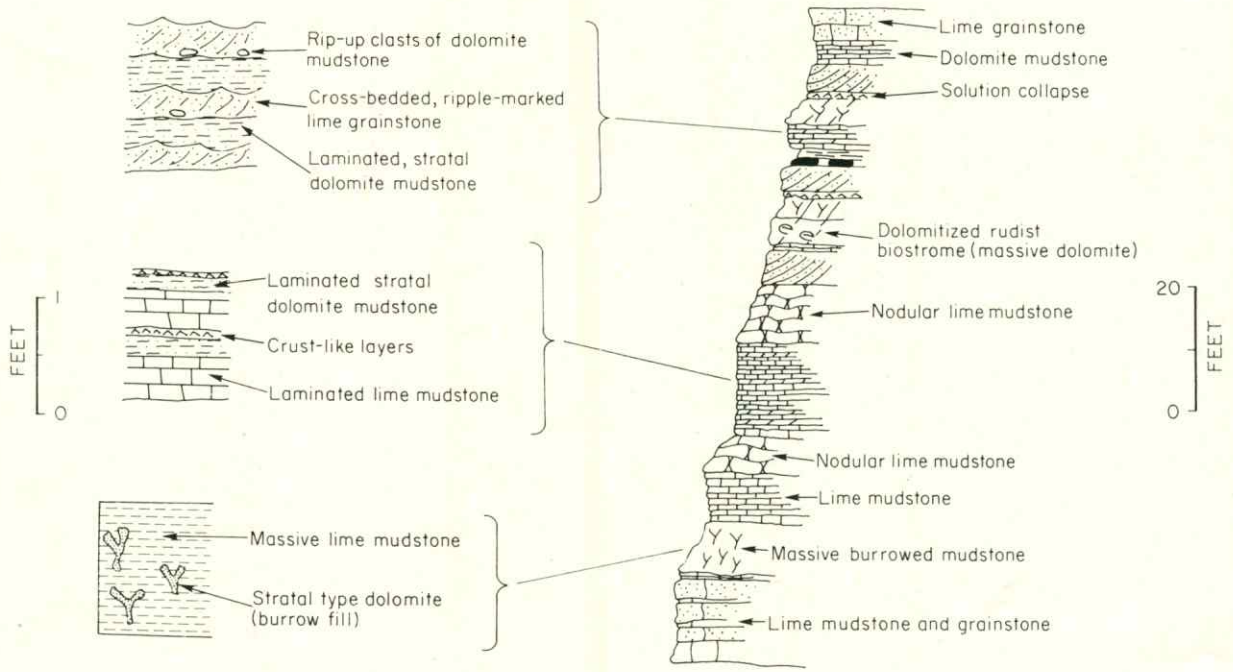

Figure 7. Stratigraphic features of stratal dolomite, Edwards Formation, Mountain Home section, northeastern Kerr County.

in a moderately to highly porous and moderately permeable rock (Fig. 6; Table 1). Massive dolomite typically replaces fossiliferous lime grainstones and displays relict structures of the host limestone. Lime mudstones or reef cores of rudist bioherms with matrix of dense lime mudstone rarely show massive dolomitization, even where adjacent grainstones are extensively dolomitized, indicating an initial permeability control for this type of dolomitization. Massive dolomite sequences are thick, commonly about 10 feet, though locally up to 80 feet thick; a variety of relict structures, indicating a variety of host limestones, may occur in a single massive dolomite sequence. Sequences consisting of several original lime grainstone types may be uniformly dolomitized. Dolomite of this type generally underlies prominent evaporite-solution units and is best developed below the lagoonward edge of the honeycombed zone and outer margin of the collapse-breccia zone (Fig. 4). Magnesium carbonate content of massive dolomites and associated limestones or dolomitic limestones is either high or low with a strong bimodal frequency among several samples (Fig. 8); similar distribution of magnesium carbonate has been reported for dolomite and dolomitic limestones from many different areas (e.g., Graf, 1960). Such distribution indicates that where conditions for massive dolomitization were suitable (i.e., permeable grainstones), dolomitization typically was thorough. Iron oxide content is generally less than that of stratal dolomites.

Origin of Edwards Dolomites

Both stratal and massive dolomites as described herein are judged the products of metasomatic replacement of calcium carbonate from contact with magnesium-enriched brines. The two dolomite types originated in similar chemical environments, the physical environments during formation and times of dolomitization differed. Stratal dolomites are most common along the southern margin of the Kirschberg Lagoon; massive dolomites are most common along the northern margin of the Lagoon. This dolomite distribution was chiefly a function of the configuration and composition of the Lagoon, its surrounding areas, and associated facies (Fig. 9).

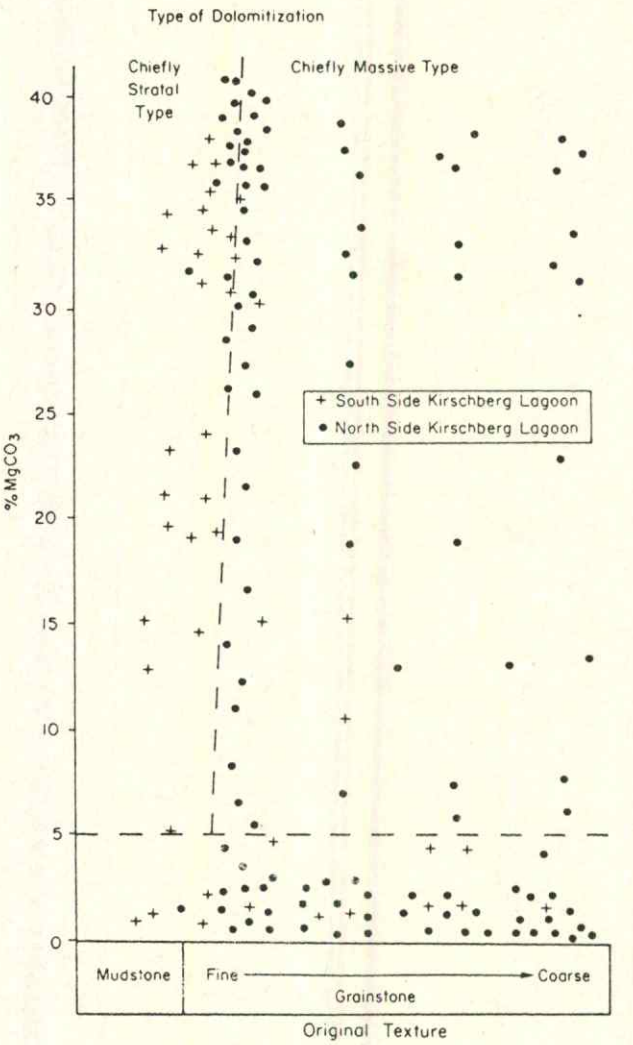

Figure 8. Distribution of magnesium carbonate content versus relict texture.

The northern margin of the Lagoon was marked by fringing, rudist, biohermal and biostromal reefs, separating the Lagoon from the shallow-water, but oceanic, North Texas-Tyler Basin. The northern reef margin was characterized by relatively high and rugged relief and was a depositional environment of moderate to high energy. Reef flank and interreef deposits are

chiefly fine to very coarse lime grainstones and reef detritus, with relatively small amounts of lime mudstone. The southern margin of the Lagoon, by contrast, was a zone of very low relief with an extensive intertidal-supratidal area; biohermal growth was sparse. Except for periods of storms, this area was an environment of low energy in which lime muds and platform grainstones were deposited.

Stratal dolomite.--Features of stratal dolomites (very fine grain size, thin bedding, mudcracks, paucity of fossils, association with thin-bedded lime mudstones and stromatolites (Table 1) suggest deposition under conditions described for certain modern carbonate supratidal and intertidal environments (Curtis et al., 1963; Deffeyes et al., 1965; Ebanks and Tebbutt, 1966; Illing et al., 1965; Kinsman, 1966; Shearman, 1963; Shinn, 1964; Shinn et al., 1965; and Skinner, 1963). These are chiefly low-latitude carbonate mud tidal flats adjacent to warm shallow seas, where dolomite forms in soft aragonitic or calcitic muds commonly in association with gypsum or halite. Requisites for dolomitization appear to be sedimentation essentially at sea level in climates that produce a relatively high net evaporation loss. Under such conditions, evaporation of water trapped at the surface, plus water brought near the surface through capillary movement of salt water, results in concentration of brines in a thin zone at and just below the sediment surface. Calcium content is reduced through precipitation either of calcium carbonate or of gypsum; the remaining heavy brine with a high Mg: Ca ratio is capable of inducing metasomatic replacement of lime muds on contact. First to form is poorly ordered, calcium-rich $Ca{\cdot}Mg(CO_3)_2$ or protodolomite. Subsequently, protodolomite crystals grow larger and better ordered and ultimately, depending on conditions of pH, salinity, and temperature, convert to dolomite. Crystals are generally 1 to 10 μ in diameter. Gypsum precipitated in this process may be removed by solution during subsequent flooding of the tidal flat or during periods of precipitation. Specific geochemical features of the process of dolomitization in supratidal sediments are given by Berner (1966), Deffeyes et al. (1965), Degens (1965), Illing et al. (1965), Kinsman (1966), Land (1966), Peterson and von der Borch (1966), Schmalz (1966), and Shinn et al. (1965).

In addition to sedimentary features of Edwards stratal dolomite which are similar to those described for modern carbonate tidal flats, several lines of evidence show that formation of these dolomites was accomplished prior to lithification. These include: (1) very fine grain size and intergrown, dense fabric, resulting from replacement in non-supported soft muds in contrast to the porous fabric derived from post-lithification replacement; (2) common nondolomitization of solid shells and protected zones beneath shells, though surrounding sediment is thoroughly dolomitized; (3) interbedded dolomitized and nondolomitized rocks of identical texture; (4) thin dolomitized units; and (5) occurrence chiefly as mudstones, a rock type with low permeability; mudstones generally are not dolomitized by refluxing brines (see later under discussion of massive dolomite).

The common replacement of thin lime grainstones or shelly mudstones by dolomite and the interbedding of these dolomitized grainstones with dolomite mudstones of the stratal type suggest that dolomitization of the grainstones could have occurred within a thin zone below the supratidal surface in a bed-for-bed manner by downward and outward sinking magnesium-enriched brines (Fig. 10). In such manner, underlying or adjacent intertidal deposits might also be dolomitized by a process involving refluxion and mechanically similar to that described below as massive seepage refluxion. Dolomitization was, however, fundamentally a part of the supratidal environment. Distinction of grainstones dolomitized in this manner from grainstones dolomitized by massive seepage refluxion is based on stratigraphic association (thin-bedded dolomite grainstones interbedded with thin stratal-type dolomite mudstones). That the heavy brine solutions did not sink far and were probably confined to unconsolidated sediments is

indicated by the characteristic thinness of stratal dolomite units (generally < 2 feet).

Dolomites similar to Edwards stratal dolomites are known from diverse areas and from practically all parts of the geologic column; some have been specifically interpreted as the product of early diagenesis in the supratidal zone. Recently reported stratal-type dolomites from ancient rocks which have features of the stratal type include: Devonian rocks, Indiana (Bluck, 1965); Permian Phosphoria Formation, Bighorn Basin (Campbell, 1962); Triassic Dachstein Formation, Salzburg (Fischer, 1964); Silurian rocks, Pennsylvania (Gwinn and Glack, 1965); Devonian Manlius Formation, New York (LaPorte, 1967); Devonian Sevy Dolomite, Utah and Nevada (Osmond, 1962); Devonian Jeffersonville Limestone, Indiana (Perkins, 1963); Ordovician Beekmantown Group, Maryland (Sarin, 1962); Ordovician Nittany Dolomite, Pennsylvania (Spelman, 1966); and Devonian Martin Formation, Arizona (Teichert, 1965).

Massive dolomite.--In contrast to the very early diagenetic, pre-lithification formation of stratal dolomite, massive dolomite is clearly secondary. This is shown by abundant relict sedimentary structures and fossils indicating that the host rock is a marine, medium- to high-energy lime grainstone or coarse bioclastic limestone rather than a low-energy tidal flat lime mudstone. The fabric is loosely knit and grain size is relatively large.

The relationship of Edwards massive dolomite to evaporite or evaporite-solution units in the adjacent Kirschberg Lagoon indicates a mode of formation of these dolomites clearly attributable to the seepage refluxion model developed by Adams and Rhodes (1960) to explain origin of Permian, shelf-edge dolomites of West Texas. Structural and petrologic features as well as depositional facies of Edwards massive dolomites are similar to shelf- and platform-edge dolomites of the West Texas Permian, and many others.

According to the seepage refluxion model, highly concentrated brines, particularly those remaining after precipitation of lower rank salts (e.g., gypsum), migrate to depressions of the lagoon floor overlying lighter waters prevent further concentration. As depressions fill, brines spill over and escape basinward through permeable substrate zones, generally formed by lime sands and clastics bordering the finging reef or other barrier at the lagoon margin; those parts of the lagoon floor covered by dense anhydrite or halite are practically impermeable. Seepage through permeable zones may be slow and not affect lagoonal circulation pattern through rapid loss of heavy brines; hence the supply of magnesium-enriched brines could be maintained. Refluxing brines are denser than connate water they replace; seepage is downward and outward toward the basin. Extent of dolomitization is limited by changes in composition and character of refluxing brine and host rock. These changes involve chiefly a lowering of the high Mg:Ca ratio as dolomitization proceeds, and alteration of brine temperature, salinity, and alkalinity due to interaction of brine and connate water. Lateral migration of the seepage zone results from transgression of the evaporite lagoon; during regression of the lagoon the previous spillway probably will be sealed by a cover of impermeable evaporites.

Application of the seepage refluxion concept to Edwards massive dolomites suggests a model as indicated in Figure 11. Anhydrite was precipitated in the central and north-central part of the Kirschberg Lagoon which was barred on the north by a series of fringing rudist reefs (Fig. 9). Heavy, magnesium-enriched brines, formed after precipitation of the anhydrite, spilled from the lower part of the Lagoon into the relaitvely permeable reef-grainstone facies along the northern reef margin. Dolomitization was accomplished by downward and outward migration of refluxing brines through permeable grainstones.

Field relationships of Edwards massive dolomites support origin by seepage refluxion. Although massive dolomites occur along the entire margin of the Kirschberg lagoonal facies, they are best developed on

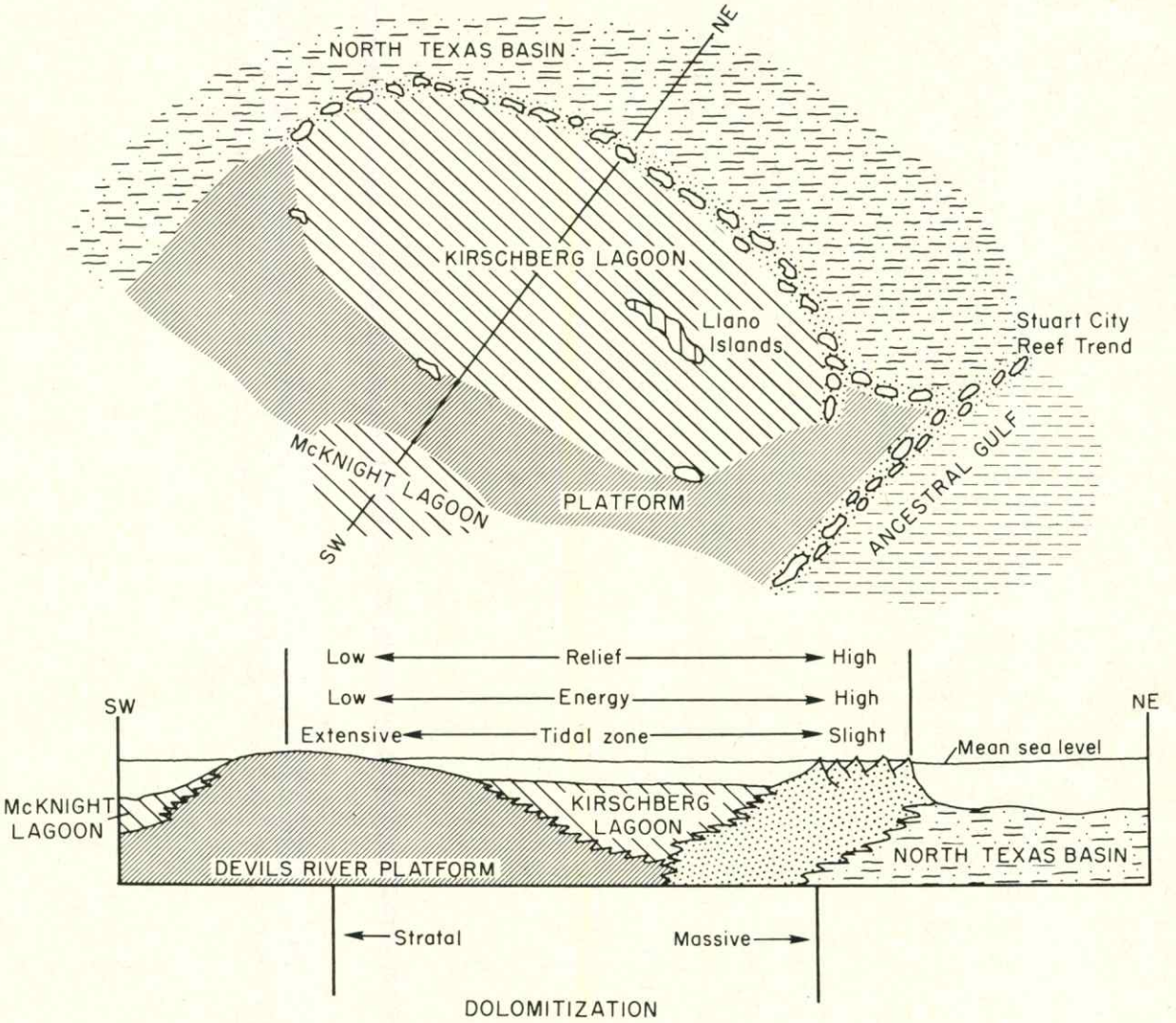

Figure 9. Reconstructed physiography and depositional system of Kirschberg Lagoon.

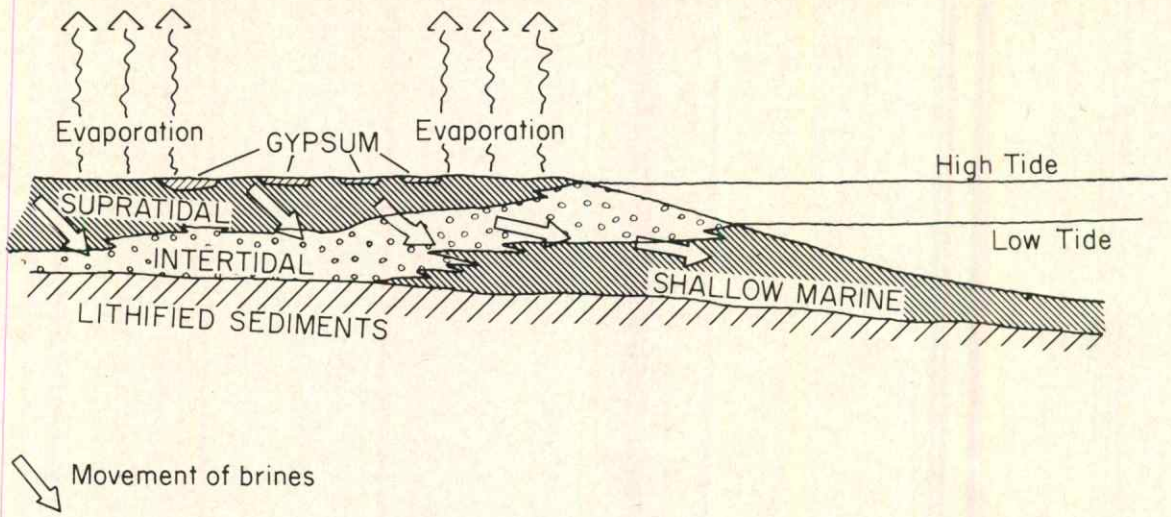

Figure 10. Stratal dolomite model, Edwards Formation (after Rose, 1966).

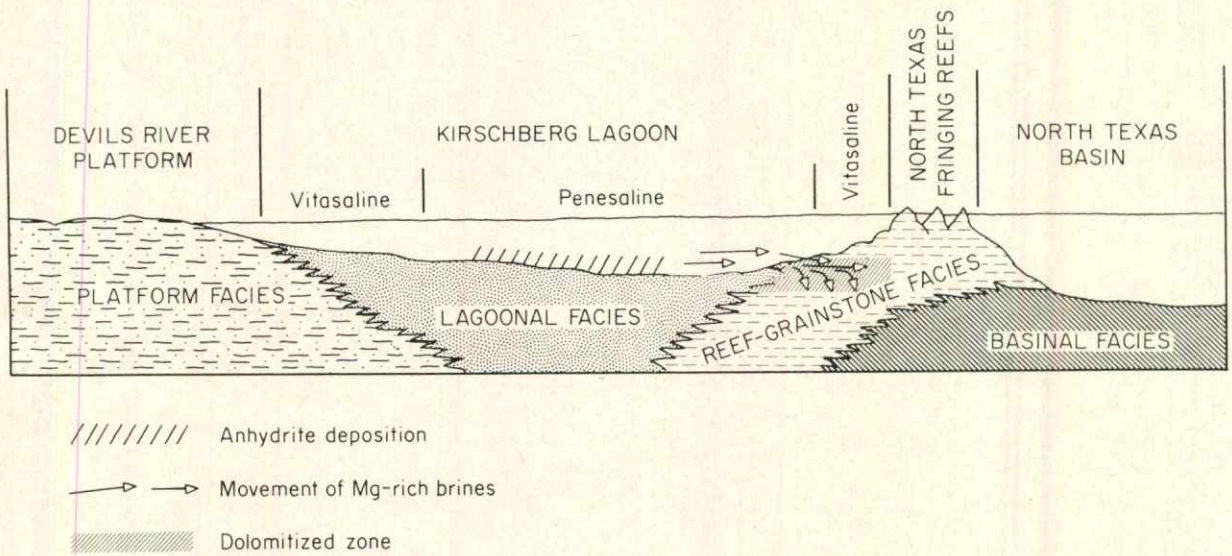

Figure 11. Seepage refluxion model, massive dolomite, Edwards Formation

the north side in a belt coincident with the nearly uniformly permeable grainstone-biohermal facies (Fig. 12; compare with Fig. 5). Within the dolomitized grainstone facies, reef cores with dense lime mudstone matrix are not dolomitized, though surrounding reef-flank and interreef deposits may be completely dolomitized. Locally, nondolomitized grainstones underlie lenses of impermeable mudstone; beyond the mudstone lens, dolomitization extends farther downward. Finally, variation in magnesium content of rocks in this facies is strongly bimodal, with values either high or low but generally not intermediate (Fig. 8). This frequency suggests that if host rock permeability was sufficient to permit any refluxing, it was sufficient for extensive dolomitization; if not, little dolomitization occurred. This bimodal variation contrasts with the irregular variation of stratal dolomites which formed in soft muds.

Massive dolomites of the Edwards Formation characteristically underlie evaporite-solution units. Thickest dolomite units generally underlie the outer part of the collapse-breccia zone and inner part of the honeycombed zone (Fig. 4), suggesting that the most extensive dolomitization occurred

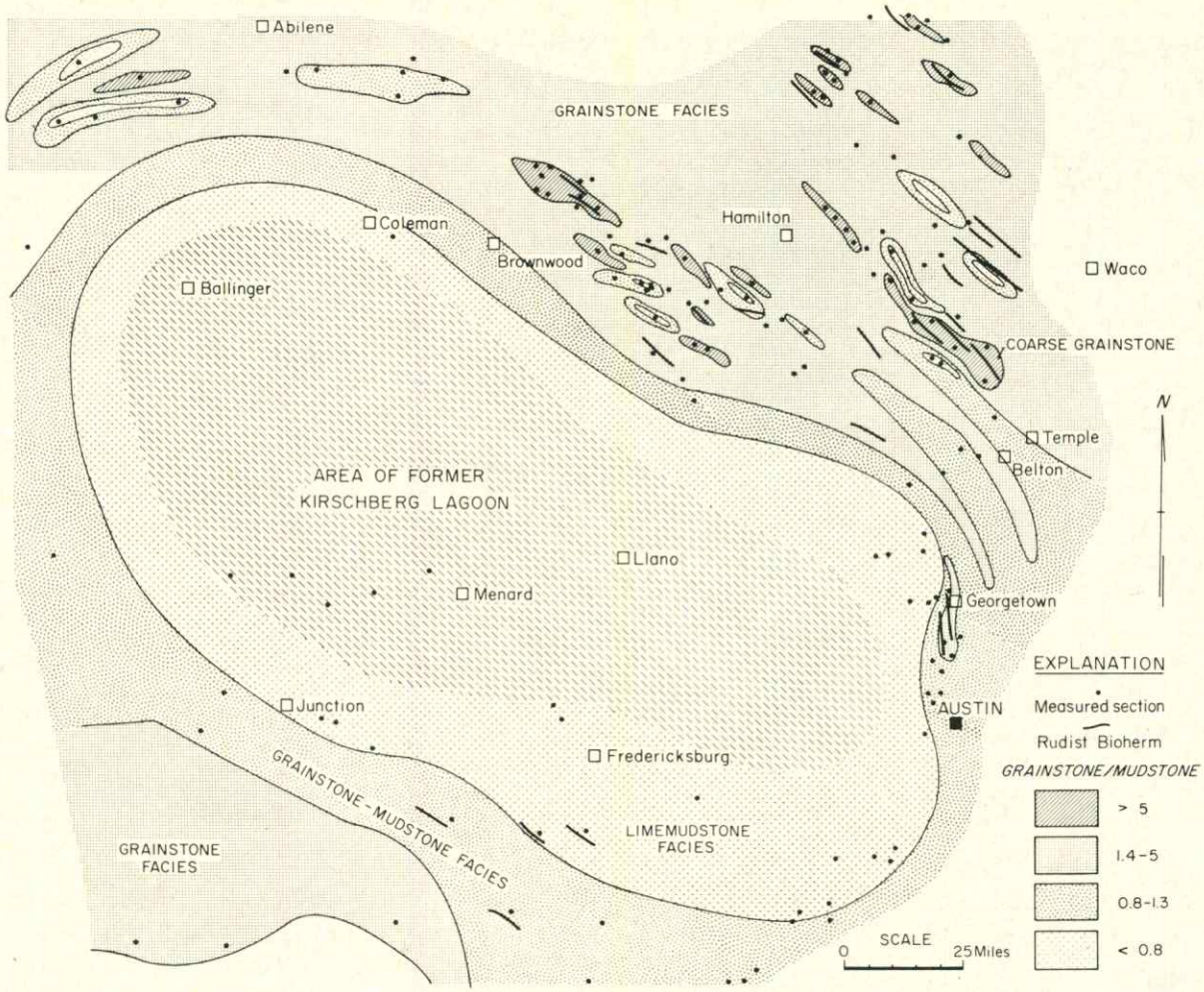

Figure 12. Grainstone:mudstone ratio, Edwards Formation

just marginal to the thicker lagoonal evaporite sequence, approximately at the boundary of the lagoonal and grainstone facies (Fig. 11). The lagoonal margin of the grainstone facies would have been the optimum zone for brine escape. Only moderately thick massive dolomite units (average of 5 feet in thickness) underlie the lagoonward margin of the collapse-breccia zone (Fig. 4), presumably due to relatively earlier seal by impervious anhydrite as the lagoon expanded. Similarly, only moderately thick zones of massive dolomite underlie the most marginal zone of the original lagoon as indicated by the thin honeycombed zone (Fig. 4). As interpreted, these zones were in the path of spilling brines for a shorter period than the intermediate zone.

Alternation of laterally persistent massive dolomite units and non-dolomitized units suggests distinct episodes of dolomitization. Alternation of disturbed evaporite-solution units and nondisturbed strata indicate further that anhydrite deposited during a specific period was chiefly removed by solution within a relatively short period of time and prior to the next period of evaporite deposition.

No modern examples of massive dolomitization by seepage refluxion are known unless the dolomitization of Pliocene-Pleistocene rocks on Bonaire, Netherlands Antilles, reported by Deffeyes et al. (1965), and certain mid-Pacific atolls reported by Berner (1965), are the products of seepage refluxion. Lack of definite modern examples is probably due to scarcity of extensive modern carbonate-evaporite shelves or platforms plus the obvious difficulty in ob-

serving such process in a modern environment. By contrast, many ancient dolomites were apparently formed by seepage refluxion. Significant parts of many ancient carbonate shelves and platforms contain dolomites having petrologic and structural properties as well as depositional relationships (lagoonal evaporites and shelf-edge dolomites) typical of those here described as massive dolomite attributed to seepage refluxion. Some recently described massive type dolomites (some specifically interpreted as the product of seepage refluxion) include: Permian rocks, West Texas (Adams and Rhodes, 1960); Mississippian Madison Formation, Wyoming and Montana (Andrichuk, 1955); Upper Devonian rocks, Alberta (Andrichuk, 1958); Mississippian Lodgepole Formation, Montana (Cotter, 1966); Middle and Lower Paleozoic rocks, Teton Mountains (Dixon and Reeves, 1965); Mississippian rocks, Saskatchewan (Edie, 1958); Devonian rocks, Montana (Lewis and Elliott, 1962); Mississippian rocks, Alberta (Murray and Lucia, 1967); Silurian rocks, Michigan (Sharma, 1966); Ordovician Nittany Dolomite, Pennsylvania (Spelman, 1966); Silurian rocks, Nevada (Winterer and Murphy, 1960).

Fault and fracture dolomite.-- Concentration of dolomite along faults, joints, and fractures has been widely noted (Fairbridge, 1957, pp. 159, 172). Locally in the Edwards, dolomite is present along small fractures or lines cavities associated with both stratal and massive dolomites; much larger grain size (100 to 200 μ) readily distinguishes this type of dolomite from surrounding finer grain dolomites. Such dolomite presumably is late secondary and a product of Pleistocene-Recent weathering. Although occurrences are widespread, late secondary dolomite is volumetrically insignificant. No regional relationship was noted between Edwards dolomites and regional fault or fracture patterns. Pulverulent limestone, another Pleistocene-Recent surficial weathering product associated with the Edwards Formation, is also widespread but volumetrically insignificant.

Distribution of Chert

Distribution of chert in the Edwards Formation is markedly coextensive with Edwards dolomite (Fig. 13). Like dolomite, chert occurs in a belt marginal to the Kirschberg Lagoon, though the chert facies is slightly more extensive. A composite lithofacies map of the Edwards shows a lagoon margin zone of cherty dolomite, grading peripherally to a narrow cherty limestone zone which in turn grades outward to limestones free of dolomite and chert (Fig. 14). Only about 3% of the chert in the Edwards is bedded; the remainder is nodular, occurring as nodules from less than 1 inch in diameter up to masses as large as 4 by 10 feet. Of approximately 150 outcrop occurrences of dolomite recently examined, 70% contain chert. Biohermal reef-flank deposits generally are not cherty but within the dolomite facies they are characteristically thoroughly dolomitized. As such, they constitute the only dolomite rock unit consistently free of chert. Absence of chert in reef-core and reef-flank deposits apparently is common in many ancient reefs. Most dolomite in the Edwards is the massive type formed by replacement of lime grainstone. A high correlation of chert and dolomite necessarily means a high correlation of chert and original lime grainstone; however, within the cherty limestone facies less than 20% of the chert occurs with lime mudstone or lime wackestone (based on approximately 250 field observations in this facies), indicating a high correlation of chert and lime grainstone independent of dolomite. Edwards chert typically contains relict structures and fossils of enclosing limestone which, with other considerations, indicate a secondary origin for most of the chert. Interstitial silica is generally < 1% in both Edwards limestones and dolomites; no significant difference exists among the several rock types (e.g., between dolomite, cherty dolomite, limestone, cherty limestone).

Explanation of the origin of Edwards chert must consider, among

others: (1) a secondary origin, (2) association of chert with medium- to high-energy lime grainstones, suggesting a permeability control in formation, (3) regional coextensive distribution of chert and dolomite marginal to a restricted carbonate-evaporite lagoon, suggesting a mode of origin related to that of dolomites, (4) consistent absence of chert in the reef-core and reef-flank environments within the cherty grainstone facies, suggesting an environmental control of the silica source (e.g., possible environmental restriction of siliceous sponges to the now cherty interreef environment). Investigations of the origin of Edwards chert by the writers are currently in progress.

Acknowledgments

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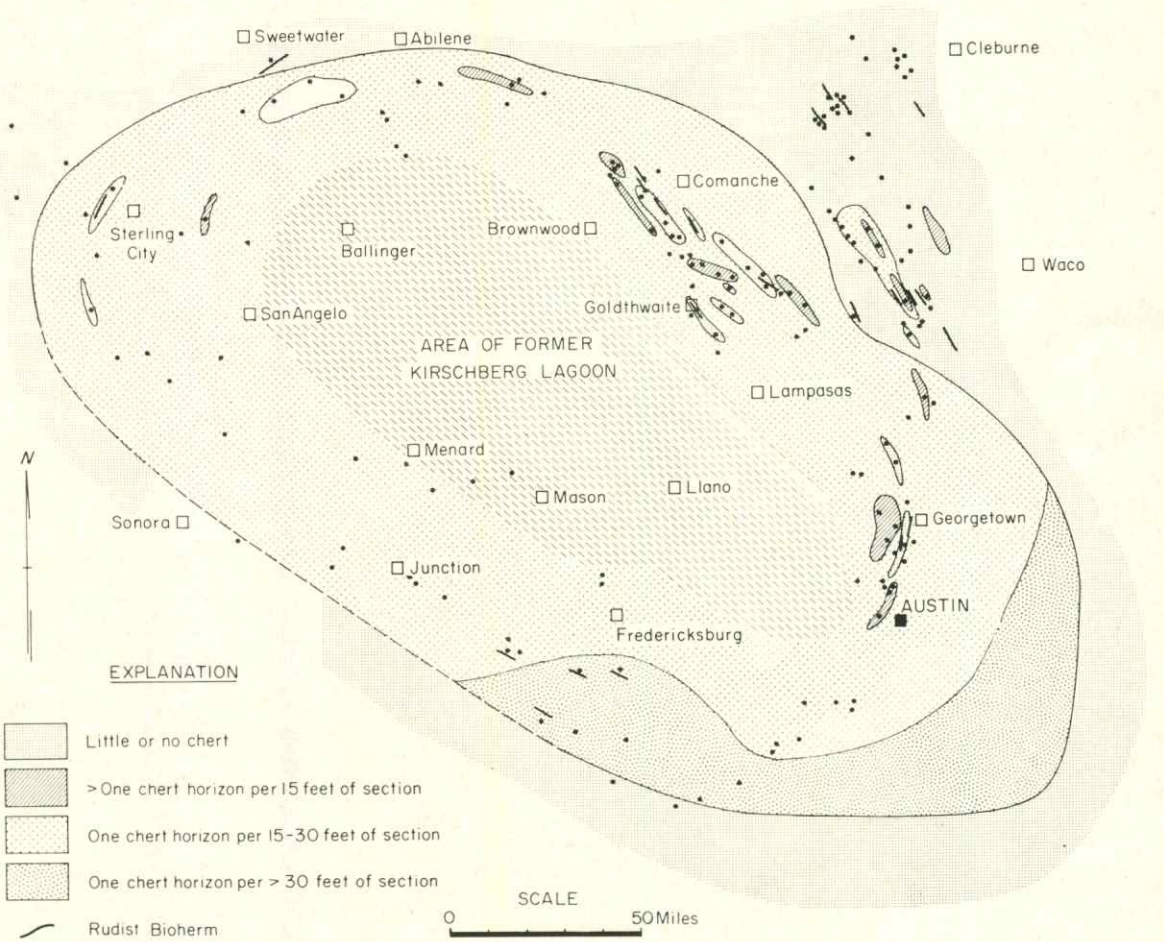

Figure 13. Distribution of chert, Edwards Formation.

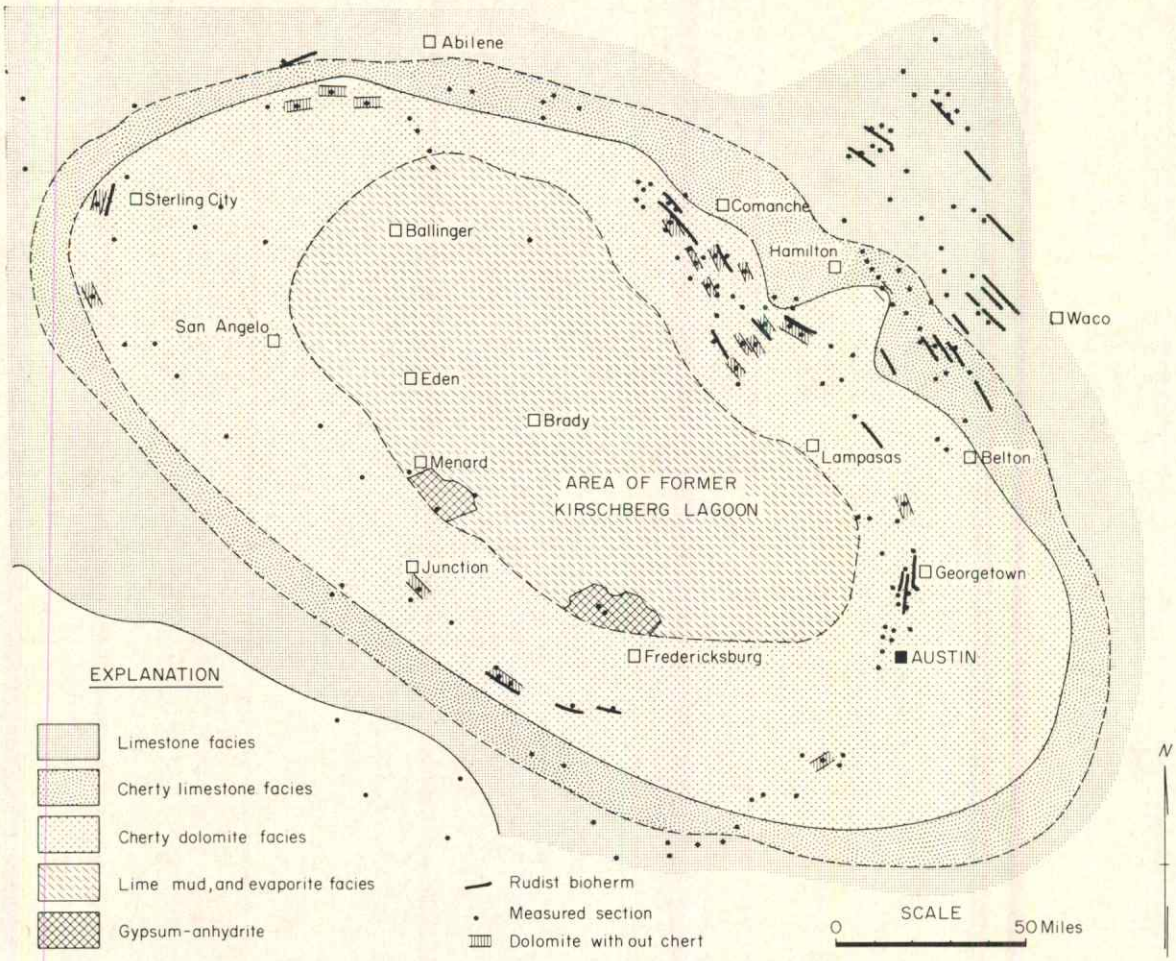

Figure 14. Composite lithofacies map, Edwards Formation.

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CEMENT RAW MIX CONTROL THROUGH X-RAY EMISSION SPECTROSCOPY

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ABSTRACT

A technique for plant control utilizing x-ray emission spectroscopy is presented which permits a rapid and accurate determination of the major elements in cement raw mix which has been formulated through a combination of varying lithologic units. The procedure utilizes the powder method thereby avoiding the use of dilution or fusion techniques. Elemental compositions are determined through the elimination of particle size effects by sufficient grinding and empirical calculations necessary due to the varying degrees of absorption resulting from fluctuations in the elemental composition of the sample. Utilization of the elemental determinations are reflected in raw mix control which is accomplished through specific oxide ratios calculated to predetermined phase compositions.

INTRODUCTION

The production of portland cement involves the quarrying, crushing, proportioning, and burning of geologic materials which may vary widely in mineralogy and chemical composition. Proportioning these materials to formulate a chemical mixture through which a high quality product of consistent uniformity may be produced is the major objective of a cement manufacturer. Uniformity of the mix and constant feed rate, regardless of variations in raw materials, must be maintained in order to provide raw mix which does not demand continual adjustments of kiln fuel or feed due to chemical fluctuations.

Elemental analysis of cement raw mix may be accomplished through x-ray emission techniques providing specific characteristics of the procedures are understood. The relative intensity between a standard and an unknown are usually just approximate measures of the unknown since matrix effects and the concentration of the element determines the intensity of its characteristic radiation. Specifically, matrix effects are generally considered as self-absorption and interelement effects. Evaluating these effects and thereby providing a useful and workable method of analysis through x-ray emission is usually approached by use of internal standards, comparison with standards approximate in composition to the unknowns, dilution with transparent materials, or the lesser used mathematical corrections (Anderman, 1961; Zemany, et. al., 1954).

Analytical determinations through x-ray emission and subsequent control of cement raw mix has been accomplished by minimizing the mineralogical and elemental effects through fine grinding and utilization of fusion (Anderman, 1961; Burnstein, 1961; and Rose et. al., 1963), and internal standard techniques (Brown, 1963). Kester (1960), in evaluating methods of control using pressed powder samples, has indicated a necessity of large libraries of standards of similar mineralogy and chemistry as the unknown samples. Burnstein (1962) in working with a common element in several minerals cites examples where fine grinding tends to reduce the difference in intensities normally associated with variations in mineralogy. The method presented by the author and used at the Chanute Plant of the Ash Grove Lime and Portland Cement Company utilizes the powder method, fine grinding, and empirical calculations for corrections due to interelement effects.

Raw mix control through x-ray emission spectroscopy is accomplished by utilization of empirical calcula-

tions for elemental oxides and oxide ratios equated to desired pre-determined phase compositions of the cement clinker. The ratio of Al_2O_3/Fe_2O_3 is used to control the sandstone and shale feeders and the tricalcium aluminate phase while the CaO/SiO_2 ratio is used to control the limestone feeder and the tricalcium silicate phase.

RAW MATERIALS

The basic raw materials for the production of portland cement at the Chanute, Kansas plant are obtained from Pennsylvanian limestone, shale, and sandstone of the Kansas City group and minor quantities of iron ore from central Texas. Specifically, the limestone which comprises approximately 80 percent of the mix is derived from varying amounts of the Lane-Bonner Springs shale and the Cottage Grove sandstone member of the Chanute shale.

Chemically, all of the basic raw materials except for the iron ore and shale tend to be highly variable as indicated on Table 1. The Raytown limestone, as illustrated on Table 1, may be divided into three distinct chemical and lithologic units. Unit 1, the uppermost 8' of the member, is heavily argillaceous and grades into unit 2 which is a 6' section of a relatively pure limestone with thin interbedded shale seams. The lowermost section of this member, designated as unit 3, is approximately 25' thick and is a relatively pure limestone with very little interbedded shale. In addition to the vertical variability, the Raytown also varies considerably in lateral attitude due to the presence of irregular clay seams filling vertical joints.

The Lane-Bonner Springs shale appears to be fairly uniform over a large area with the greatest variation as illustrated on Table 1. The Cottage Grove sandstone member, however, displays as much variability as the Raytown limestone and may also be divided into three distinct units with the top unit, unit number 1, consisting of approximately 6 to 10' of interbedded grey shale and argillaceous sandstone. Unit 2 is sharply divided from unit 1 and 3 and is a 10 to 12' section consisting primarily of a fine grained, yellow to red, quartzose sandstone which is slightly micaceous. Unit 3 is similar to unit 2 except it is blue-grey in color, partly argillaceous, and much more micaceous.

Table 1. Chemical analyses of Chanute Plant raw materials.

	Lane-Bonner Springs shale		Raytown limestone			Cottage Grove sandstone				
Unit	1	2	1	2	3	1	- -	2	- -	3
SiO_2	55.22	53.66	11.82	6.12	2.56	73.02	90.30	86.00	88.06	88.30
Al_2O_3	15.34	19.99	3.95	2.15	0.88	13.82	6.41	7.99	6.03	6.23
Fe_2O_3	4.28	3.97	1.75	1.35	0.86	3.94	1.29	1.29	1.83	1.05
CaO	7.20	5.40	43.60	48.53	52.37	0.15	tr	0.05	tr	0.25
MgO	2.26	2.31	1.77	1.47	0.94	tr	tr	tr	tr	tr
loss	11.59	9.34	36.42	39.94	42.18	4.79	1.33	1.86	1.67	1.67
Na_2O	0.80	0.88				1.16	1.24	1.48	1.16	1.60
K_2O	2.48	2.56				2.00	0.64	0.88	0.60	0.68

THEORY

A favorable attribute of material to be analyzed through x-ray emission techniques is the samples have a compositional range of elements which are reasonably small. Cement raw mix falls into this category, but consists primarily of varying combinations of geologic materials in which the elements of interest are low in atomic number and are present in a variable matrix. In order for a useful technique of x-ray emission spectroscopy to be applied to raw mix the various factors affecting the reproducibility and accuracy must be understood and adequately corrected. These factors are particle size, mineralogy, and interelement effects due to the varying chemical composition of the matrix.

Particle size

Variations in particle sizes in a single component system can often cause significant changes in the emitted intensity. Burnstein (1961) has shown that the fluorescent intensity from a pure material will increase as the particle size is decreased. In multiphase systems the intensities from several phases may all increase, decrease, or one may decrease while others increase. The latter is the case in cement raw mix as shown in Figure 1 where the intensities of calcium K-alpha and aluminum K-alpha decrease while the intensities of iron, silica, and potassium K-alpha increase with a reduction in particle size. Additionally, as the size of the individual components are reduced uniformly, the intensities appear to level off after a specific size is attained (Fig. 1). Further grinding or reduction in particle size beyond this point does not add any appreciable benefits to the samples.

During the course of calibration of the previously described standards, it was determined that sufficient grinding of all the sample virtually eliminated the effects normally attributed to mineralogy or variations in particle size. This concurred with the findings of Burnstein (1961) and applied to any sample derived from any unit as previously described. In addition, to the previous results, mineralogically different samples from another company exhibited the same results.

Interelement effects

In order for quantitative results through x-ray emission to be meaningful, it is imperative to relate the measured intensity of a particular wave length to the percent composition in a specific sample. With single component systems, free of mineralogical and particle size effects, the intensity - percent composition relationship is linear. In the multi-component system, this linear relationship is not always true, due to the presence of other elements in the system.

The phenomenon responsible for non-linearity in a multi-element system is commonly called the interelement effect. This effect can either be in the form of enhancement or absorption. Enhancement generally occurs when characteristic fluorescent wave lengths from elements in the matrix excite the characteristic radiation of the element under study. Absorption occurs when the elements within the matrix absorb the characteristic radiation of the desired element. This effect occurs when an element in the matrix possesses an absorption edge slightly greater than the wave length of the desired line or has a mass absorption coefficient significantly larger than the mass absorption coefficient of desired element.

Since cement raw mix is a multi-element system, it is logical to assume that these effects will be present. Consequently, Figure 2, was prepared in which the mass absorption coefficient vs. wave length of several elements in raw mix are plotted. By observing Figure 2, it is apparent that specific elements will have a pronounced effect on others. Calcium K-alpha radiation, for example, will be strongly absorbed by potassium since calcium K-alpha has a wave length slightly less than the absorption edge of potassium.

Additionally, aluminum K-alpha will be absorbed by iron due to the high mass absorption coefficient of iron while silica K-alpha should be slightly absorbed by aluminum due to the proximity of the aluminum K-edge. Although magnesium is not a problem at the Chanute Plant and therefore is not determined routinely, it should be pointed out that in the analysis of this element it would be expected that a correction would have to be made due to the high mass absorption coefficient of iron at the magnesium analytical line.

STANDARDS

The raw mix standards, as previously mentioned, were derived from varying combinations of the Raytown limestone, Lane-Bonner Springs shale, Cottage Grove sandstone, and iron ore. Two specific sets of standards of dissimilar mineralogies were prepared and labeled as "I" and "F" series. The "I" series were compounded from varying amounts of limestone (units 1, 2, & 3), shale, and sandstone (units 1 & 2) while the "F" series were formulated from limestone (unit 3), sandstone (unit 2), and iron ore. This particular procedure for the formulation of the standards was done since Type I cement clinker may be produced from normal materials and shale, while Type II cement clinker must be made from selected materials plus additional iron and little or no shale in order to limit the amount of tricalcium aluminate.

Five samples of each series were collected directly from the raw mill discharge. The spread in composition was obtained by varying the material feeder system to insure a range of samples which would encompass the maximum and minimum chemical limits of any future combination. Following the collection of the standards, each sample was analyzed three times through x-ray emission techniques utilizing a fusion method incorporating heavy absorber in the melt as outlined by the procedure developed by Rose, Flanagan, and Alder (1963). The average of the three analyses of each sample was then used as the true chemical value (Table 2) for purposes of calibration.

Table 2. Chemical analyses of raw mix standards.

Standard	I-1	I-2	I-3	I-4	I-5
SiO_2	17.55	16.15	13.97	12.05	10.80
Al_2O_3	4.24	4.04	3.81	3.38	3.21
Fe_2O_3	2.33	2.23	2.04	1.85	1.80
CaO	39.03	41.33	42.22	43.68	44.97
TiO_2	0.23	0.19	0.16	0.12	0.10
SrO	0.12	0.12	0.13	0.15	0.17
K_2O	0.72	0.66	0.58	0.48	0.45
Na_2O	0.28	0.29	0.26	0.21	0.20
loss	33.15	34.49	35.66	36.59	37.59

Standard	F-1	F-2	F-3	F-4	F-5
SiO_2	20.20	18.10	15.89	14.32	12.95
Al_2O_3	3.05	2.87	2.79	2.73	2.47
Fe_2O_3	2.96	2.62	2.60	2.62	1.97
CaO	38.28	39.88	41.47	42.27	43.61
TiO_2	0.17	0.14	0.13	0.12	0.08
SrO	0.13	0.15	0.16	0.17	0.19
K_2O	0.36	0.34	0.33	0.33	0.31
Na_2O	0.35	0.34	0.29	0.28	0.25
loss	32.70	34.00	35.10	35.70	36.66

SAMPLE PREPARATION

For ease of rapid powder sample preparation, a mold consisting of a stainless steel ring (½" high, 1¼" inside diameter, and ¼" wall thickness) mounted on a highly polished steel block was used in preparing the sample pellets. A stainless steel rod 0.030" diameter less than the inside diameter of the ring was used as a ram for compacting the sample. By pressing several samples of a raw mix standard, it was determined that the most reproducible results were obtained at pressures of nine tons per square inch. Samples prepared below six tons per square inch do not compact to a dense pellet and consequently have a tendency to deteriorate on the surface exposed to the x-ray beam. As the pressure exceeds eleven tons per square inch, the ring becomes strained so that upon release of pressure the pellet cracks as a result of the ring flex-

ing. Therefore, nine tons per square inch was used as the pressure for making the dry powder mount.

As previously discussed, the size of the individual particle within the sample significantly affects the intensity. Consequently all the standards and unknown samples were ground sufficiently to where the intensities of the individual elements appear to reach equilibrium which was 6 minutes as illustrated on Figure 1. In all raw mix powder samples, five grams of sample and 100 mg of dodecyl sodium sulfate were ground in a Buehler mill with a tungsten carbide vial.

INSTRUMENTATION

The instrument used by the author was a General Electric XRD-6 vacuum spectrometer with a chromium target x-ray tube which was operated at 50 KVP and 50 MA. A flow proportional counter tube with 0.00015" aluminized mylar windows plus an EDT crystal and a 0.020 x 1½" soller slit with a standard beam tunnel were used for the determinations of all the elements discussed in this report. The flow proportional counter tube was operated at 1750 volts for the determination of silica, potassium, calcium, and iron with PR gas (90% argon, 10% methane) supplied at the rate of 60 bubbles per minute as measured in one inch of water. Aluminum was determined through the aid of pulse height selection and consequently the voltage applied to the counter tube varied slightly over a period of time, but was approximately 1550 volts with a 2 volt base and a 4 volt channel width.

EXPERIMENTAL RESULTS

The graphical illustration of the calibration curves corresponding to the chemical analyses in Table 2 are displayed in Figures 3-9. In all cases, the samples were prepared in the manner previously described while standard sample F-3 was utilized as the primary standard and thereby used to correct the count levels of all other samples in the event of minor drift in the instrument.

As discussed previously, the ideal situation in x-ray emission analysis is when the intensity of the element to be determined is a linear function of the weight percentage present. Unfortunately, this situation does not always exist due to varying amounts of other elements in the matrix. In the analysis of cement raw mix using powder samples, it was determined that the intensity - percent relationship was linear for the analysis of Fe_2O_3 and SiO_2. In the analysis of CaO and Al_2O_3, however, the linear relationship did not exist and thereby necessitated a mathematical correction due to varying amounts of interfering elements in the matrix.

Ferric oxide

Figure 3 illustrates the calibration curve for the analysis of Fe_2O_3. As may be observed, the calibration standards fit the calibration curves extremely well with the exception of standard sample I-5 which displays the most deviation from the curve. Although this sample does not fit the curve perfectly, the percentage as determined by the calibration curve would only be 0.06% lower than the true value for this one sample with the other calibration standards being within 0.03% of the values indicated by the calibration curve.

Anderman (1961) in the analysis of Fe_2O_3 in raw mix through fusion techniques, applied a correction due to the varying amount of calcium among samples. The data resulting from the samples discussed in the report, however, was not improved by considering the slight correction due to calcium. Additionally, the difference in the mineralogical phases responsible for the varying iron contents among the samples did not affect the linear attitude of the intensity - percent relationship.

Silicon dioxide

Figures 4 and 5 are the graphical results of the silicon dioxide analysis. The samples illustrated on Figure 4 are representative of the fineness produced in the raw mill-85% passing 200 mesh. In viewing this figure, it may be readily observed

that a reasonable calibration curve could be drawn for each series separately. To the casual observer, this could suggest three possible conditions; 1) difference in mineralogy, 2) enhancement or absorption effects, or 3) particle size effects. By re-examining Figure 2, it could be concluded that aluminum in the matrix could promote a negative absorption effect of silica as is experienced in the analysis of ceramic materials (Zemany et. al., 1954), but this theory was discounted since the range of aluminum in the samples is extremely small. Consequently, this leaves mineralogy and/or particle size. In order to rule out these possibilities the samples were ground in the manner previously described until 100% passed the 400 mesh. The results of the finely ground samples, which plot as a linear curve, are compiled on Figure 5 and immediately reveal the necessity of adequate particle size distribution prior to calibration. Additionally, it appeared that no noticeable effects were present due to mineralogy providing the samples were ground to sufficient fineness.

Calcium oxide

The graphical results of the Calcium oxide analysis are illustrated on Figures 6 and 7. Figure 6 displays two conditions; 1) samples as received from the raw mill and illustrated by the dashed lines, and 2) samples ground to a size of 100% passing 400 mesh indicated by the solid lines. A definite improvement may be noted in the ground samples, but it is obvious that another effect is present since all the points do not plot as a single linear line. By observing Figure 2, the effect responsible for the non-linear attitude of the points is the strong absorption of calcium K-alpha radiation by the potassium K-edge. If the level of potassium remained constant, this effect would be an insignificant problem, but with a variable amount of potassium in the matrix a method of correction is necessary.

For raw mix control, potassium is not analytically determined at the Chanute plant. Therefore, a system whereby calcium could be determined in a matrix containing variable amounts of potassium was derived. Such a system merely utilized the difference of the potassium counts per second of the unknown sample and the primary standard as in the following equation with the results as illustrated on the calcium oxide calibration curve - Figure 7.

Ic = Io e EXP.(0.03156 delta k)
where
Ic = corrected intensity
Io = observed intensity
delta k = (cps potassium of unknown - cps potassium of standard)/1000

Aluminum oxide

The uncorrected aluminum oxide calibration curve is illustrated on Figure 8. The dashed line represents the best fit of the ten standards while the solid line represents the best fit by least squares. Since neither is acceptable for control analysis, a method had to be derived which would consider any interfering elements within the matrix. Observing Figure 2 again, it is apparent that iron would absorb aluminum K-alpha radiation by virtue of the high mass absorption coefficient of iron as compared to aluminum. In addition it is also apparent that a silica matrix would produce a slight enhancement effect of aluminum.

Considering these previous statements, a mathematical correction was derived in which the percentage of iron and silica in the matrix were utilized in the aluminum intensity correction. The corrected Al_2O_3 calibration curve is illustrated on Figure 9 and was computed by the following equation;

Ic = Io e EXP.(0.024 Cfe - 0.0003 Csi)
where
Ic = corrected intensity
Io = observed intensity
Cfe= % Fe_2O_3 in sample
Csi= % SiO_2 in sample

CORRELATION OF SAMPLES

The samples utilized in this procedure as standards are of two widely

dissimilar mineralogical groups as pointed out earlier. Through procedures of proper grinding and mathematical correction for interelement effects, all of these samples have been calibrated and equated to single linear curves for each element discussed. In order to further test the validity of these curves and equations, several additional raw mix samples were obtained from another company utilizing different materials. The results between the other company's wet determinations (average of 6) and the results obtained by the method described in this report are extremely good as illustrated on Table 3.

RAW MIX CONTROL

Generally, portland cement clinker is a mixture of man-made minerals which in specific combinations lead to properties such as high strength, low heat of hydration, resistance to sulfate attack, etc. Control of the minerals constituents responsible for these properties can only be accomplished by the ability to analytically determine the composition of vast quantities of highly variable raw materials rapidly.

Specifically, cement chemists are usually interested in the tricalcium silicate (C_3S) and the tricalcium aluminate (C_3A) minerals in which the phase calculation involves the utilization of the percentage of Fe_2O_3, SiO_2, CaO, and Al_2O_3. Control of these phases demands control of the raw materials responsible for the addition or deletion of these oxides in the mix. Since each raw material is fed independently into a raw mill, analysis of the resulting mixture of all the materials can be equated to the various delivery speeds of the individual raw material feeders.

Raw mix control at the Chanute plant is accomplished by initially analyzing the raw mill discharge periodically for Al_2O_3 and Fe_2O_3 and relating these figures to the expected tricalcium aluminate as determined on the nomograph, Figure 10. In the production of Type I clinker, the major materials contributing Al_2O_3 and Fe_2O_3 are shale and sandstone respectively. Since the ratio of these two materials govern the tricalcium aluminate phase, controlling the rate of delivery of these materials will control the C_3A. This is accomplished by using the nomograph, Figure 10, to determine the potential C_3A of the sample. If the sample falls outside the desired range of 10 - 12 percent tricalcium aluminate for type I clinker, the difference between the correct percentage of Al_2O_3 necessary to produce the proper C_3A and the observed percentage of Al_2O_3 in the sample is calculated. The shale feeding system is then adjusted proportionately to provide the correct amount of Al_2O_3 using an average value of seventeen percent Al_2O_3 in the shale.

Obviously the limestone tends to be rather variable depending on quarry location. If during the pro-

Table 3. Correlation of mineralogically dissimilar samples from Company X as determined on calibration curves.

	Company X-Standard #1		Company X-Standard #4	
	Wet Analysis*	X-Ray Analysis**	Wet Analysis*	X-Ray Analysis**
SiO_2	13.59	13.48	14.16	14.10
Fe_2O_3	1.94	2.03	2.12	2.18
Al_2O_3	2.90	3.06	3.08	3.21
CaO	42.60	42.55	42.15	42.03

*Average of 6 analyses
**X-Ray analyses utilizing curves and equations as illustrated on Figures 3, 5, 7, and 9.

cess of production, the limestone received is heavily argillaceous as in unit 1 of Table 1, appropriate calculations are undertaken for the additional Al_2O_3 which demand lesser adjustments of the shale feeder. During the production of Type II, a similar method of correction is utilized except the controlling factor is the sandstone feeder. In this case the sandstone feeder is adjusted proportionately utilizing an average Al_2O_3 content of the sandstone of 6.50 percent while the iron ore feeder is held constant.

Following the proper adjustment of the Al_2O_3 and Fe_2O_3 by regulating the sandstone-shale ratio on the feeding system, the tricalcium silicate phase must be regulated by correcting the ratio of CaO to SiO_2. This is done by independently adjusting the limestone feeder while keeping the shale and sandstone feeders in the ratio previously determined. Since the plant has four holding tanks, the material is ground so that every other holding tank will be slightly high in CaO while the other two will be slightly low. As the tanks are filled, they are homogenized and sampled. The four major oxides are determined utilizing the previously described calibration cruves. Following this determination, the potential C_3A is verified and the CaO/SiO_2 is calculated for each holding tank. As additional kiln feed is needed, proportionate parts of two holding tanks, a high and a low calcium, are pumped into the blending tanks with the proper proportion of each holding tank determined by the desired CaO/SiO_2 ratio as plotted on Figures 11 and 12, CaO/SiO_2 as clinker C_3S. The specific curve utilized is dictated by the type of mix being ground. For example, a mix proportioned from limestone-sandstone-shale would apply to Figure 11 (Type I raw mix) while a mix proportioned from limestone-sandstone-iron ore would utilize Figure 12 (Type II raw mix).

Utilization of this method of control applied at the Chanute Plant has yielded results of plus or minus 1.0% C_3S and plus or minus .75% C_3A in the resulting clinker over a production period of 30 days regardless of the variability of raw materials. In addition, it has allowed the plant chemist to re-adjust the material handling system due to variations in the basic components and thereby continually produce a uniform feed. Since the total time of analysis is approximately 20 minutes, the adjustments may be made rapidly enough to accomodate significant changes.

CONCLUSIONS

X-ray emission analysis of cement raw mix samples may be accomplished with little consumption of time and provide results of sufficient accuracy to be utilized for control purposes. In application of such a method, however, it is essential that particle size and interelement effects are corrected. Utilization of the method described, including the empirical calculations for absorption effects, has been applied to several samples of different mineralogy than the standards. The agreement between the wet and x-ray analyses is excellent and thereby suggests the method could be applied to other cement plant materials.

Control of the individual lithologic components in raw mix has been accomplished at the Chanute Plant and has lead to a system whereby the resulting mineralogical phases of the resulting clinker can be controlled within relatively close limits. Beyond producing a uniform product, control of the clinker mineral phases should promote more even fuel consumption plus increased production by virtue of constant kiln feed.

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cess of production, the limestone received is heavily argillaceous as in unit 1 of Table 1, appropriate calculations are undertaken for the additional Al_2O_3 which demand lesser adjustments of the shale feeder. During the production of Type II, a similar method of correction is utilized except the controlling factor is the sandstone feeder. In this case the sandstone feeder is adjusted proportionately utilizing an average Al_2O_3 content of the sandstone of 6.50 percent while the iron ore feeder is held constant.

Following the proper adjustment of the Al_2O_3 and Fe_2O_3 by regulating the sandstone-shale ratio on the feeding system, the tricalcium silicate phase must be regulated by correcting the ratio of CaO to SiO_2. This is done by independently adjusting the limestone feeder while keeping the shale and sandstone feeders in the ratio previously determined. Since the plant has four holding tanks, the material is ground so that every other holding tank will be slightly high in CaO while the other two will be slightly low. As the tanks are filled, they are homogenized and sampled. The four major oxides are determined utilizing the previously described calibration cruves. Following this determination, the potential C_3A is verified and the CaO/SiO_2 is calculated for each holding tank. As additional kiln feed is needed, proportionate parts of two holding tanks, a high and a low calcium, are pumped into the blending tanks with the proper proportion of each holding tank determined by the desired CaO/SiO_2 ratio as plotted on Figures 11 and 12, CaO/SiO_2 as clinker C_3S. The specific curve utilized is dictated by the type of mix being ground. For example, a mix proportioned from limestone-sandstone-shale would apply to Figure 11 (Type I raw mix) while a mix proportioned from limestone-sandstone-iron ore would utilize Figure 12 (Type II raw mix).

Utilization of this method of control applied at the Chanute Plant has yielded results of plus or minus 1.0% C_3S and plus or minus .75% C_3A in the resulting clinker over a production period of 30 days regardless of the variability of raw materials. In addition, it has allowed the plant chemist to re-adjust the material handling system due to variations in the basic components and thereby continually produce a uniform feed. Since the total time of analysis is approximately 20 minutes, the adjustments may be made rapidly enough to accomodate significant changes.

CONCLUSIONS

X-ray emission analysis of cement raw mix samples may be accomplished with little consumption of time and provide results of sufficient accuracy to be utilized for control purposes. In application of such a method, however, it is essential that particle size and interelement effects are corrected. Utilization of the method described, including the empirical calculations for absorption effects, has been applied to several samples of different mineralogy than the standards. The agreement between the wet and x-ray analyses is excellent and thereby suggests the method could be applied to other cement plant materials.

Control of the individual lithologic components in raw mix has been accomplished at the Chanute Plant and has lead to a system whereby the resulting mineralogical phases of the resulting clinker can be controlled within relatively close limits. Beyond producing a uniform product, control of the clinker mineral phases should promote more even fuel consumption plus increased production by virtue of constant kiln feed.

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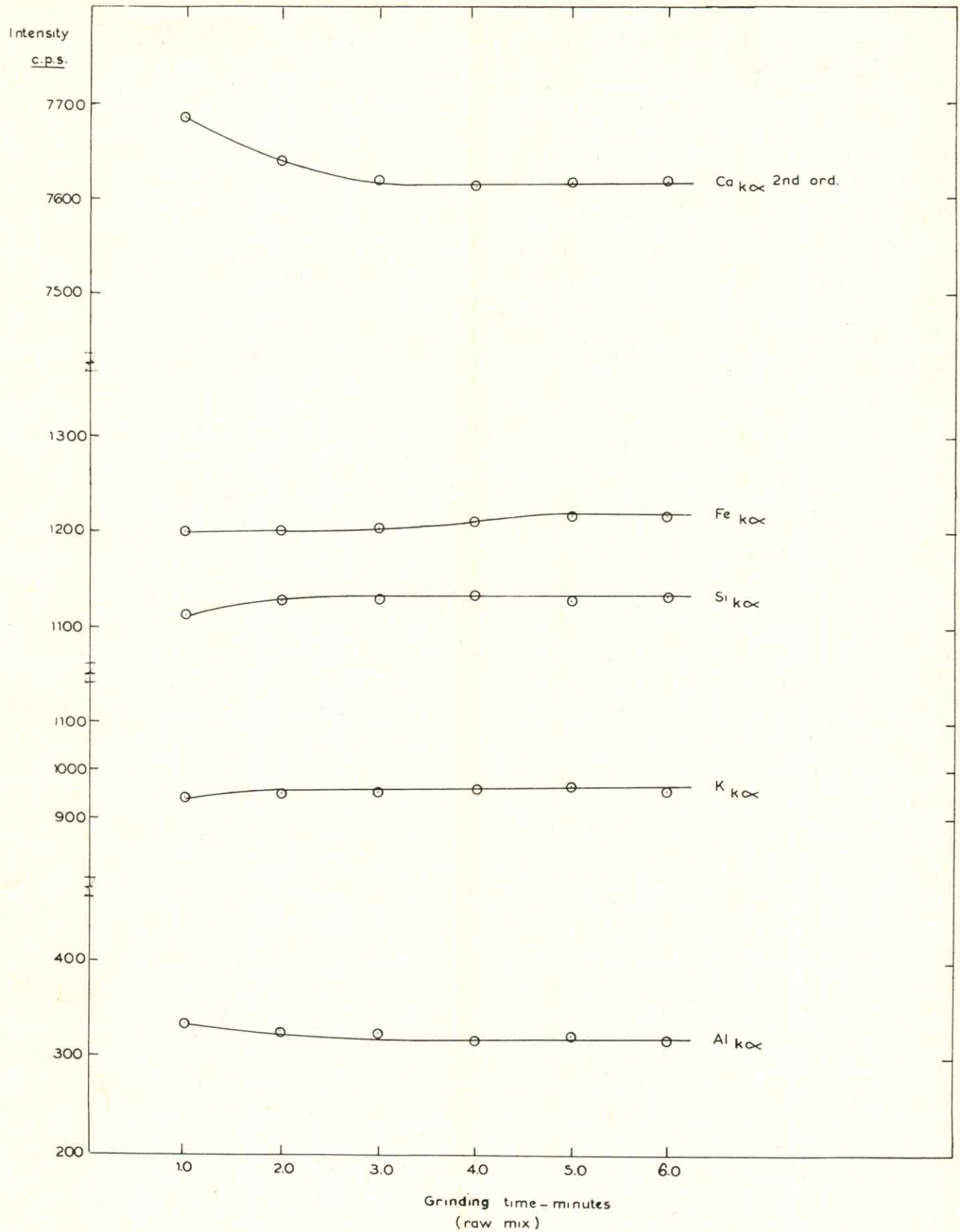

Figure 1. Grinding time vs intensity

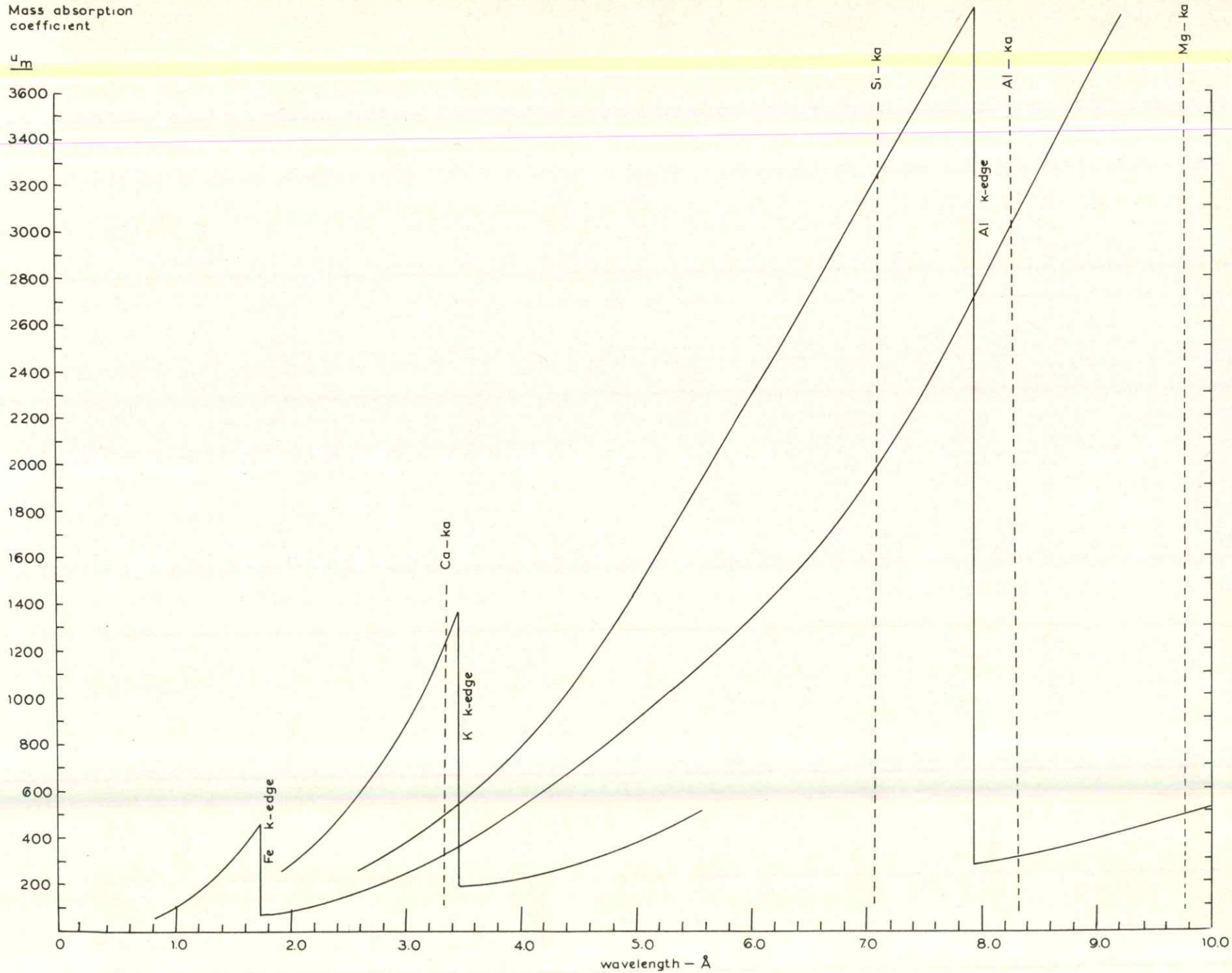

Figure 2. Mass absorption coefficient vs wavelength

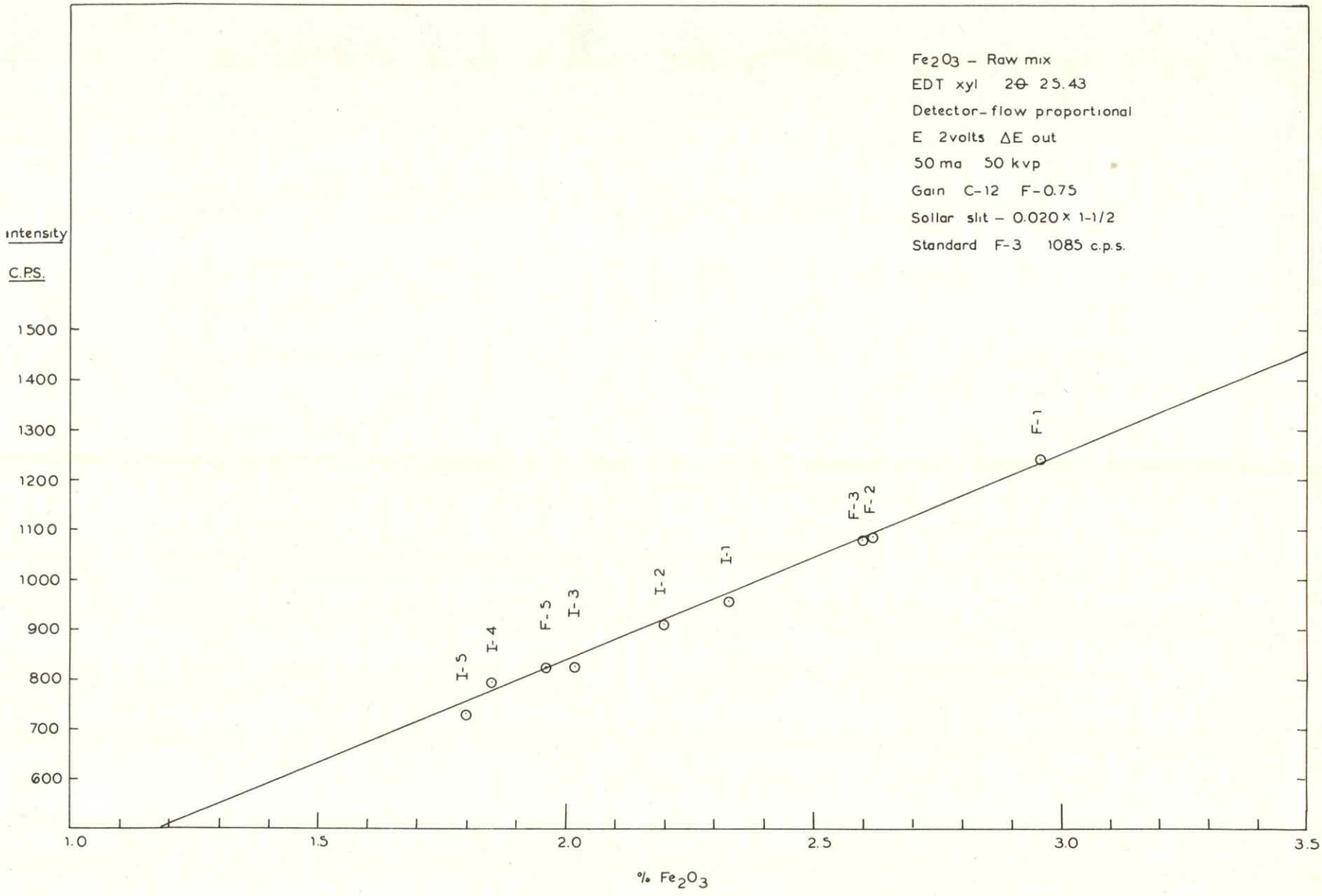

Figure 3. Percent Fe_2O_3 vs intensity

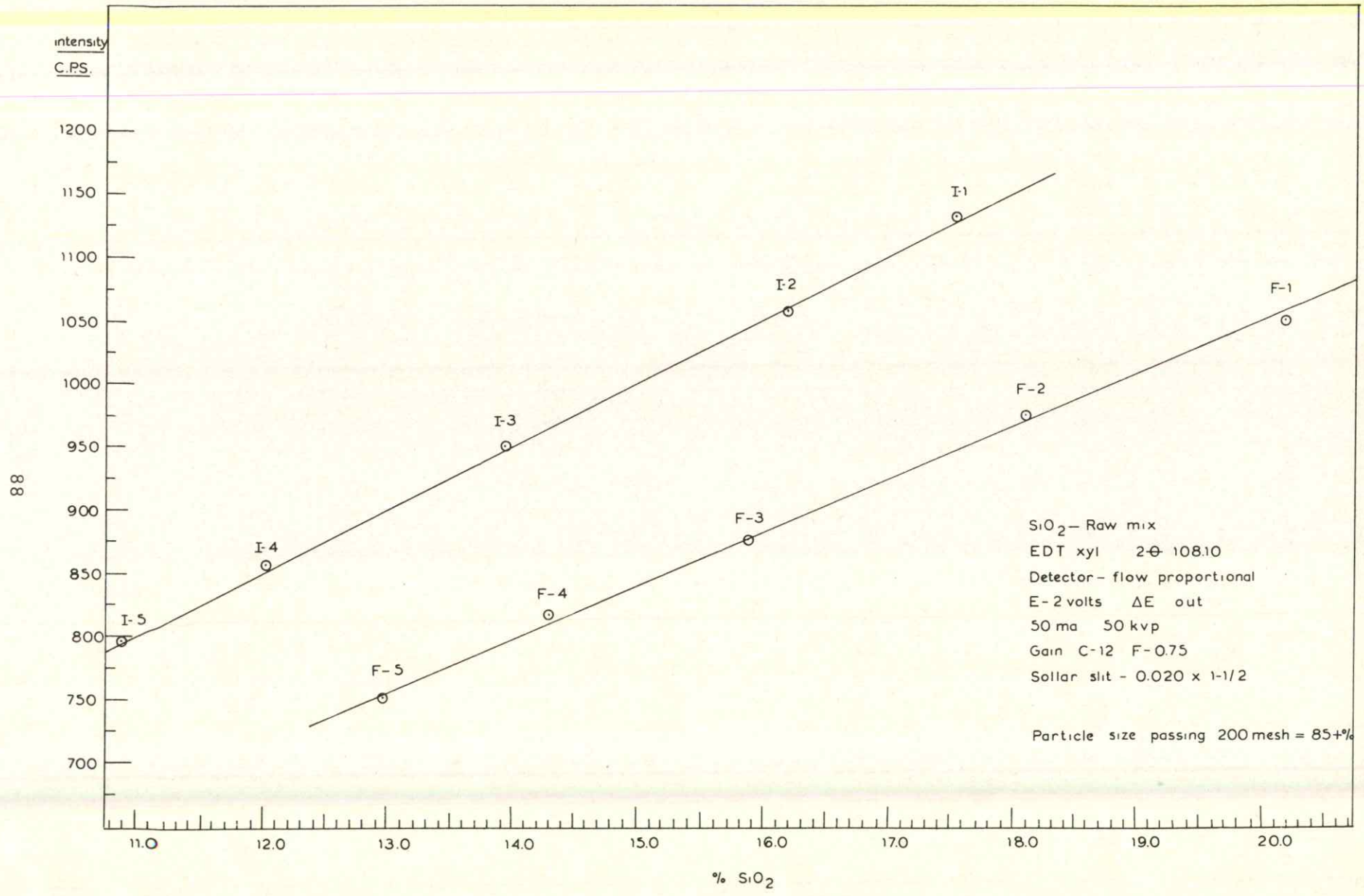

Figure 4. Percent SiO_2 vs intensity (particle size passing 200 mesh = 85+%)

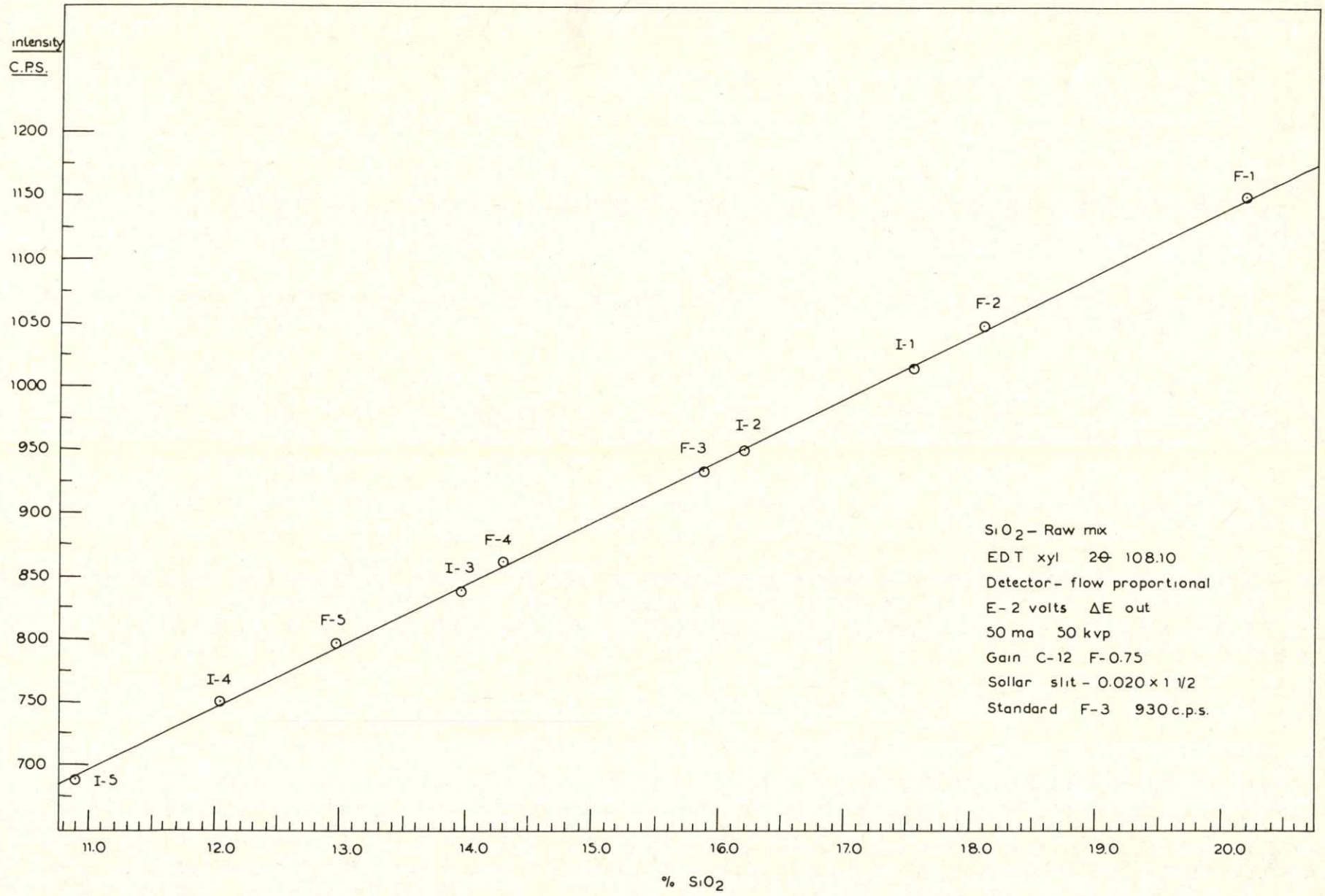

Figure 5. Percent SiO_2 vs intensity

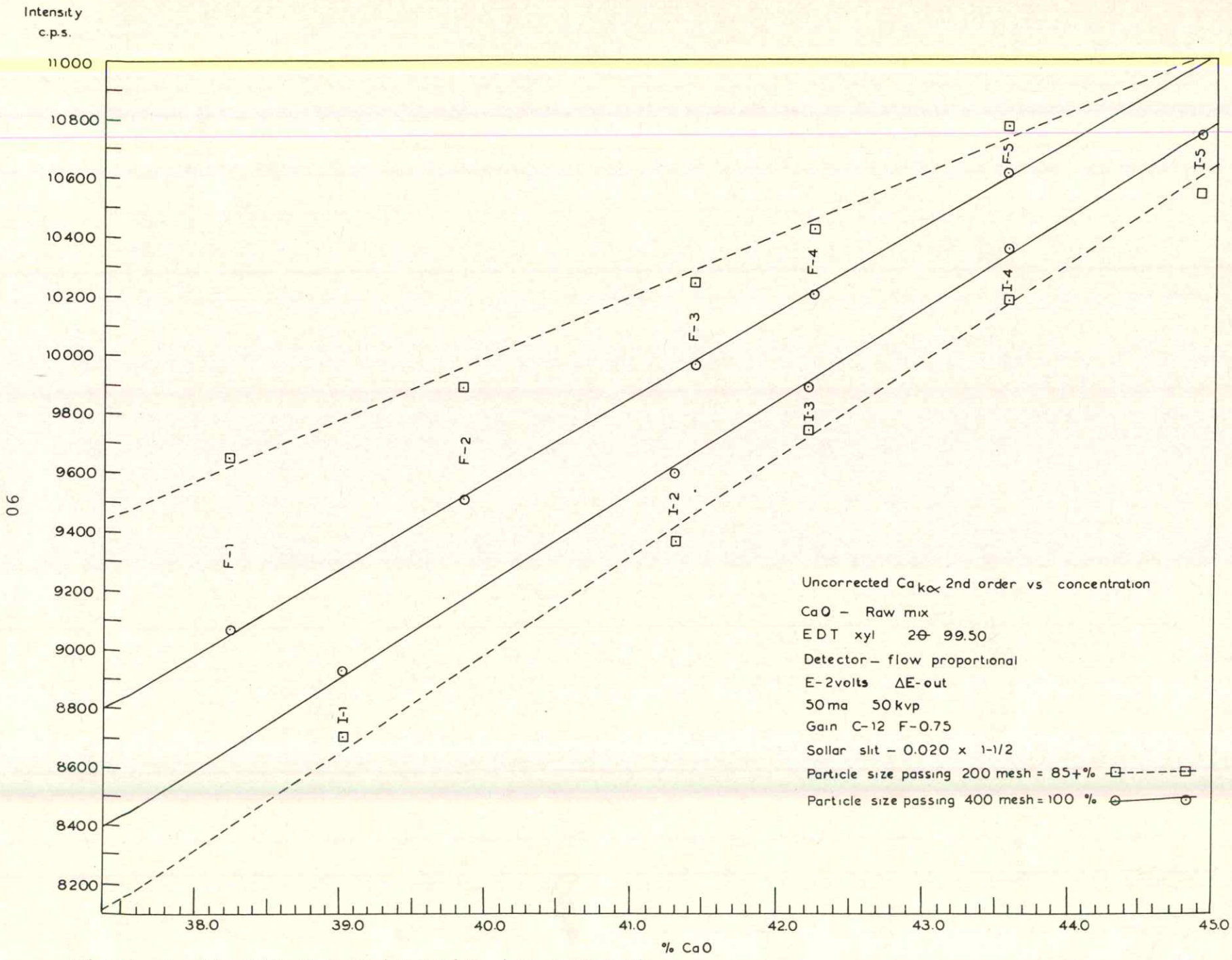

Figure 6. Percent CaO vs intensity (uncorrected)

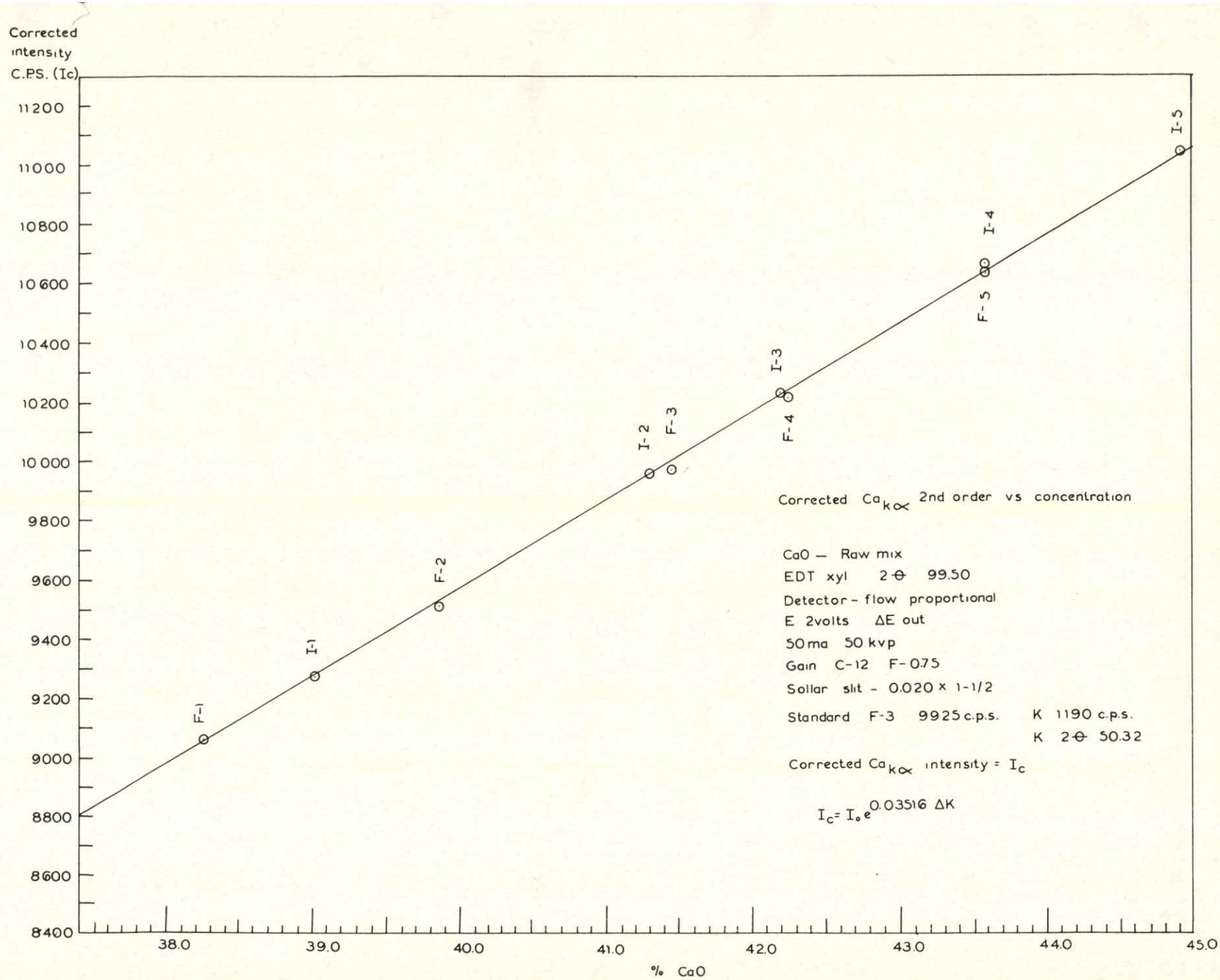

Figure 7. Percent CaO vs intensity (corrected)

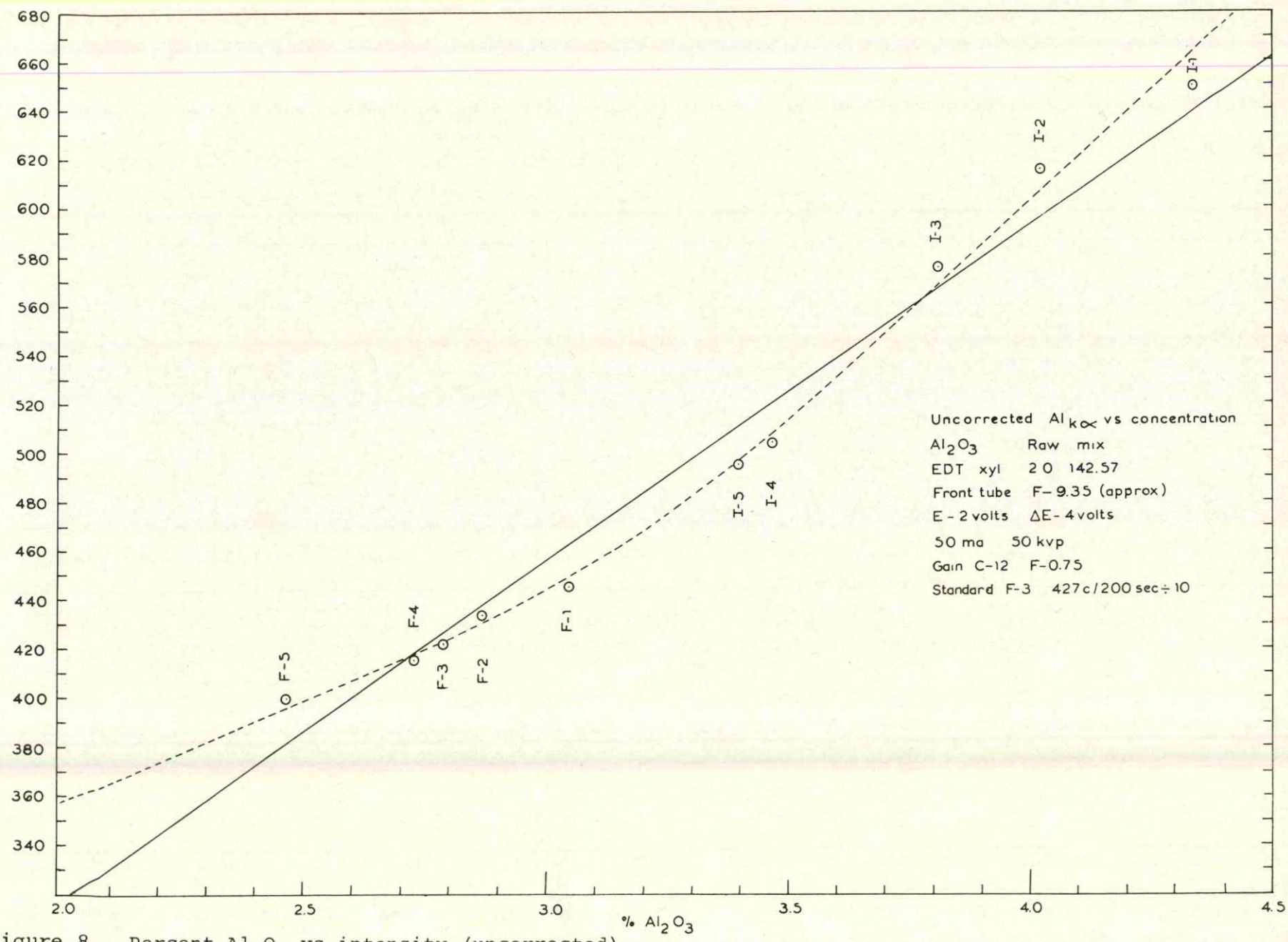

Figure 8. Percent Al_2O_3 vs intensity (uncorrected)

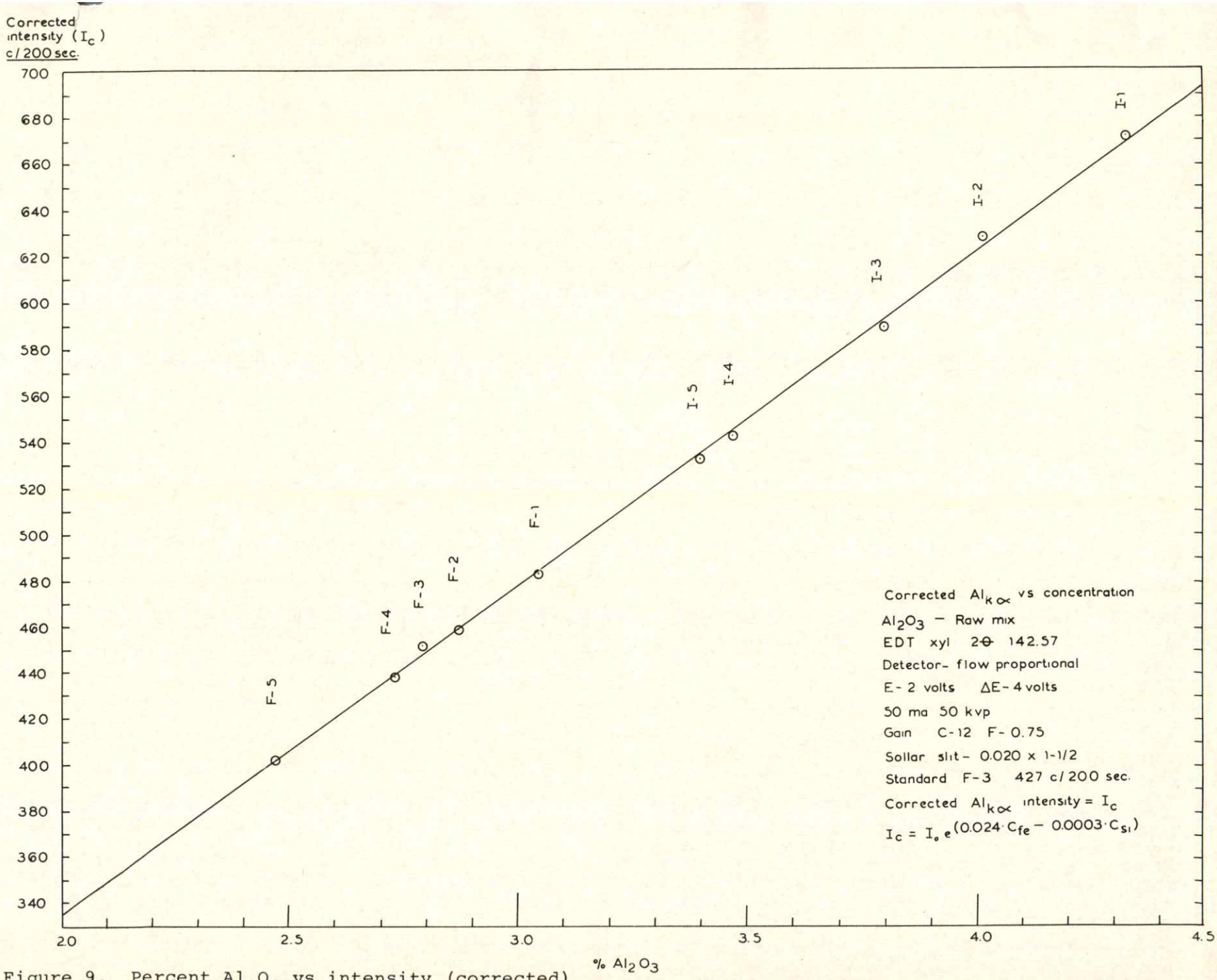

Figure 9. Percent Al_2O_3 vs intensity (corrected)

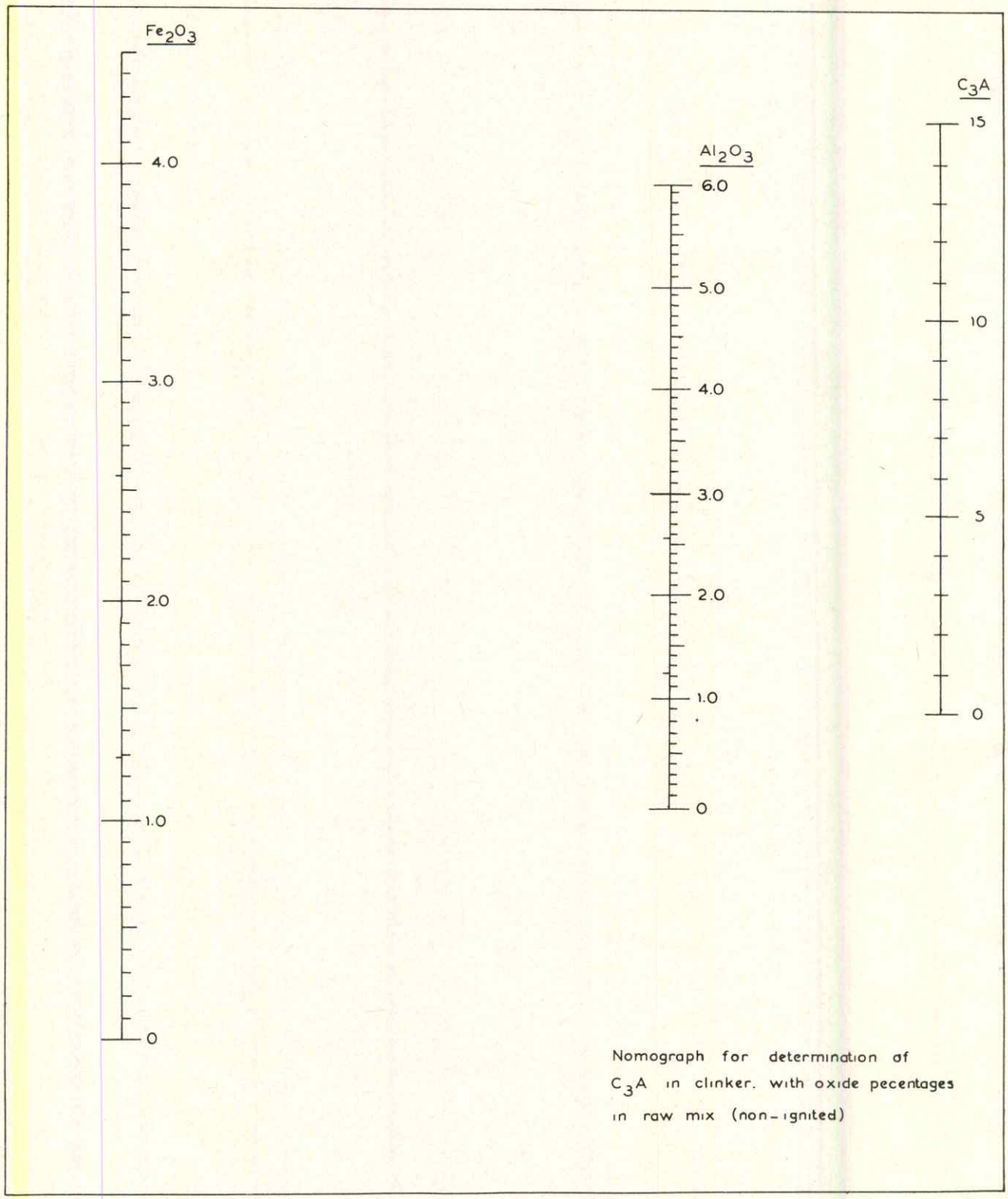

Figure 10. Nomograph for determination of C_3A in clinker with oxide percentages in raw mix on non-ignited basis

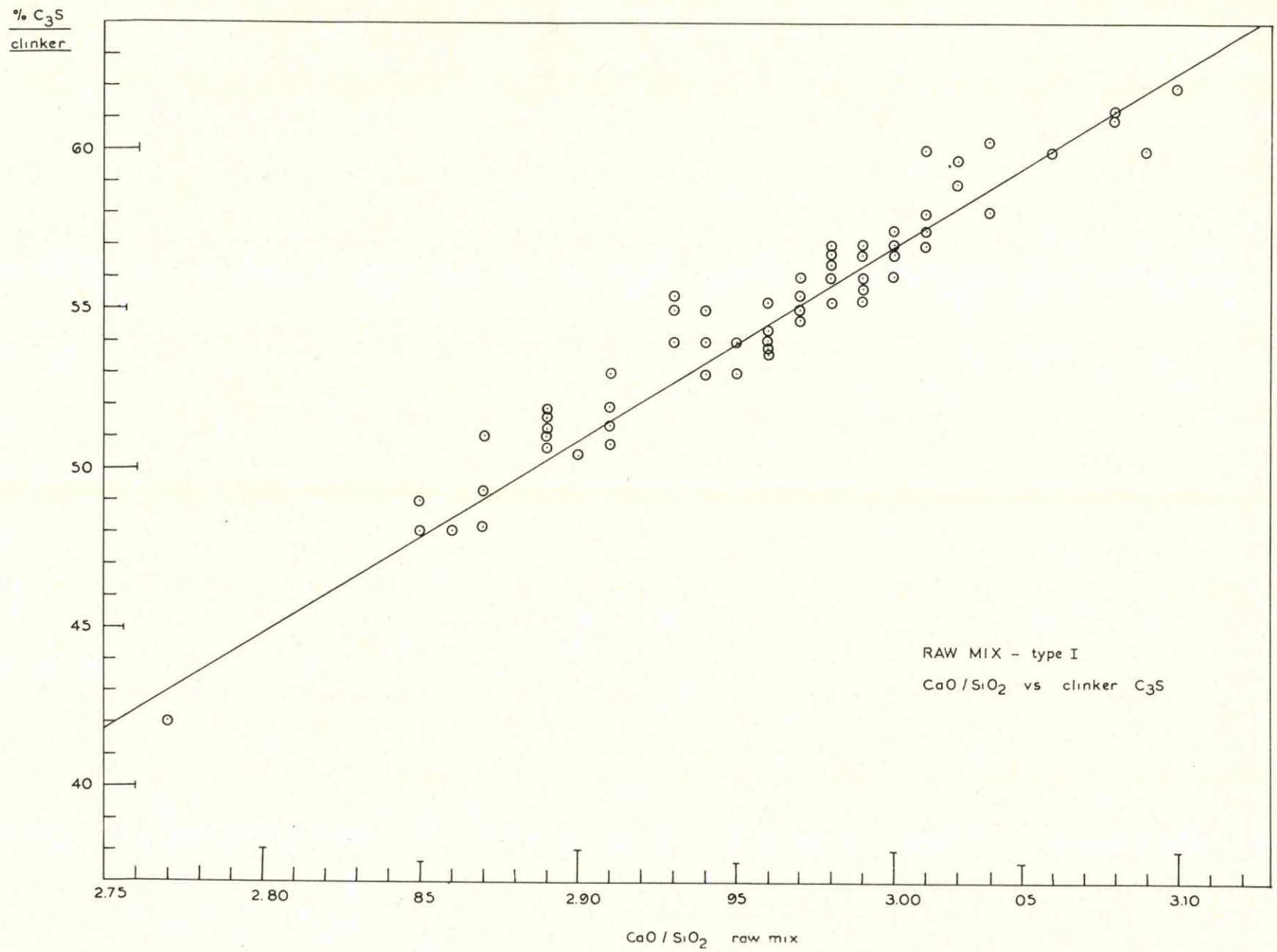

Figure 11. Percent C_3S in clinker vs CaO/SiO_2-type I

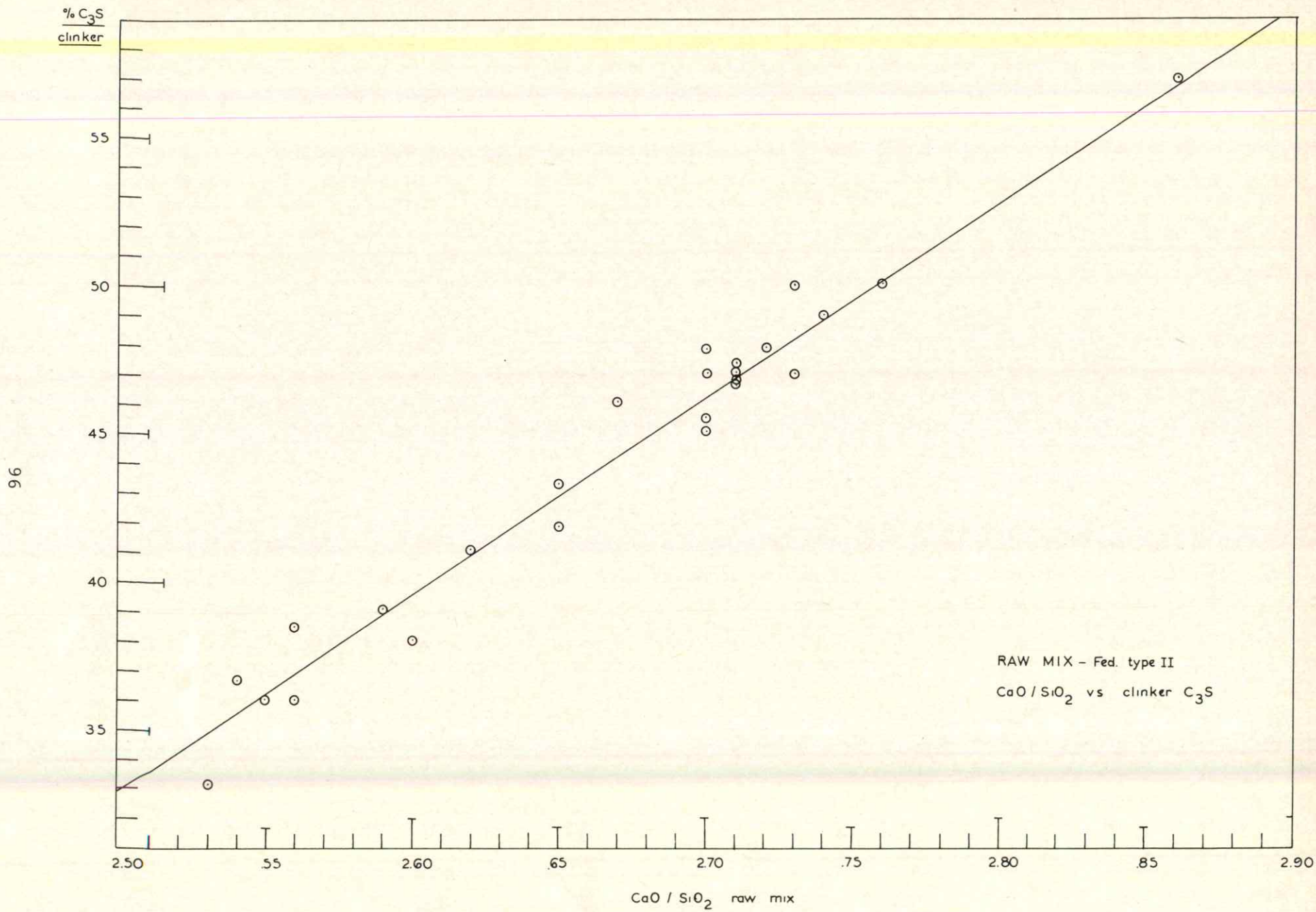

Figure 12. Percent C_3S in clinker vs CaO/SiO_2-type II

THE GEOCHEMISTRY OF THE OREAD LIMESTONE

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ABSTRACT

The four limestones of the Oread Limestone Formation, the basal formation of the Shawnee Group were systematically sampled and analyzed. The limestones (Toronto, Leavenworth, Plattsmouth, and Kereford) were analyzed for SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, SO_3, P_2O_5, K_2O, Na_2O, S, and L.O.I. Major impurities found were SiO_2 in all four limestones, dolomite ($MgCO_3$) and iron (Fe_2O_3) in the Toronto, and pyrite (FeS_2) in the Leavenworth. The SiO_2 in the Plattsmouth and Toronto is present in the form of chert. In the Kereford the SiO_2 is attributed to the apparent deposition of sand along with the limestone. In general it was noted that the purity (the amount of $CaCO_3$ present) tends to increase toward the southern edge of the outcrop area.

Included in the paper are tables of chemical analysis, graphs of various constituents, and a map of sampling locations. Specific analytical techniques are also described and significant chemical trends within the limestone noted.

INTRODUCTION

The Oread Limestone, basal formation of the Shawnee group, Upper Virgilian Pennsylvanian Age, was chosen as the first unit of a detailed study of the geochemistry of the limestones of the Shawnee Group. Our reasons for beginning with the Oread Limestone were threefold: (1) The Shawnee Group, of which the Oread is a member, was described by R. C. Moore (1935) as "clearly a cyclic repetition of beds" in terms of the theory of cyclothems as first proposed by Wanless and Weller in 1932. It was thought that a chemical study might show a similar cyclic trend in the chemical constituents throughout the formations; (2) Geochemical results might provide additional information on environmental conditions prevalent within the Kansas part of the midcontinent area during Pennsylvanian time; and (3) Three of the Oread Limestones (Kereford, Plattsmouth and Toronto) are of sufficient thickness at various locations within the state to be utilized economically. Therefore a systematic study would locate those areas where the limestone is thick enough to be quarried as well as provide information on the impurities present at these locations. Many limestones from eastern Kansas have been sampled and analyzed, but the study as reported in this paper is the first in which samples have been collected at regular intervals along the entire outcrop length of a particular limestone within the state and chemically analyzed.

Studies similar to the one described in this report are planned for the limestones of the remaining formations of the Shawnee Group. When completed, it is hoped that definite chemical trends and correlations between the formations can be established.

GEOLOGY

The Oread Limestone, as currently defined, comprises four limestones and three shales (Fig. 1). From bottom to top, these are the Toronto Limestone, Snyderville Shale, Leavenworth Limestone, Heebner Shale, Plattsmouth Limestone, Heumader Shale, and Kereford Limestone. The lower boundary is placed at the contact of the Toronto Limestone with the underlying Lawrence Shale Formation. The con-

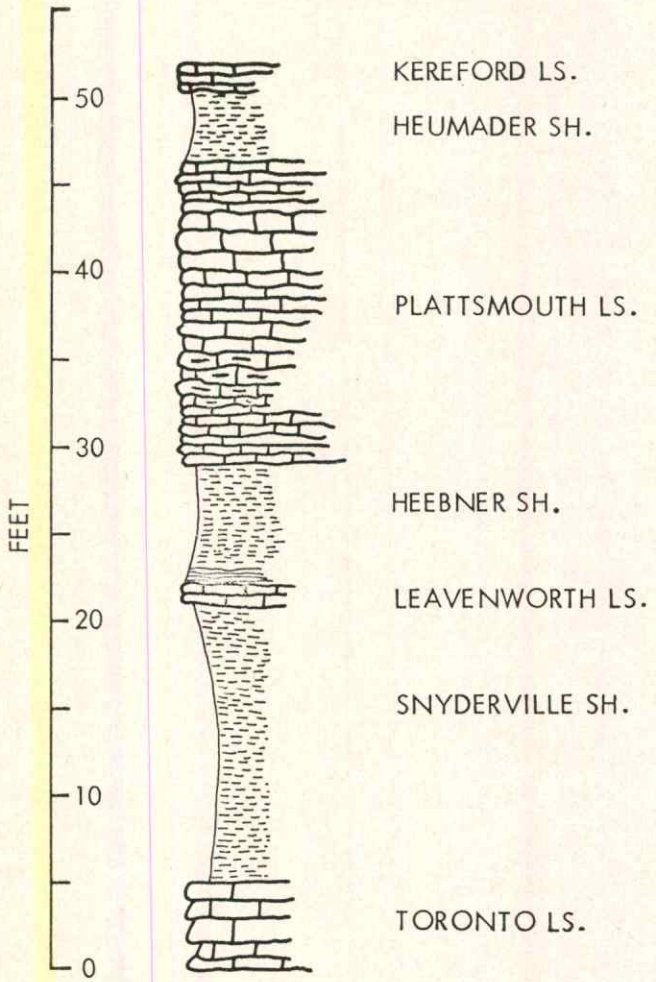

Figure 1. Measured section of Oread Limestone at Location Three, Doniphan County, Kansas.

tact of the Kereford Limestone with the overlying Kanwaka Shale Formation is taken as the upper boundary. Because the Kereford Limestone is absent in certain areas of Southern Kansas, the upper boundary of the Oread in these areas is taken as the contact of the Plattsmouth Limestone with the undifferentiated Heumader-Kanwaka Shales (Moore, 1935, p. 162). The Toronto Limestone was recognized and sampled at all locations except in the vicinity of Sedan (Fig. 2, Location 30) where no limestone outcrop could be found in the stratigraphic position of the Toronto. In the area around Sedan, many of the characteristics of the Snyderville Shale resemble those of the Lawrence Shale. Any differentiation other than an arbitrary one would be impossible. Therefore, in the area of Location 30 the Leavenworth Limestone is the lowest definitive member of the Oread Limestone and the lower boundary was placed at its base.

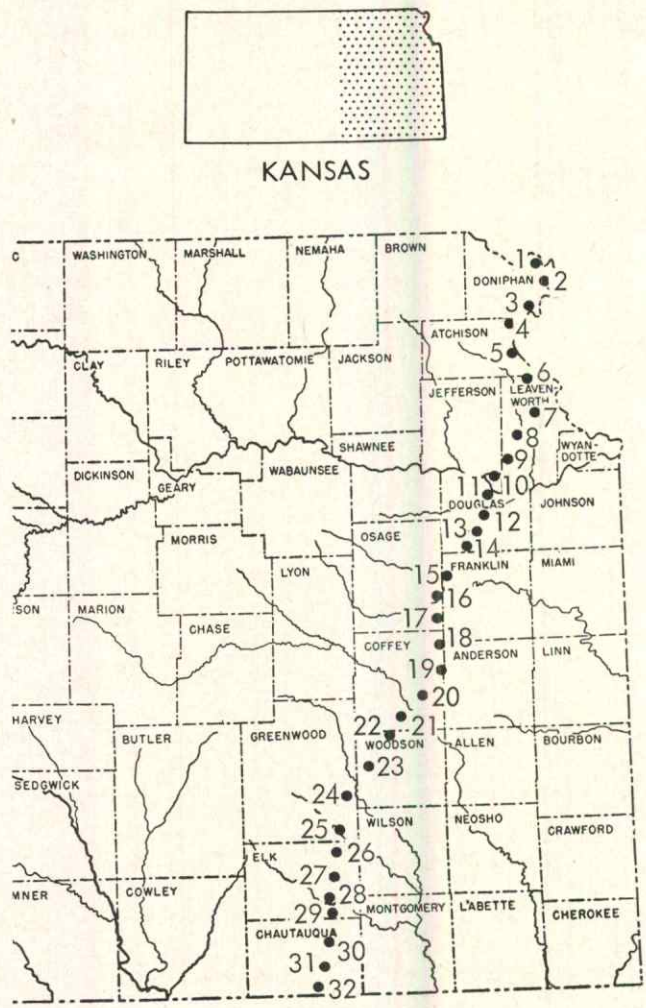

Figure 2. Map of sample locations of Oread Limestone.

Between the boundaries described above, the variations in the thickness of the Oread Limestone Formation are due primarily to variable thicknesses of the shale members. Where

all four limestones are present, the thickness of the formation varies from 44.0 ft. at location 2 in Doniphan County, to 137.5 ft. at location 19 near Waverly in Coffey County. In northeastern Kansas (location 1 to 11) the total thickness of the formation remains fairly constant, ranging from about 45 ft. to 60 ft. The Plattsmouth Ls. is quarried extensively in this area which is bounded on the north by the Missouri River and on the South by the Kansas River. In the central Kansas are the shale members of the formation and the Kereford Limestone show a marked increase in thickness. In the area bounded by the Kansas River on the north and the Neosho River on the south the Heumader Shale reaches a maximum thickness of approximately 78 ft. and the Kereford Limestone, which is quarried in Coffey and Osage counties, reaches its maximum thickness of 25.2 ft. In the area bounded by the Neosho River on the north and the Verdigris River on the south (Loc. 21 thru 25), the Plattsmouth Limestone decreases in thickness to about 0.5 ft. and the Toronto Limestone increases slightly in thickness. In this area the Snyderville Shale reaches its maximum thickness of approximately 81 ft. and the Heumader Shale throughout the area ranges from 30 to 65 feet in thickness. In this area (Loc. 21 thru 26) the Toronto Limestone is quarried extensively. South of the Verdigris River to the Kansas-Oklahoma line (Loc. 26 thru 32) the Kereford Limestone is not found, the Plattsmouth Limestone increases in thickness to about 20 ft. and the Toronto Limestone decreases in thickness to about 1 ft. at the Kansas-Oklahoma line. The Snyderville Shale remains fairly thick in the area also averaging 50 to 60 ft. in thickness. The Plattsmouth Limestone is the only member of the Oread that is quarried extensively in Southern Kansas.

METHODS OF INVESTIGATION

Samples of each limestone unit from the Oread Limestone were collected from both outcrops and quarries at different locations crossing the state from Doniphan to Chautauqua County. Six miles or the approximate width of one township was chosen as an arbitrary distance between sample locations. It has been shown that the same chemical trends can be observed with a six mile distance between samples or a spacing of 200 feet (Galle and Waugh, 1966). It was found necessary, in practice, to vary the spacing from 3 to 12 miles owing to inaccessability of outcrops, weathering of some outcrops and the absence of outcrops. Sample locations also deviated from the pattern to incorporate previously analyzed samples, or samples obtained from quarries. Thus a sample of each limestone unit of the Oread Limestone was collected, if possible, from the same location. If samples of each limestone could not be obtained from the same location, the remaining samples were collected from another area as close as possible to the other sampling sites. As a result samples of the Toronto, Leavenworth, Plattsmouth and Kereford Limestones were collected in such a way that a specific area of the outcrop was sampled. The sampling sites from each area were grouped together and given a location number. These are shown in Figure 2.

An analysis of a composite sample representing the total thickness of each limestone member was obtained. This was necessary from the standpoint of economic potential and future utilization. Each composite sample was taken from a fresh surface and, depending upon the thickness of the unit, ranged in weight from 3 to 50 pounds.

The samples were crushed, reduced by quartering and splitting, and ground to pass a 60-mesh screen. Subsequently they were analyzed for SiO_2, Fe_2O_3, Al_2O_3, TiO_2, K_2O, Na_2O, SO_3, S, P_2O_5, CaO, MgO and loss on ignition for CO_2 and other volatiles, using the methods outlined by Hill et al. (1961). The results are given in Tables 1-5.

Some of the major impurities noted in the limestones of the Oread were chert (SiO_2) in the Toronto and Plattsmouth, pyrite (FeS_2) in the Leavenworth, and varying amounts of clay in all limestones of the formation. Since clay was present in all of the limestone analyzed an arbitrary value for an illitic clay was calcu-

lated from the percent alumina found in the sample. Illite of the formula $2K_2O \cdot 3MgO \cdot (Al_2O_3, Fe_2O_3)_8 \cdot 24SiO_2 \cdot 12 H_2O$ (Imbrie and Poldervaart, 1959) was used for the calculation. Illite was chosen for the calculation because all X-ray diffractograms run on random samples of clay fractions of the Oread Limestone proved to be illitic. Quantities of the total amount of silica in the limestone not used in the calculated value of clay were then reported as excess silica.

Varying amounts of pyrite were found to be present in the Leavenworth Limestone. In the gross analysis of the limestone all of the iron is reported as Fe_2O_3. Therefore, when the iron in pyrite is reported as ferric oxide, the summation of the percentages of all components will be low because of the molecular weight difference between ferric oxide and ferrous sulfide (Waugh and Hill, 1960). For this reason, in the analysis of the Leavenworth Limestone all of the sulfide is converted to ferrous sulfide. Any iron not used in the calculation of ferrous sulfide is reported as ferric oxide and both values (FeS_2 and Fe_2O_3) are used in obtaining the total.

Chemistry of the Limestone

Toronto Limestone

A characteristic of the Toronto Limestone is the reddish-brown color as seen in many of the weathered outcrops. This color is attributed to the presence of iron oxide (Fe_2O_3) and chemical analysis of the rock showed the Toronto to have a high percentage of Fe_2O_3 (Table 1). The Fe_2O_3 content of 31 Toronto samples averaged 3.71 percent (range 0.54-8.34 percent).

Location 12 in Douglas County is an area which apparently separates the northern and southern parts of the outcrop into two different depositional environments. Table 1 indicates a larger MgO content north of location 12. South of that point the MgO content is nearer the average of the other limestones of the Oread Limestone. Calculation of the $CaCO_3$ and $MgCO_3$ using the method outlined by Galle and Runnels (1960) indicates a higher amount of dolomite present north of location 12. X-ray analysis confirmed the presence of dolomite in the samples from this area. In the area from location 12 north to the state line, the average $MgCO_3$ content is 6.03 percent while the average $MgCO_3$ south of that point is 1.34 percent.

Leavenworth Limestone

The results of the chemical analysis showed that samples taken from the area north of location 12 have a higher silica (SiO_2) content than samples collected south of that point. This area is bounded on the north by the Missouri River and on the south by the Kansas River. The average SiO_2 content of samples taken from eleven locations within this area is 7.37 percent with a range of 5.57 to 11.47 percent (Table 2). In the area extending from location 12 in Douglas County to location 32 in Chautauqua County, the mean SiO_2 content of samples taken from 22 locations is 3.19 percent (range 1.80-5.52 percent).

The lack of correspondingly high alumina (Al_2O_3) value in relation to the higher SiO_2 value for the samples from the northern part of the state (Table 2) indicates that only part of the SiO_2 is incorporated into clay minerals. Fig. 3 illustrates the comparison between a calculated clay content and the excess silica present in some other form. The graph plot of the values for the calculated clay and excess silica against sample location uses a seven-point moving average to smooth out minor variations in chemical compositions. A seven-point moving average is found by averaging a value with three values on either side of it, and the process repeated for each succeeding value. It must be remembered that the values representing the amount of clay in this particular limestone are empirical and were calculated for purposes of comparison. The excess SiO_2 in the Leavenworth Limestone appears to be present in finely disseminated form as indicated by insoluble residues run on samples of this limestone. No visible chert nodules were found

Table 1. Results of Chemical Analysis and Other Pertinent Data of the Toronto Limestone.

Loc. No.	Lab. No.	County	Locality Sec. T.S. R.E.	Thick-ness	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O
1	59268	Doniphan	SW 28- 2-22	3.1	9.60	2.34	2.69	0.10	42.83	3.74	0.41	0.16
2	58246	Doniphan	SW 21- 3-22	0.8	19.50	4.86	2.11	0.02	38.80	1.01	0.84	0.24
3	59256	Doniphan	SW 5- 4-22	4.5	9.63	2.01	3.05	0.11	40.77	4.99	0.30	0.13
4	607	Atchison	NE 18- 5-21	6.5	9.43	2.11	2.67	0.03	46.17	1.18	0.20	0.02
5	58183	Atchison	SW 32- 6-21	3.8	8.88	2.15	6.37	0.08	43.11	1.96	0.37	0.06
6	58247	Leavenworth	NE 34- 7-21	4.5	5.63	1.57	3.66	0.04	47.82	1.25	0.17	0.05
7	58127	Leavenworth	N 36- 8-22	5.2	8.98	1.85	5.33	0.11	43.83	1.78	0.20	0.10
8	58308	Leavenworth	SE 15- 9-21	5.0	4.87	0.92	7.47	0.03	40.41	6.12	0.11	0.01
9	58285	Leavenworth	NW 7-10-21	6.0	6.29	1.24	6.49	0.07	45.54	1.63	0.22	0.05
10	6169	Leavenworth	W 8-11-21	8.6	4.94	0.67	3.84	0.01	48.05	2.19	0.04	0.03
11	58119	Jefferson	E 31-11-20	13.6	12.42	1.11	2.49	0.18	44.14	2.33	0.12	0.04
12	52358	Douglas	SW 25-12-19	8.0	8.56	1.47	3.83	0.06	44.08	3.19	0.19	0.09
13	54372	Douglas	NW 35-13-19	3.6	3.62	0.79	1.53	0.06	51.97	0.73	0.07	0.03
14	54371	Douglas	SE 19-14-20	4.2	3.16	0.79	0.54	0.03	52.81	0.52	0.06	0.04
15	58159	Franklin	NW 32-15-18	11.0	5.57	1.12	3.00	0.19	49.51	0.62	0.06	0.02
16	59580	Osage	N 16-17-17	5.0	5.77	1.19	3.32	0.04	48.93	0.70	0.11	0.02
17	58182	Osage	SW 6-18-17	2.9	17.70	3.62	2.12	0.13	41.22	0.71	0.69	0.13
18	58160	Anderson	NE 24-19-17	9.0	5.14	1.00	4.16	0.19	48.88	0.97	0.05	0.01
19	5959	Coffey	N 15-20-17	2.9	4.20	0.73	5.70	0.02	48.04	1.22	0.07	trace
20	58249	Anderson	C 1-21-17	6.0	24.00	4.38	7.07	0.26	33.07	1.01	0.61	0.22
21	5960	Coffey	W 36-22-15	7.8	3.54	0.82	4.00	0.03	47.71	2.58	0.07	0.01
22	5914	Woodson	NW 4-24-15	7.9	4.13	0.76	4.10	nil	48.50	2.14	0.07	0.03
23	5915	Woodson	SE 18-25-15	7.6	5.78	1.34	3.14	0.05	47.49	1.85	0.14	0.06
24	52294	Greenwood	NW 10-26-13	9.0	4.56	0.92	3.04	0.02	50.10	0.61	0.08	0.03
25	52204	Wilson	W 23-27-13	4.0	5.85	1.60	1.34	0.07	49.92	0.80	0.18	0.03
26	58310	Elk	SE 1-29-12	6.5	8.55	2.02	2.50	0.08	47.35	0.76	0.17	0.04
27	58299	Elk	S 25-29-12	0.3	6.32	1.76	1.92	0.11	47.59	1.72	0.24	0.06
28	58300	Elk	SW 27-30-12	1.2	7.43	2.02	2.72	0.13	46.64	0.99	0.31	0.07
29	58250	Elk	SE 16-31-12	1.0	10.17	3.22	3.40	0.07	44.31	1.05	0.41	0.09
30	5916	Chautauqua	E 36-32-12	0.6	11.51	3.49	2.97	0.09	43.53	0.95	0.50	0.13
32	59267	Chautauqua	NE 3-35-11	1.0	16.72	5.34	8.34	0.16	35.80	0.90	0.80	0.15

Table 2. Results of Chemical Analysis and Other Pertinent Data of the Leavenworth Limestone.

Loc. No.	Lab. No.	County	Locality Sec. T.S. R.E.	Thick-ness	SiO_2	Al_2O_3	Fe_2O_3	FeS_2	TiO_2	CaO	MgO	K_2O	Na_2O
1	58122	Doniphan	SW 28- 2-22	2.3	6.33	1.08	0.85	0.37	0.09	49.61	1.22	0.09	trace
2	58123	Doniphan	SW 21- 3-22	1.7	7.00	0.69	0.79	0.22	0.09	50.52	0.55	0.01	0.01
3	59257	Doniphan	SW 5- 4-22	1.0	5.57	0.73	0.67	0.41	trace	50.24	1.39	0.08	0.03
4	605	Atchison	SW 18- 5-21	1.9	7.22	0.98	1.10	0.11	0.08	49.28	0.98	0.04	0.01
5	58283	Atchison	C 31- 6-21	1.7	11.74	0.88	1.41	0.15	0.06	46.50	0.85	0.08	0.04
6	58284	Leavenworth	SW 25- 7-21	1.3	9.50	0.84	0.92	0.34	0.01	48.72	0.53	0.08	0.03
7	58120	Leavenworth	NW 31- 8-22	2.0	5.86	0.55	0.57	0.82	0.10	49.98	1.26	0.05	0.02
8	58311	Leavenworth	SE 15- 9-21	1.4	6.22	0.88	0.90	1.87	0.03	48.80	1.50	0.11	0.05
9	58185	Leavenworth	C 18-10-21	1.7	7.26	1.02	0.79	0.43	0.03	49.82	0.45	0.15	0.04
10	58130	Leavenworth	W 8-11-21	2.0	8.66	1.06	1.22	0.71	0.03	47.24	1.74	0.13	0.02
11	58129	Jefferson	E 8-11-21	1.5	5.70	0.80	0.13	1.44	0.02	50.35	1.02	0.08	0.03
12	606	Douglas	NW 36-12-19	1.2	3.62	0.57	0.82	0.28	0.05	51.96	1.25	0.05	0.01
13	58128	Douglas	NE 14-14-18	1.5	4.43	0.99	1.11	1.68	0.06	48.97	1.55	0.13	0.04
14	58121	Douglas	NW 4-15-19	1.9	2.63	0.63	0.88	0.51	0.09	52.62	0.33	0.02	0.01
15	58131	Franklin	NW 5-16-18	1.1	2.06	0.57	0.74	1.23	nil	51.58	1.24	0.02	trace
16	5955	Osage	N 16-17-17	1.4	3.08	0.69	0.84	0.11	0.01	52.13	0.76	0.06	0.02
17	58161	Osage	SW 6-18-17	1.3	5.52	1.00	1.24	0.19	0.18	49.85	1.14	0.05	0.01
18	58162	Franklin	SW 13-19-17	1.2	5.02	1.03	1.44	0.52	0.11	49.75	1.32	0.05	0.02
19	5956	Coffey	S 8-20-17	0.9	3.41	0.89	0.93	0.51	0.10	51.06	1.08	0.09	trace
20	58186	Coffey	E 11-21-16	0.6	4.25	1.14	0.91	0.56	0.02	51.12	0.50	0.15	0.05
21	5957	Coffey	NE 27-22-15	0.7	3.12	0.80	1.42	0.21	0.09	51.20	1.14	0.06	0.02
22	5917	Woodson	NW 6-24-15	1.3	3.57	0.89	1.78	0.21	0.03	49.75	1.58	0.11	0.03
23	58312	Woodson	SW 16-25-14	1.4	2.46	0.70	1.70	0.21	nil	50.77	1.21	0.07	0.01
24	59266	Greenwood	SW 8-26-13	1.2	3.88	0.90	2.20	0.11	0.11	50.06	1.06	0.06	0.01
25	58313	Greenwood	NW 15-27-13	1.4	3.00	0.79	1.84	0.22	0.05	50.37	1.62	0.08	0.01
26	58314	Elk	SW 25-28-12	1.8	3.41	0.64	2.44	0.15	0.09	50.00	1.15	0.06	trace
27	58295	Elk	C 25-29-12	1.7	2.89	0.68	1.64	0.07	nil	51.66	1.09	0.06	0.03
28	58296	Elk	SW 22-30-12	1.9	2.31	0.53	1.18	0.21	0.05	52.49	0.93	0.05	0.02
29	5919	Elk	S 15-31-12	2.0	2.29	0.48	0.84	0.28	0.06	52.08	1.26	0.06	0.01
30	58315	Chautauqua	NW 31-32-12	2.0	2.40	0.87	1.32	0.94	nil	50.53	1.47	0.13	0.02
31	58297	Chautauqua	C 33-33-11	1.8	1.80	0.55	0.81	0.41	nil	52.69	1.07	0.05	trace
32	58293	Chautauqua	NW 14-35-10	1.8	3.16	1.04	1.57	0.22	0.03	51.22	0.77	0.08	trace

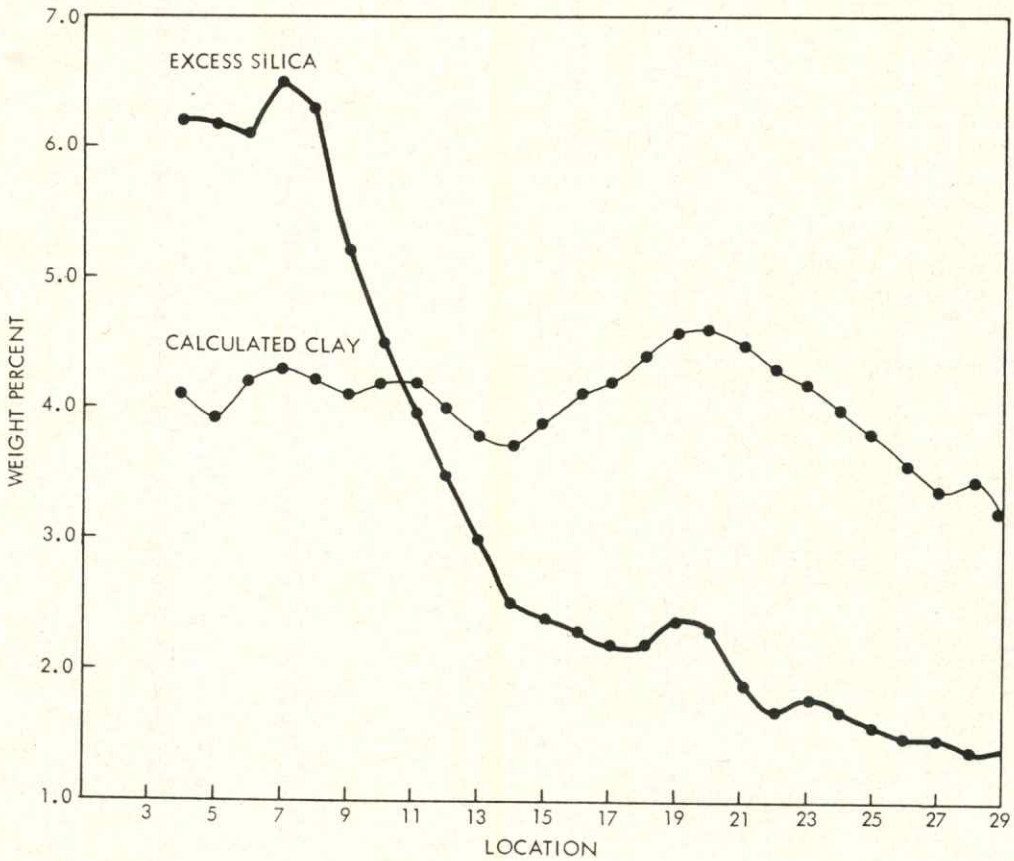

Figure 3. Graph showing comparison of calculated clay and excess silica.

in the Leavenworth.

Other minerals present in the Leavenworth Limestone which appear to be of significance are the sulfides. In the other three limestones of the Oread Limestone Formation sulfide sulfur (S) is present in only trace amounts or not at all (Table 3). However, in the Leavenworth Limestone sulfide sulfur is present in the amounts ranging from 0.06 to 1.00 percent. The sulfide sulfur in the Leavenworth was found to be in the form of pyrite (FeS_2) crystals of which can be seen easily in samples taken from the outcrop. Table 2 contains a value of FeS_2 for each sample analyzed which was calculated by converting all of the S to FeS_2. An appropriate amount of Fe_2O_3 was then subtracted from the total Fe_2O_3 to give a more realistic value for the amount of iron present as the oxide.

Also of interest is the fact that in the area north of location 12 the CaO content is slightly lower than from locations south of that point. The higher SiO_2 content in the north part of the state is the reason for the lower values of CaO. The average CaO content north of location 12 is 49.19 percent (range 46.5-50.62 percent). South of location 12 the average CaO content is 51.04 percent (range 48.97 to 52.69 percent).

Plattsmouth Limestone

Based on purity or percentage of calcium carbonate the Plattsmouth Limestone can be arbitrarily divided into four distinct areas from north to south across the state (Table 4).

Table 3. SO_3, S, and P_2O_5 data for the Toronto, Leavenworth, Plattsmouth and Kereford Limestones.

Loc. No.	Toronto			Leavenworth			Plattsmouth			Kereford		
	SO_3	P_2O_5	S	SO_3	P_2O_5	S	SO_3	P_2O_5	S	SO_3	P_2O_5	S
1	0.01	0.26	0.03	0.19	0.02	0.20	0.16	0.09	0.11	0.34	0.09	0.36
2	trace	0.05	nil	trace	0.01	0.12	trace	0.06	0.01	trace	0.07	0.03
3	trace	0.07	0.02	0.05	0.04	0.22	trace	0.05	0.02	0.06	0.26	0.01
4	trace	0.14	nil	0.04	0.03	0.06	0.09	0.06	0.06	trace	0.04	0.08
5	trace	0.02	nil	0.05	0.03	0.08	0.14	0.03	0.12	trace	0.11	0.01
6	0.06	0.10	nil	0.10	0.02	0.18	trace	0.13	trace	0.14	0.12	0.01
7	0.03	0.04	0.02	0.13	0.02	0.44	trace	0.08	0.01	trace	0.08	0.02
8	trace	0.08	0.02	0.10	0.03	1.00	trace	0.08	0.02	0.07	0.05	0.12
9	trace	0.10	trace	0.03	0.02	0.23	trace	0.06	0.16	trace	0.08	0.05
10	trace	0.08	nil	0.12	0.01	0.38	0.20	0.08	0.20	trace	0.04	0.02
11	trace	0.05	0.04	0.03	0.01	0.77	0.11	0.09	0.10			
12	nil	0.04	nil									
13	nil	0.02	trace	0.21	0.02	0.15	trace	0.04	0.06	trace	0.20	0.02
14	nil	0.01	trace	0.08	0.02	0.90	0.13	0.02	0.10	0.06	0.04	0.01
15	trace	0.08	0.03	0.09	0.03	0.27	0.09	0.07	0.08	trace	0.07	0.01
16	trace	0.04	nil	trace	0.04	0.66	trace	0.05	0.02	trace	0.01	0.03
17	trace	0.04	nil	trace	0.01	0.06	trace	0.02	nil	nil	0.03	0.02
18	trace	0.05	nil	0.22	0.01	0.10	0.16	trace	0.20	0.05	0.02	0.06
19	nil	0.02	nil	0.03	0.03	0.28	nil	0.03	trace	trace	0.03	0.06
20	0.03	0.07	nil	0.11	trace	0.27	trace	0.04	nil	nil	0.03	nil
21				0.08	0.01	0.30	nil	0.05	0.12	trace	0.03	nil
22	trace	0.07	nil	0.06	0.01	0.11	nil	0.07	nil	trace	0.20	0.01
23	trace	0.03	trace	0.12	0.05	0.11	0.02	0.07	0.04	trace	0.03	nil
24	trace	0.09	0.01	0.11	0.03	0.11	0.02	0.08	0.05	trace	0.03	nil
25	nil	0.05	nil	0.07	0.06	0.06	0.15	0.09	0.24	0.03	0.05	0.06
26										trace	0.19	0.03
27	nil	trace	0.02	0.06	0.05	0.12	nil	trace	trace			
28	0.06	0.13	0.02	0.07	0.05	0.08	0.05	0.05	0.06			
29	0.09	0.04	0.15	0.05	0.02	0.04	nil	0.01	trace			
30	0.17	0.21	0.14	0.11	0.03	0.11	trace	0.03	trace			
31	0.12	0.21	nil	0.23	0.01	0.15	trace	0.02	trace			
32	0.13	0.36	0.03	0.26	0.03	0.50	trace	0.06	trace			
33	0.13	0.36	nil	0.12	0.02	0.22	nil	trace	nil			
34				0.19	0.03	0.12	trace	0.03	0.01			

Table 4. Results of Chemical Analysis and Other Pertinent Data of the Plattsmouth Limestone.

Loc. No.	Lab. No.	County	Locality Sec. T.S. R.E.	Thick-ness	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O
1	6130	Doniphan	NW 24- 2-21	19.8	14.44	1.34	1.89	0.16	41.07	3.43	0.21	0.11
2	58163	Doniphan	SW 21- 3-22	16.5	9.46	1.12	1.14	0.08	48.41	0.66	0.09	0.02
3	6129	Doniphan	SE 26- 4-21	17.5	14.11	1.19	1.04	0.13	45.66	0.79	0.09	0.03
4	604	Atchison	SW 18- 5-21	16.0	12.77	1.40	1.60	0.05	45.08	1.31	0.10	0.03
5	6170	Atchison	NW 32- 6-21	13.0	9.30	1.28	1.50	0.01	45.27	3.17	0.15	0.09
6	58252	Leavenworth	SW 25- 7-21	14.0	15.32	1.11	1.18	0.16	44.09	1.01	0.05	0.01
7	58254	Leavenworth	C 33- 8-22	11.0	7.97	0.86	1.12	0.10	49.17	0.57	0.02	0.01
8	6166	Leavenworth	SE 14- 9-21	13.5	10.74	0.86	1.28	0.01	47.55	1.14	0.07	0.03
9	58251	Leavenworth	NW 7-10-21	14.0	11.47	1.28	1.87	0.14	43.82	2.75	0.11	0.05
10	6167	Leavenworth	NW 7-11-21	16.5	11.45	1.21	1.80	0.07	43.40	3.01	0.18	0.09
11	6171	Douglas	NE 1-12-19	16.0	9.80	1.09	1.56	0.01	46.39	1.87	0.13	0.07
12	6168	Douglas	SW 4-13-19	15.0	5.47	0.74	0.92	0.01	50.48	1.16	0.10	0.05
13	54370	Douglas	C 22-14-18	10.3	6.41	1.43	0.44	0.01	50.44	0.97	0.10	0.03
14	59112	Douglas	NE 15-15-18	14.0	6.52	1.10	1.24	0.01	48.69	1.41	0.08	0.05
15	59113	Franklin	SW 7-16-18	6.0	6.04	0.83	1.06	0.03	50.47	0.43	0.05	0.04
16	5998	Osage	SW 6-17-17	10.6	3.00	0.64	0.95	0.02	52.83	0.34	0.03	0.02
17	54224	Osage	SW 3-18-16	20.2	3.89	1.00	1.32	0.04	49.59	2.15	0.11	0.04
18	5999	Franklin	NW 14-19-17	3.0	5.85	1.49	3.12	0.05	48.69	0.84	0.11	0.03
19	59100	Coffey	S 8-20-17	3.7	4.88	1.09	2.05	0.04	50.44	0.63	0.08	0.02
20	52278	Coffey	SW 14-21-15	13.0	4.04	1.08	1.29	0.06	49.99	1.92	0.15	0.06
21	52316	Coffey	SE 2-22-15	12.0	6.48	1.28	2.77	0.13	47.85	1.64	0.18	0.06
22	59265	Woodson	NW 6-24-15	0.5	8.41	3.22	3.11	0.08	45.27	1.12	0.25	0.03
23	59263	Woodson	S 17-25-14	0.5	8.79	3.15	3.68	0.11	45.14	0.90	0.24	0.06
24	59262	Greenwood	NW 1-26-12	2.0	9.05	3.59	3.20	0.25	42.13	2.89	0.42	0.12
25	52205	Wilson	SW 23-27-13	3.0	3.64	1.23	1.35	0.07	51.30	0.72	0.13	0.01
26	53174	Greenwood	NE 3-28-12	7.1	3.36	0.97	1.30	0.07	51.24	1.28	0.09	0.03
27	52361	Elk	SE 21-29-12	9.0	1.61	0.41	0.64	0.01	53.96	0.43	0.07	0.03
28	58293	Elk	SW 22-30-12	17.5	2.45	0.61	0.92	0.01	53.04	0.34	0.05	0.01
29	58256	Elk	NE 29-31-12	18.0	2.55	0.63	1.23	0.01	52.79	0.34	0.10	0.01
30	58294	Chautauqua	NE 36-32-11	6.0	2.54	0.67	0.61	0.03	53.19	0.30	0.05	trace
31	52270	Chautauqua	C 33-33-11	20.0	1.15	0.30	1.51	0.07	52.67	1.44	0.06	0.04
32	58293	Chautauqua	NW 14-35-10	17.4	3.45	0.75	0.94	0.18	51.91	0.41	0.02	trace

In the northernmost area from location 1 through 11 the average calculated CaO_3 is 45.45 percent and the average MgO_3 is 1.79 percent. In the area from location 12 through 20 the CaO_3 average is 50.18 percent and the average magnesium carbonate is 1.09 percent. At locations 21 through 24 the Plattsmouth exhibits its greatest chemical and lithologic change within the state. In the area studied the limestone at location 21 is 12 feet thick and at location 22 and 23 it is a 6-inch calcareous fossiliferous zone. At location 24 the thickness is two feet. The average calcium and magnesium oxide at these locations is 45.10 percent and 1.64 percent which is generally less than at other locations in the state. In the southernmost area, location 25 through 32, the Plattsmouth gradually thickens to a maximum of 20 feet at location 31. The calcium oxide shows a marked increase to an average of 52.51 percent and the magnesium oxide decreases to 0.66 percent.

A predominant feature of the Plattsmouth Limestone is the presence of black or gray chert, spotted with white or gray siliceous replacement of fossils in the area north of the Kansas River (Loc. 1 thru 11). Some chert is found in Douglas County and in lesser amounts southward into Coffey County. The chemical analysis as shown in Table 4 indicate, as might be expected, when the SiO_2 increases the $CaCO_3$ decreases. The four areas, as outlined previously in relation to the $CaCO_3$ content, can also be distinguished on the basis of SiO_2 content. In the area of location 1 through 11 the average SiO_2 content is 11.53 percent. From location 12 through 20 the SiO_2 averages 5.12 percent. The area from location 21 through 24 has an average SiO_2 content of 8.18 percent. In this area the increase in SiO_2 is not due to chert, but due to the extreme weathered and shaley appearance of Plattsmouth Member throughout the area. In the area of location 25 through 32 the average SiO_2 content drops to 2.59 percent.

Kereford Limestone

The calculated CaO_3 of the Kereford Limestone (Table 5) ranges from 50.96 to 21.74 percent. The amount of CaO_3 decreases generally to the south as the Kereford thins and becomes more arenaceous. The areas containing the highest percentages of CaO_3 are from location 2 through location 9 and location 13 through 18. In the southern half of the Kereford outcrop area the percent of CaO_3 decreases because of apparent sand deposition along with the limestone. Silica in the form of quartz comprises more than 21 percent of the Kereford at locations 21 through 23.

Comparison of Results

There are two general statements which can be made in regard to the results of the chemical analyses of the Oread Limestone. (1) the lateral variation of purity of the limestone is great and relatively unpredictable from location to location. (2) parallelisms do occur in the chemical constituents of superimposed limestones deposited at different times. An outstanding example of this may be seen in Figure 4. Using a seven-point moving average, this figure shows a comparison of the amounts of $CaCO_3$. The similarities are obvious.

The following general statements may also be made with regard to the physical appearance and geology of the Oread Limestones. The limestone of the middle Oread (Leavenworth) varies the least. The lower (Toronto) and upper (Kereford) show the greatest variation. The Toronto Limestone in Southern Kansas exhibits a lithofacies similar to the Leavenworth. In the area of the type section of the Toronto (Woodson County), the bedding, color, and general appearance of the Toronto is similar to that of the Plattsmouth Limestone. The Leavenworth does not undergo a major lithofacies change at any point along the outcrop. The Plattsmouth varies primarily in degree of induration, weathering characteristics, the presence of chert and the color of shale partings. The Kereford is discontinuous and more variable than any of the other limestones. It resembles the Leavenworth and Plattsmouth Limestones in specific areas but does exhibit a facies which is unique as exemplified by the "Waverly Flags."

Table 5. Results of Chemical Analysis and Other Pertinent Data of the Kereford Limestone.

Loc. No.	Lab. No.	County	Locality Sec. T.S. R.E.	Thick-ness	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O
1	59254	Doniphan	NW 24- 2-21	2.0	10.01	2.91	4.20	0.20	36.26	7.19	0.47	0.15
2	59255	Doniphan	SW 21- 3-22	2.0	7.45	2.31	2.42	0.20	47.38	0.73	0.22	0.07
3	6128	Doniphan	SE 26- 4-21	1.6	4.18	1.06	3.58	0.30	49.09	1.06	0.11	0.03
4	602	Atchison	SW 6- 5-21	1.5	3.51	1.20	1.73	0.08	50.96	0.81	0.04	0.01
5	59253	Atchison	NE 32- 6-21	3.5	11.05	3.12	2.56	0.17	44.44	1.00	0.47	0.10
6	59252	Leavenworth	SW 27- 7-21	3.0	2.66	0.75	2.67	0.01	50.84	0.70	0.06	0.02
7,8	59251	Leavenworth	SW 32- 8-21	2.0	8.60	2.54	2.07	0.16	46.57	0.83	0.26	0.09
9	59250	Leavenworth	NW 34- 9-20	3.7	9.41	2.56	1.72	0.16	45.38	1.71	0.33	0.17
10	59249	Jefferson	NE 12-11-19	6.6	9.49	2.32	2.20	0.11	46.48	0.62	0.14	0.08
11	59260	Douglas	NW 2-12-18	6.8	11.53	2.46	2.86	0.22	44.64	0.83	0.47	0.15
12	60109	Douglas	SW 31-12-19	2.2	18.94	3.36	2.76	0.28	38.51	1.09	3.23	0.26
13	60132	Douglas	SW 18-14-19	0.8	12.06	3.28	2.57	0.18	43.67	0.85	0.44	0.13
14	60111	Douglas	C 3-15-18	2.0	16.07	4.85	2.93	0.19	39.74	0.88	0.76	0.13
15	59101	Osage	NE 15-16-17	12.0	7.33	1.89	1.72	0.06	48.54	0.80	0.10	0.04
16	59102	Osage	SW 35-16-16	8.2	7.84	1.90	1.94	0.10	48.11	0.64	0.10	0.06
17	60110	Osage	E 4-18-16	25.2	6.74	1.63	1.21	0.28	49.36	0.80	0.14	0.06
18	59103	Osage	W 36-18-16	12.2	6.21	0.88	1.17	0.14	50.47	0.56	0.06	0.04
19	59104	Coffey	E 11-20-16	11.0	48.91	1.97	2.12	0.22	25.23	0.36	0.24	0.12
20	60114	Coffey	SW 11-21-15	8.6	6.93	1.52	2.88	0.09	48.38	0.72	0.14	0.06
21	60113	Coffey	SW 2-22-15	0.5	27.23	6.21	4.76	0.45	31.40	0.76	0.89	0.12
22	60115	Woodson	C 14-24-14	6.3	29.99	1.37	1.48	0.10	36.78	0.27	0.10	0.06
23	5912	Woodson	S 8-25-14	2.9	19.22	0.82	2.56	0.15	42.49	0.43	0.05	0.02
24	58307	Greenwood	SW 8-26-13	7.0	10.11	2.45	2.55	0.08	45.92	0.65	0.23	0.02
25	59261	Greenwood	C 6-27-13	2.0	51.32	3.49	2.42	0.45	21.74	0.45	0.38	0.52

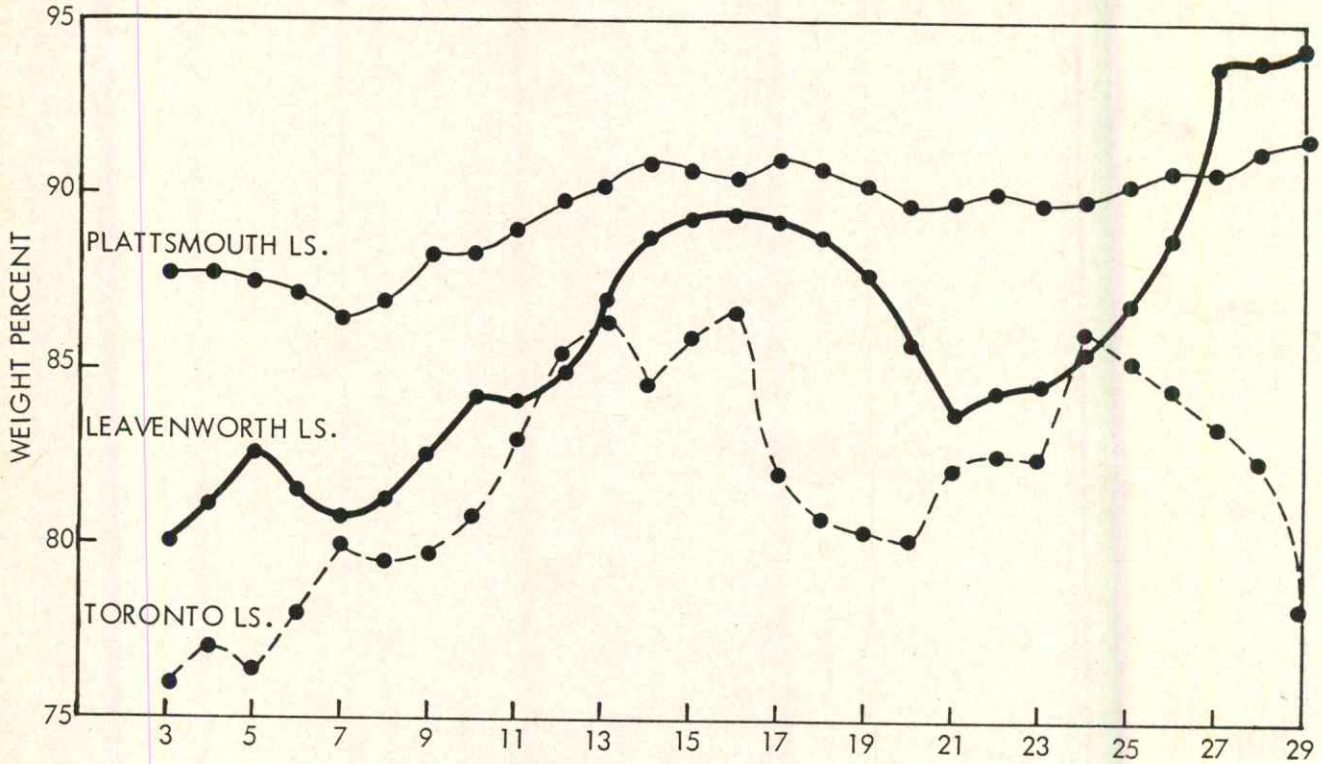

Figure 4. Comparison of $CaCO_3$ in three limestones.

It is also of interest to note the way in which some of the rivers or natural boundaries within the state also act as dividing lines denoting changes in chemistry along the outcrop. As pointed out earlier, the outcrop of the Plattsmouth Limestone can be divided into four distinct areas in relation to the percent $CaCO_3$ and SiO_2. The boundary of each area coincides with a river except the extreme southern boundary which is the Kansas-Oklahoma line. The Leavenworth and Kereford Limestones do not follow this pattern. There are only two general areas which can be distinguished in these limestones and the dividing line is the Kansas River. The results as listed in the tables show the difference of the two areas. The Toronto Limestone has three areas which should be noted. The area north of the Kansas River has already been mentioned. The other two areas are south of the Kansas River to the Marais des Cygnes River (Loc. 13 thru 15) and the area between the Neosho River and the Verdigris River (Loc. 21 thru 24). In these areas, the SiO_2 content is the lowest and the $CaCO_3$ content reaches its maximum. Also in the area of Loc. 21 thru 24 the thickness of the limestone is consistently seven to nine feet.

Economically speaking, all limestones of the Oread Formation, except the Leavenworth, have been quarried. The Plattsmouth Limestone is quarried most extensively. The only area in which the Plattsmouth is not quarried is in Woodson and Greenwood counties (Loc. 22-26). The primary uses of limestone quarried from the Plattsmouth is that of road metal, concrete aggregate and agricultural lime. In the northeast part of the state it has also been used for rip-rap along the Missouri River. The Toronto is quarried extensively in Woodson and Greenwood counties (Loc. 22-26). The primary uses being road metal, agricultural lime and concrete aggregate. The Kereford is utilized economically in Coffey counties with most usage again being road metal and agricultural lime. In the area of Burlington, Kansas the site of a flood control dam on the Neosho River, the Kereford limestone was used for rip-

rap along the John Redman Dam.

The conditions present at the time the Oread Limestone was deposited were not fully explored during the course of this study. While it is obvious that the environment of deposition influences the chemical composition of the limestone, such a study was not included within the scope of this paper. It is possible that as the analyses of the limestones of the other formations of the Shawnee Group are completed, a more detailed picture of the environmental conditions present at the time of deposition will be obtained.

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AGGREGATE SOLUBILITY RELATED TO CHERT PETROGRAPHIC TEXTURES AND ELECTRON SURFACE MORPHOLOGIES[1]

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ABSTRACT

Solubility, petrographic and electron optical studies were made on chert from ten different localities in Ohio. The distribution of electron optical surface morphologies and petrographic textural types were determined respectively from 6000 replicas and 550 thin-sections. The surface morphologies observed are porous, spongy, intermediate, polygonal, and "crystallite," whereas the petrographic textural types observed are amorphous, cryptocrystalline, microcrystalline, fibrous, and mosaic (megaquartz). In addition, chert pore size distributions and solubilities in solutions ranging in pH from 8.0 to 13.0 were determined. A marked correlation occurs between the surface morphologies, petrographic textures, and the solubilities and routine engineering tests.

The chert morphologies and textures represent possible stages of devitrification and polymerization of fine-grained silica. A change of surface area, packing density, and crystallinity occurs with grain growth and influences the physical, chemical, and optical behavior of the chert.

The degree of devitrification and polymerization is a function of the following geological factors: (1) time; (2) depth of burial; (3) tectonics; and (4) metamorphism or diagenesis. If the concrete durability of a chert aggregate is to be ascertained with any fidelity, it is necessary to study in detail the geologic occurrence of the chert.

Cherts with amorphous, cryptocrystalline, and fibrous textures and porous, spongy, and "crystallite" surface morphologies exhibited: (1) the least freeze-thaw durability; (2) the highest solubilities; and (3) the greatest expansion due to alkali-chemical reactivity. In addition, cherts which possess variable texture and grain size and exhibit partial replacement tend to be deleterious in concrete.

The cherts with a homogeneous matrix composed of uniform size microcrystalline quartz and with an intermediate to polygonal surface morphology exhibit better cryothermal durability and lower solubility and chemical reactivity.

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[1] The paper by William A. Kneller was not submitted for publication.

RELATIONSHIPS BETWEEN α-QUARTZ CELL PARAMETERS AND SOME PHYSIO-CHEMICAL PROPERTIES OF CHERT AGGREGATES

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ABSTRACT

Cell parameters of 22 chemically analyzed chert samples have been determined by least squares computer analysis of x-ray powder photographs before and after a double heating to 1000°C. In most chert pairs both of the lattice parameters ***a*** and ***c*** increased with the largest increase in ***a*** . There is a correlation between a large increase in ***a*** of the heated sample and deleterious behavior of the unheated chert in a high alkali cement. A less pronounced correlation is apparent between expansion of heated samples and two properties of the unheated chert, silica solubility and effective porosity.

Studies of quartz cell parameters by other investigators have led to the conclusion that an interstitial type of solid solution mainly causes ***a*** to increase. Large increases in this parameter upon heating suggest that some of the tested cherts have more structural disorganization (unspecified) than others. This may permit a larger amount of foreign ion interstitial admission as the structure expands upon heating, and the retention of foreign ions in the structure instead of exsolution at the β to α-quartz inversion.

The recognition of this behavior may be useful in predicting chert reactivity in concrete.

INTRODUCTION

The environmental conditions of formation of fine-grained silica (chert) are well-known. Most cherts are formed in an aqueous environment and are generally believed to have crystallized from a colloidal "silica-gel". Because the amount of detritus entering this type of environment can vary markedly, cherts characteristically have a wide range in SiO_2 content. Variations in species, degree of crystallinity, grain size, and porosity of fine-grained silica in chert can be found within adjacent zones of a single hand specimen. These variations would be expected to produce changes in the behavioral properties of chert, as well as changes in the more salient characterizing feature, cell parameters. In this investigation an attempt is made to determine whether a quantitative study of the cell parameters of the α-quartz in chert can be correlative to certain behavioral properties when chert is used in concrete. Specifically, the investigation has led to an evaluation of many parameters, including chemical composition, porosity, solubility, and mortar bar expansion phenomena in relation to changes in cell dimensions.

SAMPLE PREPARATION AND DATA ANALYSES

Twenty-two chert samples were crushed, sieved, and the 325 mesh fractions were retained. A portion of the sample was designated for chemical analyses. Self-supporting sample spindels for x-ray purposes were prepared by mixing 2/3 (volume) chert with 1/2 amorphous low absorbing binder. The mixture was rolled, while moist, to the desired thickness. The spindel, when dry, was aligned in a 22.5 cm diameter General Electric powder camera.

Each of the 22 cherts was divided into two fractions. One was x-rayed without further treatment and the other was subjected to a double heating to 1000°C in a DTA furnace before x-ray investigations were carried out. Computations in the computer program

demanded the film be mounted in the "regular" position following the method of Bradley and Jay (see Klug and Alexander, 1954). The samples were exposed to filtered copper radiation for a period of 20 hours. The tube was operated at 40 kv and 30 ma. Radiation was directed to the sample through a 20 mil diameter beam collimator. Laboratory temperature was maintained at 25°C during the exposure.

After development and drying, the films were read in a film reader which permits line definition to the nearest 0.02 mm. Front and back reflections were used in computation of the a_o and c_o cell parameters of α-quartz by a least squares program with an IBM 1620 data processing unit.[1]

Most cherts gave excellent powder diffraction patterns with well-resolved α_1 α_2 doublets in the high-angle region. In these cherts a high precision (standard deviation value of 0.0005A or less) was regularly attained. Samples which gave broadened reflections in the back reflection region were computed to have higher standard deviations (0.0005A up to 0.0014A) due to errors introduced in measuring the exact center of the lines and to the decrease in the total number of reflections used in the computation. Each reflection was examined and its d-value computed according to the observed value of θ and a calculated value computed by the program based on the formula for the hexagonal system where the hkl values are known. If the residual between $d_{calc.}$ and $d_{obs.}$ was large, the reflection was discarded and the data resubmitted. This procedure was continued until the standard deviation remained constant for the specimen. The accuracy of the determined cell parameters cannot be independently determined as there is no reference chert. However, the d-values for the quartz standard agreed with those reported by Frondel (1962, p. 25-28) and yielded parameters for a_o and c_o with standard deviations of 0.0001A.

VARIATIONS IN CELL PARAMETERS OF NATURAL QUARTZ

Variations in the cell parameters of α-quartz have been attributed to the presence of foreign ions, structural vacancies, structural disorder, and environmental variables such as temperature and pressure. Significant variations in the chemical composition of quartz have been reported in the literature and evidence has been presented which relates change in composition to variation in cell parameters. Wittels (1953) reported a quartz sample such that the parameters a_o and c_o increased when subjected to a neutron flux. The change was attributed to a dislocation phenomenon whereby some of the atoms were housed in an interstitial position. The quartz structure was restored on annealing.

Measurement of unit cell parameters of cherts in paired samples, one of which had been sufficiently heated so as to "reorder" the structure or drive off excess or combined OH, should provide the investigator with a set of data which may yield some additional information concerning the reactivity of the sample - especially if it has been characterized chemically and physically. With this assumption as the main basis of investigation, the discussions which follow are presented with two ultimate goals in mind: (1) to explain the variation in cell parameters in cherts caused by heat treatment (Table I). and (2) to relate these data to any significant trends which may be useful in determining the value of a specific chert as an aggregate in concrete.

VARIATION IN CELL PARAMETERS IN CHERTS DUE TO ION SOLUTION

Dennen (1966) has demonstrated that substitution of foreign elements for silicon or oxygen in quartz results in electrical neutrality as a result of the interchange. Table II summar

[1]Original program received from D. Peacor, Department of Geology and Mineralogy, University of Michigan, Ann Arbor, Michigan.

Table I. Cell parameters of 22 chert specimens from Ohio.

No.	Before Heating a_o(Å) (S) (1)	Before Heating c_o(Å) (S)	Before Heating c_o/a_o	After Heating a_o(Å) (S)	After Heating c_o(Å) (S)	After Heating c_o/a_o	Variation(3) in a_o	Variation(3) in c_o	SiO_2 (Wt.%)	CaO (Wt.%)	Al_2O (Wt.%)	FeO (Wt.%)	Fe_2O_3 (Wt.%)	Ti PPM	Ge PPM	Li PPM	K PPM	Na PPM	$\frac{CaO+Al_2O_3}{SiO_2}$
1L	4.9112 (0.0009)	5.4036 (0.0008)	1.1002	4.9114 (0.0006)	5.4073 (0.0008)	1.1003	+0.0002Å	+0.0037Å	92.31	2.22	1.15	0.18	0.08	150	0.7	5	2000	500	0.03
2HD1	4.9151 (0.0007)	5.4048 (0.0009)	1.0996	4.9153 (0.0012)	5.4049 (0.0011)	1.0996	+0.0002Å	+0.0001Å	90.06	2.68	0.80	0.12	0.74	175	0.1	2	1750	350	0.03
2MD2	4.9137 (0.0014)	5.4032 (0.0013)	1.0996	4.9154 (0.0013)	5.4041 (0.0012)	1.0994	+0.0017Å**	+0.0009Å*	82.20	5.73	0.85	0.18	1.01	170	0.3	6	1280	420	0.08
2HD2	4.9141 (0.0007)	5.4048 (0.0007)	1.0998	4.9142 (0.0006)	5.4049 (0.0005)	1.0998	+0.0001Å	+0.0001Å	82.98	4.93	0.72	0.15	1.17	220	0.2	7	2200	650	0.06
3L	4.9101 (0.0006)	5.4019 (0.0006)	1.1001	4.9121 (0.0006)	5.4037 (0.0007)	1.1000	+0.0020Å**	+0.0018Å**	90.21	2.55	1.18	0.15	0.39	20	0.2	1	400	150	0.04
3MW	4.9138 (0.0005)	5.4020 (0.0006)	1.0993	4.9142 (0.0008)	5.4036 (0.0008)	1.0995	+0.0004Å*	+0.0016Å**	75.43	9.47	0.98	0.16	0.25	45	0.6	1	750	300	0.13
4AL	4.9134 (0.0006)	5.4039 (0.0004)	1.0998	4.9172 (0.0012)	5.4047 (0.0010)	1.0991	+0.0038Å**	+0.0008Å**	84.12	5.03	1.21	0.15	0.25	94	0.5	3	1070	400	0.07
4BM	4.9109 (0.0005)	5.4020 (0.0005)	1.1000	4.9146 (0.0005)	5.4025 (0.0003)	1.0992	+0.0037Å**	+0.0005Å**	83.92	6.45	0.36	0.31	0.09	83	0.3	3	2300	660	0.08
5HD	4.9140 (0.0004)	5.4074 (0.0004)	1.1000	4.9178 (0.0006)	5.4066 (0.0006)	1.0993	+0.0038Å**	-0.0008Å**	61.06	18.73	2.01	0.24	0.22	100	1.0	1	2500	1500	0.33
5HG(2)	4.9110 (0.0005)	5.4027 (0.0006)	1.1000	4.9130 (0.0007)	5.4028 (0.0007)	1.0996	+0.0020Å**	+0.0001Å	55.23	21.95	1.26	0.16	0.26	110	0.3	6	1100	570	0.42
6L	4.9118 (0.0003)	5.4033 (0.0004)	1.1000	4.9145 (0.0005)	5.4040 (0.0005)	1.0996	+0.0027Å**	+0.0007Å**	94.82	0.12	1.72	0.18	0.65	80	0.1	2	900	400	0.01
6M	4.9114 (0.0003)	5.4028 (0.0004)	1.1000	4.9135 (0.0004)	5.4035 (0.0003)	1.0997	+0.0021Å**	+0.0007Å**	93.23	0.35	1.76	0.24	2.13	150	0.05	4	1500	500	0.02
6H	4.9106 (0.0003)	5.4016 (0.0004)	1.0999	4.9126 (0.0002)	5.4048 (0.0003)	1.1001	+0.0020Å**	+0.0032Å**	94.67	0.25	1.25	0.14	1.52	150	0.1	2	500	300	0.01
7L	4.9111 (0.0003)	5.4030 (0.0003)	1.1001	4.9127 (0.0006)	5.4037 (0.0007)	1.0999	+0.0016Å**	+0.0007Å**	90.74	0.54	1.14	0.14	1.73	75	0.2	6	960	320	0.03
7M	4.9110 (0.0004)	5.4031 (0.0004)	1.1002	4.9122 (0.0005)	5.4044 (0.0005)	1.1001	+0.0012Å**	+0.0013Å**	89.85	3.00	1.66	0.15	0.41	180	0.2	10	1500	300	0.05
7H	4.9109 (0.0011)	5.4016 (0.0013)	1.0999	4.9135 (0.0008)	5.4018 (0.0008)	1.0993	+0.0026Å**	+0.0002Å	77.81	8.17	1.81	0.17	0.39	230	0.2	9	770	600	0.12
8L	4.9141 (0.0003)	5.4045 (0.0003)	1.0997	4.9135 (0.0002)	5.4050 (0.0002)	1.1000	-0.0006Å**	+0.0005Å**	95.82	0.14	1.45	0.15	0.59	10	0.1	1	180	210	0.01
8M	4.9120 (0.0003)	5.4043 (0.0003)	1.1002	4.9128 (0.0003)	5.4043 (0.0003)	1.1000	+0.0008Å**	0.0000Å	96.30	0.37	0.76	0.13	0.49	5	0.01	0	160	100	0.01
8H	4.9121 (0.0004)	5.4031 (0.0004)	1.1002	4.9107 (0.0006)	5.4020 (0.0007)	1.1000	-0.0014Å**	-0.0011Å**	96.71	0.40	0.73	0.10	0.48	6	0.05	1	110	110	0.01
9HD	4.9098 (0.0008)	5.4036 (0.0006)	1.1005	4.9148 (0.0014)	5.4043 (0.0013)	1.0995	+0.0050Å**	+0.0007Å	75.54	11.39	2.20	0.15	0.22	333	0.3	3	1000	1000	0.17
10M	4.9140 (0.0008)	5.4052 (0.0008)	1.0999	4.9158 (0.0012)	5.4034 (0.0009)	1.0992	+0.0021Å**	-0.0013Å**	79.66	9.08	1.44	0.19	0.70	2	0.1	1	280	280	0.13
10H	4.9105 (0.0002)	5.4035 (0.0003)	1.1003	4.9120 (0.0002)	5.4037 (0.0003)	1.1001	+0.0020Å**	+0.0002Å	90.65	3.06	1.15	0.13	0.74	190	0.1	1	210	210	0.04

Analyst: J. T. Wilband

(1) Standard deviation

(2) Chemical analyses of sample 5HG do not represent that of the sample used for cell parameter determination. The x-rayed specimen was hand picked from a large nodule in the uncrushed chert because of the dilution effect of the carbonate minerals.

(3) ** - Significant at $\alpha = 0.01$ (t Test).
* - Significant at $\alpha = 0.05$ (t Test).

izes the most generally accepted replacement ions in quartz and the effect of their admittance into the structure upon the cell parameters. Of special significance in the discussion of foreign ion admissions is the conclusion reached by Dennen

> "---the dominant contaminants of quartz are just those ions which are abundant in tne environment and not necessarily those of best structural fit."[2]

Investigations on lattice expansion as a result of impurity ion solution (Keith, 1955; and Cohen and Sumner, 1958) have led to the conclusion that two main types of impurity positions exist in α-quartz: replacing Si^{4+} and interstitial (Table II). Electrical neutrality is preserved by a concomittant entry of a univalent cation in the interstitial position, when a trivalent cation such

[2]Our emphasis.

as Al substitutes for Si^{4+} (Table IIb). Other replacements such as Al^{3+} in the tetrahedral site with a proxy of $(OH)^-$ for O^{2-}, or two tetrahedral Al^{3+} with one interstitial Al^{3+} or Fe^{3+} have been proposed (Dennen, 1966). Results of a combined impurity analysis and parametric study of natural and synthetic α-quartz specimens by Cohen and Sumner (1958) led to the conclusion that a gradational change in cell parameters exists due to impurity ion concentration. They found that substitutional impurities for Si result in an increase in the values of a_o and c_o, and interstitial impurities result in an increase mainly in a_o.

Increase in the value of the a_o direction probably results when an atom is housed in the interstitial spaces which form long channels parallel to the c-axis. Stuffing of these channels is believed to produce a small stress in the structure (Keith, 1955). The effect of the interstitial impurity will be greater in a plane normal to the c-axis (i.e., containing the a_o axis) than in a plane parallel to the c-axis.

The determination of absolute assignments of foreign ions into the quartz within cherts is an extremely difficult task based only on chemical analysis and cell parameter studies because of the varying mineralogy of the cherts. Foreign ions are probably derived from the aqueous environment as well as from minerals which are intimately associated with the fine-grained quartz. Other minerals present in the cherts which have been identified from x-ray powder diffraction patterns are, in general order of decreasing abundance, calcite, dolomite (some ankerite), clay minerals (kaolinite and illite), hematite, and pyrite.

VARIATIONS IN CHERT CELL PARAMETERS RELATED TO CHEMICAL COMPOSITION

The data tabulated in Table III show that 17 of the 22 specimens underwent a significant change in the a_o parameter, whereas only 13 specimens showed a significant increase in c_o after heat treatment (t test, levels of significance taken at 0.01 and 0.05.).

The effect of heat treatment can be indirectly evaluated by determination of mean values of change in cell parameter for the specimens. Group a (Table III) shows that 22 specimens have a mean expansion of 0.0017A and 0.0006A in a_o and c_o, respectively. A study of these data has indicated six groupings (b to g - Table III) whose mean expansions in a_o and c_o vary significantly from these values.

Further study is needed to explain all the variations that exist between the different chert groupings. However, some trends are apparent and warrant discussion.

Al_2O_3 AND CaO CONTENT OF THE CHERTS

At elevated temperatures the solid solubility of Al^{3+} and alkali ions is reported to be considerably greater than at lower temperatures in coarsely crystalline quartz. Data presented in Table III suggest that in cherts, clay mineral and calcite (or dolomite) content, i.e., high Al_2O_3 and CaO content, are responsible for the increase in a_o. Most foreign ions are probably located in the interstitial positions because the mean expansion in a_o is nearly five times that of c_o in specimen groups b, c, and d (Table III).

The main transition in the cherts at the temperature range used in this study is the high-low displacive type inversion at 573°C. The resultant change in bond angles between adjoining silica tetrahedra is accompanied by a volume increase in the order of 0.86%. This reaction should be accompanied by the solution of calcium ions and the alkalies Na^+ and possibly K^+ (group f, Table III). At 870°C, high quartz may invert to tridymite. The x-ray powder diffraction films do not indicate the presence of a tridymite phase as a result of heating; however, in specimens rich in CaO strong peaks of $CaSiO_3$ indicate that the lime-silica reaction, $CaO + SiO_2 \rightarrow CaSiO_3$, does take place.

Groups c and f in Table III, based on CaO content of > 3% and chert samples with > 0.05% mortar bar expansion in high alkali cement respectively, are correlative with respect to the mean cell parameter expansion. Furthermore, 11 of 13 specimens whose

Table 2. General replacement ions in quartz and the effect of their admittance into the structure upon the cell parameters.

TYPE OF IMPURITY	BALANCING IONS (Position)	CHANGE IN CELL PARAMETERS
A. Substitutional Impurity replaces Si^{4+}		
a) Ti^{4+}, Ge^{4+}, B^{4+}		Expansion in a_o and c_o.
b) $Al^{3+}, Fe^{3+}, Mn^{3+}, B$	H^+, Li^+, Na^+ (interstitial)	Unequal expansion in a_o and c_o, greatest in a_o.
c) Al^{3+}	OH^- for O^2 (tetrahedra)	Expansion in a_o and c_o.
d) $2Al^{3+}$	1 Mg^{2+}, 1 Ca^{+2} (interstitial)	Unequal expansion in a_o and c_o, greatest in a_o.
e) $3Al^{3+}$	1 Al^{3+}, 1 Fe^{3+} (interstitial)	Expansion in a_o and c_o.
B. Interstitial Impurity "Stuffing"	Most rock forming elements ($K^+, Ca^{+2}, Mn^{+2}, Mg^{+2}, Fe^{+2}$) and others(2)	Expansion mainly in a_o

(1) Data compiled from Dennen (1966), Frondel (1962), and Cohen and Sumner (1958).

(2) Frondel (1962) reports Rb, Cs, Ba, Pb, Ag, Sn, Cu, Zn, V, Cr, Zr, and U.

Table 3. Chert groupings based on certain chemical and physical properties.

	Number of Specimens	Mean Expansion of a_o upon heating (Å)	Mean Expansion of c_o upon heating (Å)
a. All Specimens	22	0.0017	0.0006
b. Specimens with more than 1.4% Al_2O_3	8	0.0025	0.0006
c. Specimens with more than 3% CaO	12	0.0024	0.0006
d. Specimens with $CaO+Al_2O_3/SiO_2$ values greater than 0.10	6	0.0026	0.0005
e. Specimens with high expansion [(ΔL of 0.05% in a high alkali cement (>1.5% Na_2O)] (1)	13	0.0024	0.0006
f. Na+K content greater than 0.18%	8	0.0020	0.0008
g. Specimens with effective porosity and solubility greater than 10% and 900 PPM SiO_2 respectively (2)	6	0.0019	0.0015

Analysts: J. T. Wilband, W. A. Kneller, et al

(1) Mortar Bar Test (Modified ASTM C227) The mortar bars were placed in a standard cement autoclave on a rack above a reservoir of water. The temperature in the autoclave was raised gradually over a two hour period to 390°F with a steam pressure of approximately 200 psi. The temperature and pressure were maintained for a period of 5 hours, after which the power was shut off and the sealed autoclave was permitted to cool for 15 hours. The bars were then withdrawn and stored in a 73°F room at 50 percent relative humidity for 9 hours. The bars were then weighed and measured. This modification is deemed necessary to accelerate the test.

(2) Solubility measurement at an average pH of 13.3±.3 after 13 months.

cements showed high mortar bar expansion have a CaO content which is less than 3%.

Five of eight specimens in chert rich in Al_2O_3 (1.4% - group b, Table III) have a CaO content greater than 3%. The remaining three specimens have the least amount of CaO of all 22 specimens (6L - 0.12%; 6M - 0.35%; and 8L - 0.14%) and with the exception of specimen 8L the parameter a_o significantly increased in the heat treated specimens. The anomalous samples, 6L and 6M, have higher than average Fe^{3+} and Fe^{2+} concentrations. The solution of these during heating into the interstitial sites in chert may have resulted in the increase in a_o.

The chert group with high CaO + Al_2O_3/SiO_2 values (group d, Table III) is correlative to those with the high CaO content (seven of the eight specimens contain 3% or more CaO). The mean increase in the a_o and c_o parameters in both groups is essentially identical within the experimental error.

ALKALI METAL CONTENT OF THE CHERTS

If the substitutional impurity Al^{3+} replaces Si^{4+} in the tetrahedral sites, the charge deficiency theoretically is balanced by univalent cations housed in interstitial positions. In cherts the univalent alkalies Li^+, Na^+, and K^+ are available for solution into the quartz structure at elevated temperatures concommitant with a substitution of Al^{3+} for Si^{4+}. This reaction may be inferred in some cherts as 4 of 8 specimens rich in Na+K (group f, Table III) are also rich in Al_2O_3 (group b, Table III). The four remaining specimens contain Al_2O_3 in amounts ranging from 0.34% to 1.15%. Na+K rich cherts have a lower mean increase in a_o and higher expansion in c_o after heat treatment when compared to the CaO rich cherts (group c, Table III).

POROSITY AND SOLUBILITY OF CHERTS RELATED TO CELL PARAMETERS

An excellent correlation between effective porosity and solubility of silica can be made in six of the twenty-two specimens. These data when coupled with measurements of the a_o and c_o parameters yield a distinctive grouping whose cell expansion properties are significantly different from all other groupings. Group g (Table III) has a larger increase in the c_o dimension than all others, and a value for a_o which is essentially equivalent to that of mean expansion in that direction for the twenty-two specimens (group a). The high porosity coupled with the effect of temperature during heating apparently favors ionic solution of both the substitutional and interstitial type.

STRUCTURAL "DISORDER" RELATED TO CELL PARAMETERS

Disordering in α-quartz can be discussed in two broad categories. The first deals with disturbances in the bonding among the (SiO_4) tetrhedra which define the structure and is generally considered to be the physical manifestation of mechanical deformation. The second observed disordering in quartz has been related to dislocation of atoms from their normal sites into interstitial positions. This requires great amounts of energy, and the efficiency by which this type of disordering can be produced in nature is not known.

Stress induced by disordering phenomena would be expected to be relieved, cell parameters reduced, and the structure of quartz restored upon annealing. Our data indicate, however, that only one sample showed a significant reduction of the a_o and c_o parameters after annealing. Other samples showed reduction of one of the two parameters, the other expanding or remaining essentially unchanged.

Data summarized by Frondel (1962) indicate that a thin surface layer of disoriented material is formed by mechanical action such as grinding. During the crystallization process of chert a similar phenomenon may be experienced where a disordered layer of silica is formed as adjacent crystals grow together or against foreign minerals which crystallize contemporaneously with quartz. The large surface area of fine-grained cherts would favor the existence of a much greater volume of disordered material than a single crystal or polycrystalline aggregate of coarse-grained quartz.

Surface disordering, if present, would be expected to be restored to a less strained configuration upon annealing. In addition, depending upon the concentration of impurity ions at the disoriented layer interface, the possibility of solid solution of impurity ions should be greatest in these zones.

CONCLUSIONS

A study of cell parameters, chemistry, and routine engineering tests of twenty-two Ohio cherts has led to the following conclusions: (1) A comparison of chert groupings indicates that most cherts expand along a_o and c_o directions upon heating. This is best explained as a result of impurity ion substitution, probably Al^{3+} for Si^{4+}, and interstitial stuffing.

Our data indicate that Ca^{2+} (ionic radius = 0.99A) is probably stuffed into the interstitial spaces in chert upon heating. A weaker correlation can also be shown for Na^{+} (0.97A) and K^{+}(1.45A). Iron may be accommodated into the silica structure if Ca^{2+} is not abundant. (2) Following Dennen's (1966) conclusions for quartz, we conclude that the dominant impurities in α-quartz of chert are those ions which are abundant in the environment and not necessarily those of best fit.

The mineralogical content of the cherts, particularly the carbonate and clay mineral content, has a direct relationship to the α-quartz cell parameters when the chert is heated to 1000°C. Generally, the relationship may be stated as follows: The higher the carbonate and clay mineral content in a specimen of chert, the greater the possibility that the α-quartz will expand along the a_o direction. In most of the cherts studied the CaO content was greater than the Al_2O_3 content; thus the absolute effect of CaO and Al_2O_3 on the cell parameters cannot be quantitatively ascertained. (3) Six cherts with high effective porosity were found to have the greatest silica solubility of all the specimens studied. The cell parameters of these specimens indicate foreign ion solution by the α-quartz so that there was expansion along a_o and c_o as a result of heat treatment.

High temperature favors substitutional solution in highly porous cherts, whereas in highly calcareous cherts the dominant type of ion solution is interstitial. (4) The change in a_o and c_o parameters of quartz in chert from unheated and heated specimens may be used as a measure of the reactivity of cherts in concrete. A good correlation exists between unfavorable mortar bar expansion of chert and large changes of cell parameters. The common factor in this correlation is the CaO content. These trends suggest that highly calcareous cherts should be suspect when used as aggregate in high alkali cements.

On the other hand cherts with high silica, and low alumina and lime content did not significantly expand along a_o and c_o. Furthermore, these cherts did not expand significantly in high alkali cements. We conclude, therefore, that a pure SiO_2 chert is the least deleterious choice for concrete aggregate, unless it has a high porosity or spongy morphology (Kneller, 1965, 1966). (5) Chert reactivity at high temperatures may be due to surface disorientation in some cherts. A reordering of the chert structure at high temperature and in the absence of impurity ions would result in a decrease of cell parameters. Conversely, reordering in the presence of impurity ions would cause expansion in one or both of the parameters.

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DISSOLVED SALTS IN OIL-FIELD BRINES-A WASTED RESOURCE?

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ABSTRACT

The recovery of several elements contained in oil-field brines has recently assumed greater importance as a means of satisfying new industrial demand. Fresh water as a by-product of such extraction procedures could well be an additional revenue source. Presently, processes for the production of calcium, magnesium, sodium, potassium, iodine, chlorine, and bromine from many brines are being successfully applied. Iodine, for example, is extracted from California oil-field brines having an iodine content of only 10-200 ppm.

Of particular interest are those processes recently developed for the removal of calcium and magnesium from brines by precipitation in the form of magnesium ammonium phosphate and dicalcium phosphate which can then be used as fertilizer.

Billions of barrels of oil-field brines are brought to the surface yearly in the United States. About 50% of these brines are returned to the subsurface without any attempt of stripping the contained salts. The volume of this brine is such as to warrant greater consideration of the economic feasibility of extracting much, if not all, of the metallic salts dissolved therein. As an illustration of the possible economic value of the metallic content of oil-field brines, the results of a detailed study will be presented for their potential value in just one Kansas County (Butler) for 1966.

INTRODUCTION

With the greater attention now being paid to the two problems of water pollution and useage and natural resource utilization, the possible recovery of dissolved minerals from oil-field brines takes on greater importance with each passing year. Oil-field brines contain, in some measure, all of the common elements present on earth.

Many processes have been proposed for stripping dissolved salts from sea water, and new techniques are being applied constantly. Several of these processes can, with some modification, probably be applied to the recovery of specific elements or compounds from oil-field brines. Study of the feasibility of the application of some of these techniques to recovery of dissolved salts in highly concentrated brines is needed. An excellent review of the subject of mineral recovery from sea water with applicability to oil-field brines is presented by Tallmadge et al (1964).

According to Collins (1966), more than 250 billion gallons (i.e. $> 6 \times 10^9$ barrels) of salt water are brought to the surface yearly in the Continental United States. These brines contain more than 100 million tons ($>10^8$ tons) of dissolved salts, of different compounds such as the chlorides, sulfates, bromides, carbonates, etc. of calcium, magnesium, sodium, potassium, strontium, barium, etc.

Table 1 presents data on the concentration of some elements in oil-field brines and compares their concentration with that present in sea water. Several of the dissolved salts contained in oil-field brines are in short supply in the United States and their economic value will increase with time. Several elements (e.g. iodine, bromine, chlorine, sodium, and magnesium) are presently being recovered from brines. For example, Dow Chemical Co. produces iodine, magnesium sulfate and hydroxide

and the chlorides of calcium, magnesium, and potassium from subsurface brines, and The Michigan Corporation strips bromine from oil-field brines in Arkansas.

In most instances, however, oil-field brines are either used for secondary recovery operations (water flooding) or are reinjected into some producing subsurface formation without any attempt at recovery of the dissolved mineral content. A review of the dissolved salt content of many oil-field brines (Table 2 lists some typical values) strongly suggests that in the not too distant future it will become economically untenable to return most brines to the subsurface without first stripping the dissolved minerals from them.

DISCUSSION

Caustic Soda, Soda Ash, Chlorine

To illustrate the possibilities let us examine the composition of two brines (Table 2). These brines contain large amounts of chlorine. The high Cl content is obvious and is typical of many oil-field brines. Brines are an essential starting raw material in the production of soda ash, caustic soda, and chlorine, three of the most important chemicals produced in the chemical industry. Future requirements for these chemicals show a definite upward trend continuing well into the 1970's an beyond. Raw materials for the Solvay process way of making soda ash (Fig. 1) for example, are sodium chloride, lime, and ammonia (Shreve 1956). Salt is used in the form of a brine which can be made from rock salt, natural brine, or sea water. Limestone is burned in the kilns to furnish both the CO_2 for the soda ash and the lime for the recovery of ammonia. Other than a minimum of SiO_2, Al_2O_3, and Fe_2O_3 as impurities, no specific requirements for the limestone are indicated. Many areas (such as Kansas and Oklahoma) where large quantities of oil-field brines are available or can be produced easily have abundant limestone resources. The uses for caustic soda and soda ash are myriad (Fig. 1). The principal reactions of the Solvay Process are given on the next page. Caustic soda can then be produced from the soda ash or by electrolysis of salt brines.

It should be economically possible to precipitate the calcium and magnesium impurities of oil-field brines for use as fertilizer (discussed later) and use the remaining brine, high in chloride, as a con-

Table 1. Comparison of dissolved solids in sea water and high values reported for different brines.*

Element	Sea Water, ppm	Oil-Field Brines (ppm)	Concentration Ratio
Chlorine	18,980	270,000	14.2
Sulfate	2,560	8,000	3.4
Bromine	65	5,500	84.6
Iodine	0.05	260	520
Sodium	10,560	150,000	14.2
Calcium	400	120,000	300.0
Magnesium	1,272	25,000	19.7
Potassium	380	10,100	26.6
Strontium	8	4,500	562.0
Barium	0.05	1,000	20,000
Lithium	0.18	150	836.0
Rubidium	0.2	7	35.0

*From many sources

Table 2. Major Element Composition (ppm) of Two Highly Mineralized Kansas Oil-Field Brines

Composition	Topeka Formation Pennsylvanian Age	Cherokee Formation Pennsylvanian Age
TS*	236,500	169,000
Cl	130,300	86,900
Na	51,500	45,400
Ca	13,400	14,500
Mg	4,050	3,160
SO_4	3,500	5,800

*Total Dissolved Solids

Solvay Process Reactions

(1) $CaCO_3(c) \rightarrow CaO(c) + CO_2(g)$;

(2) $C\ (amorph.) + O_2(g) \rightarrow CO_2(g)$;

(3) $CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(c)$;

(4) $NH_3 + H_2O(l) \rightarrow NH_4OH(aq.)$;

(5) $2NH_4OH(aq.) + CO_2(g) \rightarrow (NH_4)_2CO_3(aq.) + H_2O(l)$;

(6) $(NH_4)_2CO_3 + CO_2 + H_2O \rightarrow 2NH_4HCO_3$

(7) $NH_4HCO_3 + NaCl \rightarrow NH_4Cl + NaHCO_3$

(8) $2NaHCO_3(c) \rightarrow Na_2CO_3(c) + CO_2(g) + H_2O(g)$;

(9) $2NH_4Cl(aq.) + Ca(OH)(c) \rightarrow 2NH_3(g) + CaCl_2(aq.) + 2H_2O(l)$;

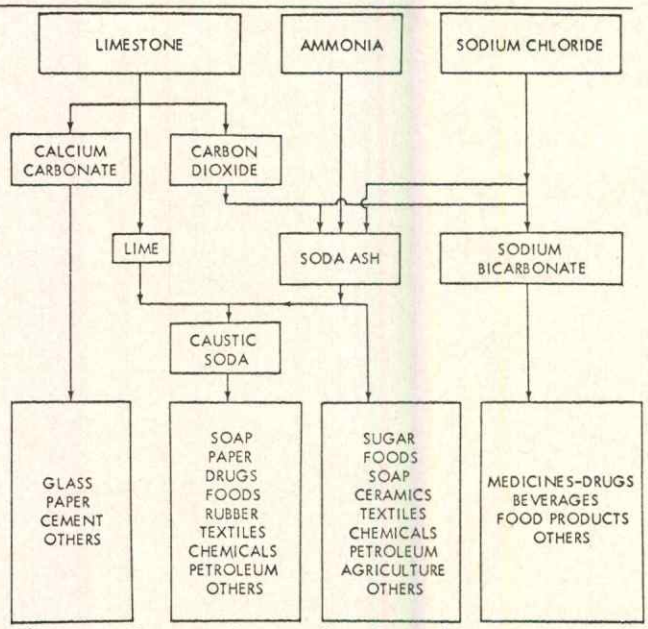

Figure 1. Schematic drawing of production steps for making soda ash and caustic soda. Some uses in the manufacture of other products are indicated.

venient source of chlorine. The process for electrolytic recovery of chlorine and caustic soda from naturally occurring brines is widely employed. Brine solutions can also be purified by addition of Na_2CO_3 to remove the calcium and magnesium. Owing to its uses as a base chemical and for water and sewage purification, manufacture of chlorinated rubber, etc., the demand for chlorine has developed phenomenally in the past few years. The recent conversion to hydrochloric acid (HCl) from sulfuric acid (H_2SO_4) as a pickling liquor in the steel industry has accelerated this demand.

The introduction of modern know-how, such as the use of weak acid resins to pretreat natural brines for chlorine-caustic soda manufacture increases the economic possibilities of greater use of oil-field brines as a base chemical raw material.

It should also be possible to strip the sulfate from certain oil-field brines (See Table 1) for use

in the production of sulfuric acid (H_2SO_4), another base chemical with a steep growth curve. A recent Bureau of Mines publication describes a process for desulfating brines that has economic possibilities (George et al 1967).

Bromine, Iodine, Sodium, Magnesium

More bromine and iodine can also be recovered from oil-field brines than presently. Bromine is recovered by displacement with chlorine. This results in free bromine dissolved in the water. The bromine can then be stripped by reaction with SO_2 and adsorption into an aqueous phase. A similar replacement method is used for the recovery of iodine. The recovery of magnesium from brines is so well known as to require no comment here. Similarly, for sodium little need be said. A high quality grade of NaCl can be obtained by first treating the brines with Na_2SO_4, $CaCO_3$ and $Ca(OH)_2$ to precipitate the alkaline earth salts, and then evaporating the remaining brine solution.

Fertilizer

A recent process developed by W. R. Grace Co. allows for the removal of calcium and magnesium from sea water in the form of magnesium ammonium phosphate (MAP) and dicalcium phosphate which can then be used as a fertilizer. An analysis of this material (Cox 1967) gives: N 7%, P_2O_5 43%, MgO 21%, CaO 5%, trace elements + water 24%.

The applicability of this method to oil-field brines has yet to be demonstrated but the possibilities are intriguing. A proposed procedure is illustrated in Figure 2.

W. R. Grace Co. has studied the economics of a plant processing one million gals. of sea water per day. If one compares the concentrations of the dissolved salts of oil-field brines and sea water, then it is clear that only 1/10- 1/25 of this volume per day would be required using oil-field brines as a source to produce a given amount of fertilizer. Conversely, treatment of one million gals. oil-field brine per day would, of course, increase the output considerably.

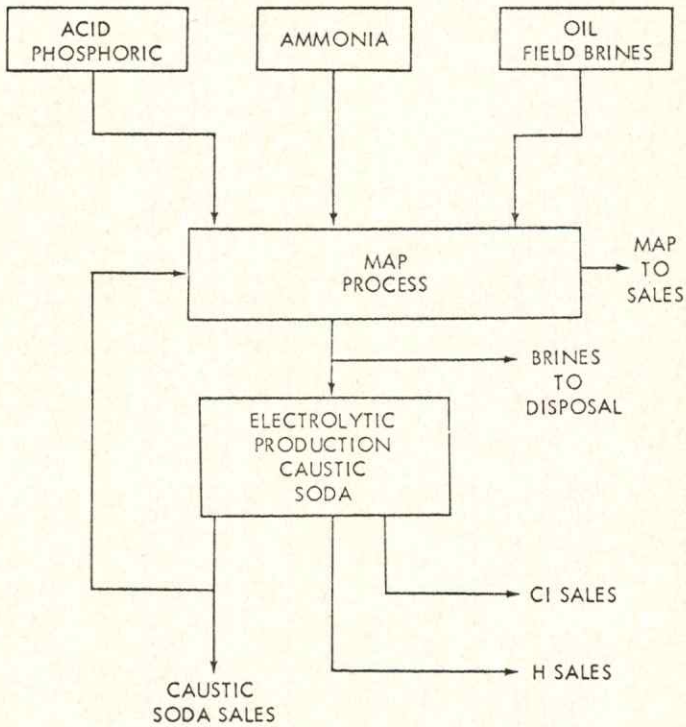

Figure 2. Schematic box diagram of potential fertilizer production from brines (Cox 1967).

For example, in the El Dorado Field of Kansas some 84,000 bbl/day were being produced daily as of Jan. 1, 1966 (B.C. Latta personal communication). Considering the volume involved, the possibilities of mineral recovery from these and similar brines definitely deserves greater economic consideration. Most oil-field brines contain more calcium than magnesium; consequently fertilizer produced from these brines should have a higher CaO content than that given in the W. R. Grace MAP analysis.

This fact could be an asset in those areas where acidic soil conditions exist. Use of a fertilizer high in both CaO and the usual nutrient components would allow a liming and fertilizing operation to be carried out in a single application. If this were the case, considerable economic benefit would accrue the users of such a fertilizer mix.

Additional research into the feasibility of producing fertilizers from oil-field brines seems warranted.

CONCLUSIONS

Considering both the yearly volume of oil-field brines produced in the United States and the potential economic value of the salts dissolved therein, then it can safely be said that we are wasting a natural resource. In many instances the salts dissolved in oil-field brines could be extracted profitably if modern extraction techniques were utilized. The close proximity in several petroleum provinces of many of the raw materials, used in the manufacture of caustic soda and soda ash is fortuitous, but this advantage has not been exploited to any great extent. The midwest is, of course, centrally located in relation to marketing and transportation costs. Extended research on the economic possibilities of locating plants for extraction of dissolved salts from brines in the source area is needed. Inasmuch as the cost of producing the brines is already covered by bringing them to the surface with oil, surely the brines should be stripped of all possible dissolved salts prior to reinjecting the spent brines into the subsurface. Lastly, the production of a useable fertilizer from oil-field brines seems feasible. Additional research on this possibility definitely is warranted, and should be encouraged.

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SECTION THREE

PRACTICAL EXAMPLES OF INDUSTRIAL MINERAL DEVELOPMENT

OPPORTUNITIES IN THE BENEFICIATION OF FELDSPATHIC SANDS

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ABSTRACT

Glass plants that utilize as raw materials rather pure forms of feldspar and quartz are often located near natural sand deposits that contain mixtures of these minerals along with various impurities. Depending upon the nature of the impurities, it may be possible to refine these sands so that they may be substituted for the pure quartz and feldspar products. Savings on production cost and freight may give such sands considerable economic potential.

Problems encountered in the production and use of such refined sands are discussed along with some methods that may be used to solve them. The current geographical distribution of such operations is outlined and flowsheets of typical plants are shown.

INTRODUCTION

Quartz and feldspar or a feldspar substitute are the main mineral ingredients used in making some kinds of glass, especially that for containers and glass wool. These are ordinarily supplied as rather pure materials and mixed together in the glass batch. Feldspar or other alumina bearing mineral, either in its natural form or as a flotation concentrate, is used to provide the alumina content of the glass together with part of the alkali and silica requirements. Glass sand, after various washing and purification steps, comprises nearly pure quartz, and this is used to provide most of the silica in the glass. Smaller amounts of other minerals or chemicals are added to obtain the desired composition.

These two minerals make up the major part of rocks such as granite and similar igneous rocks as well as sands derived from them. Such rocks may also contain numerous accessory minerals, and sand deposits may be still less pure because of admixture of material from other sources. Nevertheless, it may be possible to beneficiate such rocks or sands to produce mixtures of feldspar and quartz, or even concentrates of these minerals, which may be used in glassmaking. The economical refining of feldspathic sands is a challenge to the mineral engineer because in general no two deposits will present exactly the same problems.

A change from using pure glass sand and pure feldspar to the use of a mixed product generally presents problems and uncertainties for any glass maker. The possibility of savings in costs must be a major incentive in securing the cooperation of a glass manufacturer, and this is generally necessary in the commercial development of a new mixed quartz-feldspar product. This cooperation, besides including the testing of samples and the disclosure of information, should extend to a willingness to modify specifications, within reason, to accommodate the material available for refining. Existing specifications for the quartz and feldspar concentrates may have been written to describe these materials rather than the minimum requirements of the glass making process. New specifications based on actual requirements may make it possible to produce a satisfactory substitute material at a cost sufficiently less than the materials replaced, to provide profit incentives to the sand producer and the glass maker alike.

ECONOMIC POTENTIAL OF FELDSPATHIC SANDS

In order to estimate the savings that may be achieved by substituting a feldspathic sand for other materials,

it is necessary to consider the value of the materials being replaced and the cost of producing, refining, and delivering the substitute. If the minerals are not to be separated, the proportions of feldspar and quartz in the finished sand will depend upon their proportions in the crude sand, and this in turn will determine the value of materials replaced by a ton of the mixed product.

The cost of feldspar delivered to a glass plant will include the price at the point of production plus freight charges. The current E/MJ quotation (June, 1967) for glass spar is $9 per ton and, to some glass plants at least, the freight is about equal to this, making feldspar cost such plants a total of about $18 per short ton. Workable glass sand deposits are more widely distributed than those of feldspar, and the cost of processing is generally less. Hence, both the price and freight on quartz may be less than for feldspar, with delivered costs ranging from about $3 to about $7 per ton.

The delivered cost of a mixed mineral substitute may vary widely depending upon raw material, processing, and freight charges. Since by-product fines from construction sand plants may sometimes be refined, a raw material unit value equal to that of construction sand may be used for an example. Thus, if the unit value were $1 per ton and one third of the sand were discarded during refining, the raw material cost would be $1.50 per ton of finished product. One objective in the location of a feldspathic sand refining plant should be to achieve low freight costs. While freight by truck or rail will depend upon local circumstances and delivery distance, a useable estimate of freight costs might be $2 per ton of delivered product.

Processing requirements will depend both upon the character of the feed sand. Naturally the cost of processing will depend upon what must be done and the tonnage treated, and since this could vary from extremely low values to prohibitively high ones, no general estimate can be given. In order for the substitution of refined feldspathic sand in place of feldspar and quartz to be economically attractive, the difference between the value replaced and the cost of raw material and transportation of the substitute must be greater than the cost of treatment.

Values of this difference are calculated in Table I for sands with various proportions of feldspar and quartz, assuming that feldspar costs $18 per ton and quartz costs $3, $5, or $7 per ton delivered. These values range from $1 to $9 per ton, and it is evident that there is a greater economic potential for sands rich in feldspar because of its higher unit value. On the other hand, however, there might be a smaller total market for a sand high in feldspar than for one low in feldspar, and this could affect the unit processing cost adversely.

SPECIFICATIONS AND REFINING TECHNIQUE

The specifications for feldspathic sands generally include maximum limits for the content of iron, titanium, phosphorus, arsenic, sulfide sulfur, or other impurities, but these may vary widely depending upon the purpose of the glass. Iron appears to be the most serious of these specifications to meet because techniques for removing iron to the required content usually also result in adequate removal of the others. Maximum iron specifications may range from 0.04 percent Fe_2O_3 in a 25 percent feldspar sand used for container glass to 0.4 percent Fe_2O_3 in a sand containing 30 to 50 percent feldspar used for glass wool. The refining technique used should be the lowest cost one which will meet the specification.

Where the excess iron and titania content are present in discreet high-iron mineral particles, these may often be removed by flotation. This is the classic iron flotation in an acid circuit using sulfonated reagents and oil. Where it is amenable, this appears to be the preferred method of iron removal.

The magnetic susceptibility of iron-bearing particles in some sands covers the enormously wide range from that of magnetite to that of very weakly magnetic particles. The former may be removed by a hand mag-

Table 1. Economic potential for refining of sands with various fractions of feldspar, assuming that feldspar costs $18 per ton, that quartz costs $3, $5, or $7 per ton, and that raw materials and freight cost a total of $3.50 per ton of product.

Fraction of feldspar in product.	1/10			1/5			1/3			1/2		
Value of feldspar per ton of product	$1.80			$3.60			$6.00			$9.00		
Price assumed for glass sand per ton	$3	$5	$7	$3	$5	$7	$3	$5	$7	$3	$5	$7
Value of quartz per ton of product	2.70	4.50	6.30	2.40	4.00	5.60	2.00	3.33	4.67	1.50	2.50	3.50
Value of material replaced by a ton of product	4.50	6.30	8.10	6.00	7.60	9.20	8.00	9.33	10.67	10.50	11.50	12.50
Difference available for processing costs and profit, assuming other charges of $3.50 per ton of product	1.00	2.80	4.60	2.50	4.10	5.70	4.50	5.83	7.17	7.00	8.00	9.00

net or by relatively weak magnetic separators, but maximum removal of slightly magnetic particles requires a high intensity machine. While the separators presently used for sands containing very weakly magnetic iron-bearing particles are of the dry induced-roll type, high intensity wet separators are being developed and may soon be used for glass sands.

When either flotation or magnetic separation is used to remove en masse particles that are high in iron, the remaining non-float or non-magnetic sand generally still contains iron. However, this iron is distributed rather uniformly among the sand grains and no large part of it may be removed by selectively removing part of the sand, this sort of refining having been accomplished in the flotation or magnetic separation. If further lowering of the iron content is required, the disposition of the residual iron in the sand particles may be important. Iron, generally as oxides or clay, that occurs as surface stains on sand particles may often be removed by vigorous attritioning of the sand followed by desliming to remove the detached impurities. If the stains are located in surface pits, or iron compounds fill cracks in the mineral particles, attritioning will not remove them. In this case acid leaching may be necessary for more complete iron removal. Even acid can not remove deeply locked iron compounds, iron substituted for other elements in a mineral structure, or iron in some mineral forms, especially those that are ferro-magnetic.

Besides the removal of impurities in the refining of feldspathic sands, it may be essential to maintain certain proportions of feldspar and quartz in the finished product. While a glass batch can be designed to use almost any ratio of feldspar to quartz in the feldspathic sand, it is important to the glass maker that these proportions remain within limits that are generally specified. Thus, for example, it appears that for use in making container glass, the feldspar content of the sand should not vary more than half a percent from its known average value. On the other hand, in the making of glass wool, the batch may be adjusted to accommodate the general composition of the sand and minor variations in feldspar proportions are ignored.

Size specifications are those usual for glass raw materials. The top size may be from 20 to 48 mesh and this is generally limited by a scalping screen. A bottom size of about 150 mesh may be limited by air or water classification to remove fines. In some places natural sands may have the desired size distribution, or material of the desired size may be separated from coarser sand. In other cases, it is necessary to grind and size to produce the required product.

FELDSPATHIC SAND OPERATIONS

While the amount of feldspathic sand used by the glass industry is small compared to its total requirements for feldspar and quartz, there are a number of operations producing such materials. On the Pacific Coast there are three or four companies supplying feldspathic sands. Del Monte Properties Company of Pacific Grove, California, produces a 50 - 50 mixture of quartz and feldspar by a combination of grinding and scrubbing together with desliming followed by flotation of iron minerals as shown in the flowsheet of Figure 1. Not shown are additional steps that can produce feldspar and quartz concentrates from part of the iron-free feldspathic sand.

Glass plants in the Los Angeles area are supplied with low-feldspar sands that provide nearly the required proportions of feldspar and quartz. In western Washington, a feldspathic sand is used by a local glass plant. On the East Coast, there are two or three operations that produce mixtures of quartz and feldspar from granite fines.

There are at least two producers of feldspathic sands in the Midwest. One at Kansas City produces a non-magnetic sand for use in making glass wool, as shown in one of the flowsheets of Figure 2. Part of this product is ground and sized to obtain a more desirable size distribution. In Oklahoma, a similar sand is treated by magnetic separation and acid leaching, as also shown in Figure 2, to

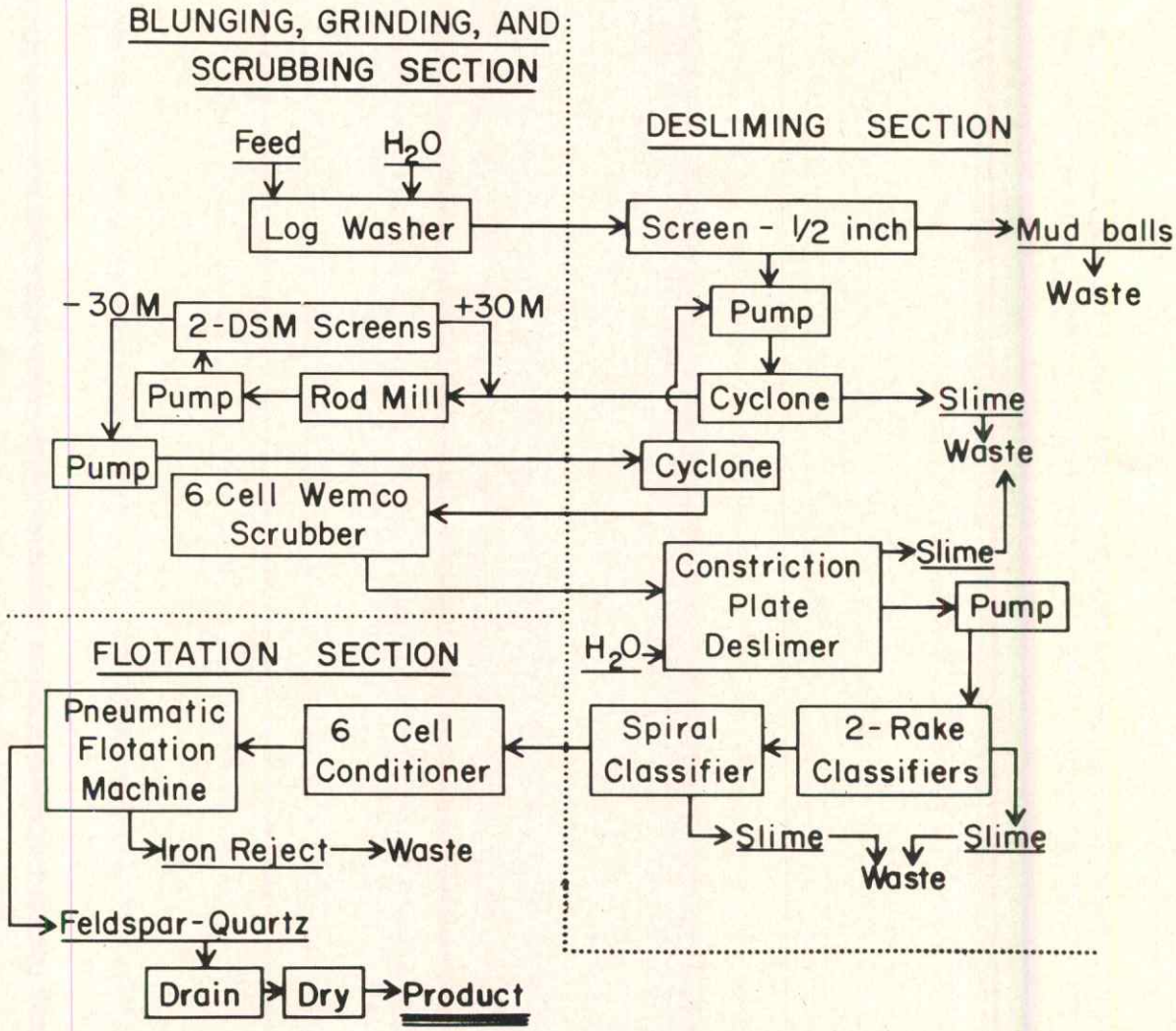

Figure 1. Flowsheet for beneficiation of feldspathic sand by Del Monte Properties Company at Pacific Grove, California using blunging, grinding, scrubbing, desliming, and flotation.

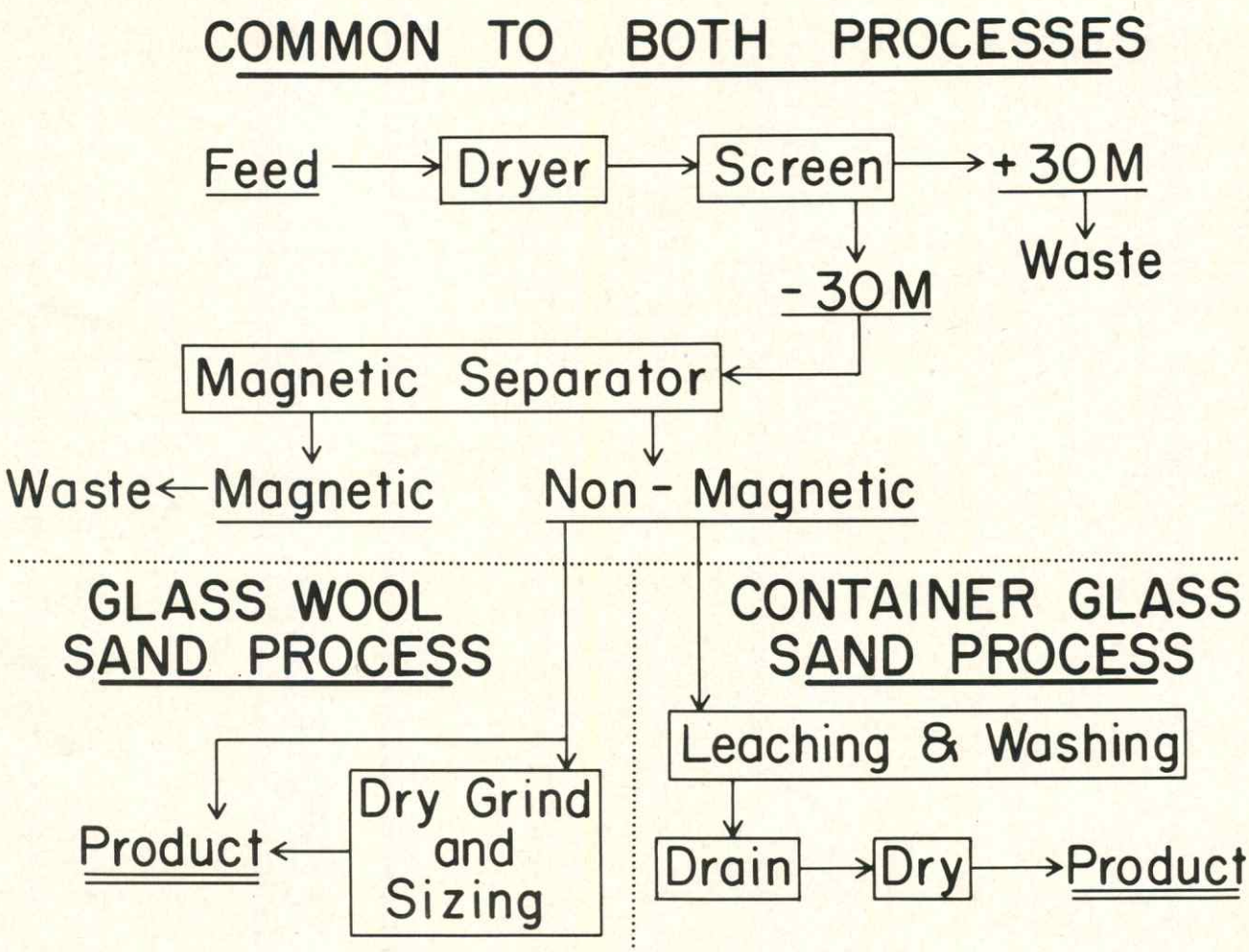

Figure 2. Flowsheets for beneficiation of feldspathic sand by Stewart Sand and Materials Company at Turner, Kansas using magnetic separation only, and by Yahola Sand and Gravel Company at Muskogee, Oklahoma using magnetic separation and acid leaching.

obtain a very low iron product suitable for making colorless container glass.

SUMMARY AND PREDICTIONS

Although the glass industry is accustomed to using rather pure feldspar and quartz as separate products, there are situations where savings in cost may be achieved by substituting for these a mixture of quartz and feldspar refined from a local material. Reductions in freight and raw material costs play a part in these savings. The materials most commonly used for this are of granitic origin, either solid rock or clastic sands. The refining methods used depend upon the raw material and the specifications that must be met. Major iron removal may be achieved by sulfonate flotation or by magnetic separation, with acid leaching being required for production of the lowest iron contents.

There are probably fewer than a dozen plants in the United States producing feldspathic mixtures for the glass industry, and most of these are in areas distinct from traditional sources of feldspar but where local feldspathic sands are found. It seems likely that there are other places where this might be done, but each case would probably present a different set of technical and economic problems.

PITFALLS IN THE ECONOMIC EXPLOITATION OF INDUSTRIAL MINERALS

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ABSTRACT

Innovation and change have created pitfalls for the entrepreneur who would economically exploit industrial minerals. Technological advances have necessitated more stringent quality standards and realigned markets for mineral products. The need to reduce costs has dictated the use of large equipment, and this in turn has increased production. Improved transportation and handling of the increased production has expanded market areas and opportunities but also has fostered more competition. Government and the general public now expect more from industry relative to land use, clean surroundings, clean water and clean air. What may be pitfalls to one organization may prove to be windfalls to another.

INTRODUCTION

The geologist has always played an important role in firms that seek to exploit mineral wealth but the importance and scope of the role has increased as the complexities of mineral extraction have increased. Sound business decisions can be made only when enough information is available to effectively evaluate alternative courses of action. Geological data definitely is part of that information whenever mineral deposits are involved.

GEOLOGICAL SURVEYS

The scope of a geological survey of a mineral deposit and its environment must be commensurate with the anticipated committments and results. For example, the survey of a sand and gravel deposit to supply a one-time demand for a road paving job need not be as extensive as a survey to delineate a twenty year source of supply for the large cement kilns that are being built today; but in either case, adequate information must be obtained. Geology is a partially hidden book. Because the work is expensive, a tendency exists to severely limit geological surveying, often with costly consequences. Nothing is apparently more worthless than a hole in the ground that has merely confirmed our expectations. But what of the hole that proves us wrong? All of us know of mineral deposits that were abandoned by one firm only to be successfully exploited by another group. Other companies have suffered lower mineral reserves or additional exploitation costs because inadequate geological surveys did not disclose discontinuities in the deposits. The physical and chemical characteristics of a mineral deposit may vary sufficiently to render part of the material in a deposit unsuitable for its intended use and again may result in decreased reserves or added exploitation costs.

The environment of a deposit may affect its profitability of exploitation. Surface considerations will be considered later in this dissertation, but here let us look at geological conditions and underground water. For example, a large base metal mining company owns a large deposit which cannot presently be mined because technology to hold overlying strata has not been developed. Another firm is faced with the purchase of additional equipment and higher mining costs because the expensive, highly specialized mining equipment purchased cannot penetrate a tough rock layer overlying the mineral deposit. Stripping of the overburden on the deposit now requires two separate operations. That ground water can cause serious economic and exploitation problems was well illustrated by the experience of underground potash miners in Saskatchewan when the treach-

erous Blairmore formation was penetrated. A midwest firm was forced to abandon a newly opened quarry because the quantity of water encountered would have entailed excessive pumping costs, and furthermore, the pumping would have adversely affected the level of the ground water table in its area. Another firm was forced to deepen the wells of its neighbors when the water table was lowered by its operations. The alternative to the well deepening was a spate of law suits that might be lost, and a group of irate neighbors. Obviously, all of the illustrations have involved dollars -- the common denominator.

PROBLEMS OF SCALE

In order to reduce operating costs, equipment continues to increase in size and price at a fantastic rate. The giant 40 ton off-road haulage units of yesterday have been replaced by the 85 and 100 ton units of today only to be challenged by the 160 and 240 ton capacity units now coming on the scene. Kilns being erected today are longer than a football field and each easily replaces 10 or more of the kilns that formerly were considered efficient operating units. Not only has size been increased but reliability and useful life have been improved through better designs and materials. Computers and automated controls are used to reduce production inputs and costs and at the same time to improve product quality and throughput. The net results of these innovations are greater production of a better and more uniform product at a decreased cost. Of course, lower unit costs can come only if the expensive equipment is fully utilized. The fixed charges continue regardless of the amount of output.

High productive capacity from expensive plants require large, stable, and durable markets. Some firms have solved their marketing problems by signing long-term sales contracts. Producers of coal for large electrical utilities have increasingly dedicated large reserves of fuel to a single customer. Producers of iron-ore pellets, coal and flux stone also obtain long-term sales contracts from steel companies, but steel companies quickly acquire captive facilities if dependable independent producers are not available. Other firms have improved their marketing posture and area by using innovative handling and transportation concepts.

Giant strides have been made in the handling and transportation of commodities. The Japanese have achieved a freight cost of 50 cents per thousand ton-miles by using vessels of 100,000 tons capacity to haul iron ore to their steel mills located at deep water ports. The ships are automated to the point where the size of the crew required cannot be further reduced because the work would become too lonely to retain manpower. The Japanese will achieve even lower transportation costs when the 160,000 ton behemoths currently being built become operational. Compare the transportation costs of the Japanese with our cost of $3.87 per ton to transport iron ore from Minnesota to Lower Lake Ports. Our costs for handling and transporting bulk commodities will be reduced, and efforts in this direction are already being made. Litton Industries has united several of its divisions into a team with the assigned task of devising cheaper handling and transportation modes for bulk commodities. Significant progress has already been made.

Air slide barges, trucks and jumbo rail cars used in conjunction with terminal storage silos have appreciably altered the market patterns for cement. Small producers have also suffered as strong competitors have entered their market areas. Unit trains have lowered handling costs for materials moving between a relatively few fixed points. Self-loading ships and barges and highly mechanized storage yards have helped to reduce handling and transportation costs. A well conceived plan now in operation involves the shipment of coal by river barge from Illinois to a storage and transfer facility in New Orleans for transshipment in ocean going barges to Florida. The return trip is used to haul phosphate rock thus cutting delivery costs for both commodities.

Another example of imaginative planning involves a sand and gravel producer who bested his competitors by supplying material to storage yards in a large metropolitan area by waterway barge operating from a large and easily exploited sand and gravel deposit located on the waterway beyond the congested limits of the urban area. Sometimes, the nearest deposit is not the most economical to develop and utilize.

MARKETING ORIENTATION

Many producers of minerals have failed because of inadequate marketing know-how and information. Simply because a mineral deposit exists does not mean that it can be economically exploited. Any entrepreneur considering the economic exploitation of a mineral deposit might profitably consider a market survey before spending large sums of money. Making a market survey is quite simple but interpreting the results can be a bit more difficult. The first step is to clearly define the area that might profitably be served from the deposit. Careful consideration should be given to existing and potential competitors that might serve the area being studied. The status of competitive materials should also be explored. A survey questionnaire should then be devised to obtain pertinent information about quantities purchased, specifications, prices, present suppliers, and whether or not the respondent would buy from a new supplier. Answers to the last question indicate the strength of the competition in the market area. The questionnaire should also ask what percentage of total requirements might be purchased from a new supplier immediately, in one year and within two years. Some firms insist on more than one supplier. The actual survey can be made by mail, by telephone, in person, or by a combination of methods. When surveying a larger area, we at Northern use a mail approach first because it is faster and cheaper, and then supplement the mail survey by telephone and personal calls. We have received from 60-80 percent returns on our mail surveys; and of course telephone and personal calls will raise the percentage. But don't expect a 100% return. I recently had the misfortune of calling a man while he was filling out his Federal and State income tax forms and quarterly business reports. His language to me was unprintable although my contributions to the Bureau of Internal Revenue qualify me as only a part-time employee for the government. By the way, many utilities have departments that will help with a market survey if the proposed operation is within their market area.

Space should be provided for remarks on a market survey questionnaire. The remarks given will help in interpreting the results obtained in the survey. The questionnaire might also ask for the names of other consumers of the product in the area. On several occasions in talks with businessmen from this area, we found that minerals were being imported from a distance when local supplies of adequate quality were available.

Making a market survey does not sell a product but merely indicates that a potential for sales does exist. A way to sell a product is to ask potential customers for orders and then provide good products and good service. Selling may also involve letting customers know that a need for the materials to be produced exists, and where the materials can be obtained. Advertising can be effectively used in this task. The Iowa Limestone Producers Association successfully conducted an advertising campaign to promote the use of agricultural limestone. Several producers of dimension stone for building purposes have effectively increased the size of their markets by the use of advertising.

Another aspect of being market oriented is to give the customer what he wants. Customers are demanding closer tolerances on physical and chemical specifications for raw mateials. The demands in most cases are not arbitrary but are based on the needs of the more sophisticated processing procedures being used in the constant struggle to reduce finished product costs. Added expenditures for the beneficiation of raw materials

may make greater savings possible in subsequent processing procedures. Sizing of raw materials has assumed greater importance to manufacturers and this is one area where the producer of industrial minerals can exercise good control if he so desires. Often the sized material rejected by one customer will fit the requirements of another. Many raw materials used today must be beneficiated by chemical or physical processes for the removal of impurities in order to meet specifications for one group of customers. Again, products that are below specifications for one group of customers may be sold to other customers whose requirements are less stringent; and some product may not be salable. Producers in such cases must carefully weigh the costs and profit potentials against the revenues that may be derived from the various groups of customers.

Technology is changing the markets for industrial minerals. The producers of fluxstone for open hearth steel furnaces are now being asked to produce burned lime for basic oxygen converters. The producers of refractories are also being asked for products that will withstand the higher temperatures and more severe corrosion experienced in the basic oxygen converters. Because of public demands for cleaner air, the electrical utilities are asking coal producers to find means to remove sulphur compounds from the coal before it is burned. Again, electrical utilities have devised means of converting fly ash into lightweight aggregates that compete directly with mineral products. Low grade aggregate deposits which were once not usable for road construction ceramics in some electrical insulators. The silicon chip used in an integrated circuit is replacing glass, metal and plastic. As is obvious from the above, technological advance presents the producer of industrial minerals with both opportunities and pitfalls.

MANAGEMENT CONSIDERATIONS

The greatest pitfall to the successful economic exploitation of industrial minerals is managerial inadequacy, the main cause of failure in all businesses. Managerial inadequacy runs the gamut from inattention and neglect to misdirected efforts and wrong decisions. Inattention and neglect are difficult to overcome, but poor management can be aided by careful planning and control.

Good planning begins with an awaremess of an economic opportunity and a clear statement of the objectives to be achieved in pursuing the opportunity. Planning which can seriously affect the success or failure of an enterprise must be done thoroughly and carefully. Generally, the amount of resources to be committed and the length of time involved for the attainment of the objective determine the importance of a decision. Sound decisions are based upon the study of factors or premises that may have a serious impact upon the attainment of objectives.

Premises may be internal or external to the firm and also may be controllable or noncontrollable by management. Important noncontrollable external premises are the state of the general economy, the status of customer industries, the availability and cost of money, population and economic growth rates, regional business conditions, political climate, taxation rates and policies, labor attitudes and unions. Noncontrollable internal premises include the nature of resources already committed and the nature and location of the mineral deposit. Controllable internal premises involve the use to be made of uncommitted resources that are either owned or can be attained. Premises that can be stated in numbers should have values assigned to aid in decision making, but because a premise cannot be quantified does not mean that it is not important. The number of premises that could affect a business decision are almost endless, so only limiting premises or those critical to the decision should be studied to develop alternate courses of action.

The most difficult task in planning is to discover all alternative courses of action that may lead to the desired objectives. Generally, when only one or two alternatives

appear as possible courses of action to follow, the hard, tough thinking required for good decision-making has not been done. Sometimes the best alternative remains hidden until a considerable amount of digging has been done. Consider the case of a company that was losing its business because it owned obsolete machinery and a financial situation that precluded bank loans. The first alternative seemed to be going out of business. Then a dealer was found who would finance overpriced second-hand machinery at a high interest rate. Further digging disclosed that a new machinery manufacturer had some items that would replace the most obsolete equipment and again make the firm competitive. The machinery manufacturer was willing to sign a lease-purchase agreement with a reasonable rate of interest. Obviously, the last alternative presented the best course of action, but it was the hardest alternative to find.

Sound financial planning is imperative for the success of a firm because it forms the basis for the proper allocation of resources and it enhances the opportunities to borrow money when that course of action is necessary. Realistic budgeting is the first step in sound financial planning. Budgeting should be done on a monthly basis for the coming year and on a yearly basis for longer range plans. The budget should cover units of input and output as well as money, and a separate budget should be made for capital expenditures for effective control purposes. The budget should be supplemented by a cash forecast where total money income and outgo are quantified and timed. Intended borrowing and loan repayment and capital expenditures must be included in the cash forecast. One caution on budget and cash forecasts -- they will be only as accurate as the estimates used in their making.

The final step in achieving objectives is implementing the plans and controlling action to see that results conform to plans or that deviations can be satisfactorily explained and corrected if necessary.

Many managements have difficulty controlling costs when production goals vary considerably. Marginal analysis is a useful tool to use in analyzing the most profitable level of operations for a firm. Because of variable and fixed costs, each unit of production does not cost the same. When production reaches a certain level, costs per unit increase disproportionately because inefficiencies creep into the operation. Similarly, as production increases, the revenue obtained per unit may decrease because of competitive reasons. The concept of marginal analysis states that a firm will produce its greatest profit when production is at a level where the cost of adding one unit of product will exactly equal the revenue derived from the product. Any level of production above or below this point will yield a decreased profit to the firm.

Pricing policies cause problems for many managements. One of the most common misconceptions is that pricing should be related directly to costs, when as a matter of fact, the two are only indirectly related. Prices are influenced by competition from firms producing the same products and also from competition with substitute materials. Sound pricing policies can be set only when the total service and product package to be delivered to the customer have been considered. Most of the time, customers will pay for improvements in products and services.

We, the people of the United States, have opted for clean air, clean water and a beautiful and unmarred landscape. That option is likely to affect minerals producers far more than most industries. Some areas of the country have already been closed to minerals extraction operations and more areas are likely to be closed. The efforts to clean air and clean water and to eliminate scars from the surface of the earth cost money but there may be compensations in the form of economic by-products. As indicated before, the electrical utilities sell products made from the fly ashes taken from the gases emitted into the atmosphere. Smelters have recovered valuable products from stack gases for a long

time. The paper companies are now recovering salable products that were formerly dumped into rivers. The products will pay for part of the anti-pollution treatment that is now required by law. One firm has opened a game farm on the land holding its mineral reserves. Undoubtedly that arrangement nets the company both profits and excellent public relations. Boise Cascade reaps good will by opening its vast timber holdings to the general public for recreational purposes. A coal company in Indiana recouped its costs in mined-out lands by forming a chain of man-made lakes and selling the surrounding land as building lots. Another firm has developed a vineyard on its mined-out land. A firm in Kansas uses an abandoned limestone mine as a bonded warehouse having 85 acres of refrigerated space with direct rail access. Think of the cost of erecting and maintaining this facility on the surface -- and then it might be subject to an atomic blast. Other firms in Missouri are also storing material in mined-out areas. One can see that what is a pitfall and costly operation for one firm is an economic opportunity for another.

SUMMARY

The pitfalls and opportunities encountered in the minerals industries were discussed in a brief and general way. Some of the problems and opportunities encountered are unique to the minerals industry but most are shared in common with all industries. Pitfalls develop when management fails to get all of the pertinent information, plan properly and control operations in order to make results conform to plans. Pitfalls can be turned into opportunities by imaginative management.

ORE RESERVE CALCULATIONS

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ABSTRACT

Various methods of calculating ore reserves and inherent problems in the use of each method are discussed. Several examples are given to show how the amount of information on a deposit can be increased by using statistical techniques for calculating ore reserves.

Models Based on Geometry

A calculation of grade and tonnage in a mineral deposit is usually made by an analysis of sample data framed in a polygonal, triangular, cross-sectional, or other geometric pattern. Figure 1 shows a number of geometric patterns used in assigning areas of influence to drill-hole samples (Patterson, 1959).

Sketches (a) and (b) illustrate a system of rectangular blocks constructed around uniformly spaced (a) and randomly spaced (b) drill holes with the area of influence of each sample in a drill hole extending halfway to the adjacent drill holes.

Sketches (c) and (d) illustrate polygons constructed around each drill hole and the area of influence of each sample within a drill hole extending halfway to the adjacent drill holes.

In the rectangular and polygonal methods of ore reserve calculations, it is assumed that the grade of ore of an assay in one drill hole extends halfway to any adjacent drill hole. Obviously, this is an incorrect model of the true situation which exists for the mineralization at the midpoint between the two drill holes. Even if the mineralization were to

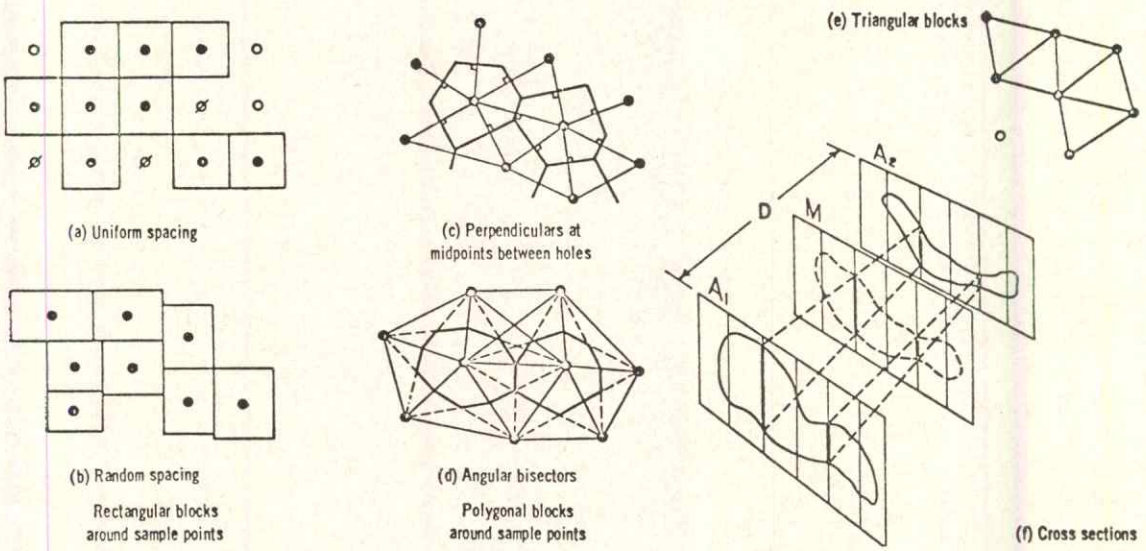

Figure 1. Geometric Patterns Used in Assigning Areas of Influence to Drill-Hole Samples from Patterson (1959).

consist of podlike and lenslike segments, the exploration drilling would not penetrate exactly at the center of each pod or lens, and the drill-hole spacing would not equal the pod or lens lengths. If this were true, then boundaries of pods or lenses would fall halfway between all holes, at least in one dimension, and the polygonal model could apply for assigning grade of ore in this special situation. However, in situations where other types of mineralization are present, the polygon method serves as only a rough approximation of the true grade of ore within its area of influence.

Sketch (e) illustrates the triangular method of estimating grade of ore between drill holes. This method is also an approximation model, because it assumes an exact linear change of grade of ore in direct proportion to the distance between drill holes. A correlation between successive assays would have to exist to assign a linear change in grade with distance. Mineralization is seldom so simply constructed that a linear model can represent its complexities. Often, a combination of various nonlinear correlations exist over short distances; thus the problem of predicting grade for blocks of ore between drill holes resolves into a problem of curve fitting for a complex distribution of assay values which exist between the drill holes (Hewlett, 1964b).

Sketch (f) illustrates the cross-sectional method of calculating ore reserves. Again, geometric areas are assigned grades for ore reserves based on averages of assays for adjacent drill holes.

In summary, the polygon, triangular, and cross-sectional methods used for calculating ore reserves assume that the area of influence of an assay in any one drill hole is a function of the distance to any other adjacent drill hole. In using these methods, no consideration is given to the mineralization which actually exists between the drill holes. The methods are a function of geometry, which simplifies the calculations. They are not a function of the mineralization which the methods propose to predict.

Table 1 presents a few facts about the percent of total volume of a deposit that is actually tested by a drill-hole sample. In constructing this table, it was assumed (Nemec, 1965) that a drill-hole sample can only be unequivocally accepted as representative of grade of ore for a peripheral distance of 10 feet. Data presented in this table emphasized how little is really factually known about a deposit when the deposit is drilled in the usual grid of 100 to 500 feet.

Ore reserve calculation is thus an exercise in taking 0.1 to 3.0 percent positive information, and determining within acceptable limits the values of 100 percent. This

Table 1. Percent of total volume actually tested by a drill-hole sample, assuming a 10-foot area of influence for the sample.

Distance between adjacent drill holes, feet	Area of grid, Square feet	"Known" area of grid	
		Square feet	Percent
500	250,000	1/ 300	0.1
400	160,000	300	.2
300	90,000	300	.3
200	40,000	300	.7
100	10,000	300	3.0

1/ Rounded to nearest hundred feet.

statement is true if the assumption made in calculating the table is true that the area of influence of a sample, or assay value, is a maximum of 10 feet.

An investigation has been made in determining the "area" of influence of an assay (Hazen, 1967) by use of the statistical techniques of correlation and the mean-square-successive-difference test. Constructive runs of assays from drill holes and from drifts, crosscuts, raises, and some stopes have been tested from five hydrothermal deposits. Results are summarized in Table 2. The area of influence of an assay has been determined by testing for a sample interval length at which the grouped assay values are no longer related, that is the groups are independent. A series of assays along a drift or in a drill hole, as shown in Figure 2, can be grouped into lengths representing successively longer sample or assay intervals. Each new grouping length is tested for independence between groups. When the tests indicate independence, the distance or sample interval length represented by the group is considered as the maximum distances that can be assigned for an area of influence for an assay. If data are available grouping can be done in all three dimensions, drifts, raises, and stopes.

When assay values are independent at intervals less than the drill-hole spacing, the best estimate of grade of ore for the area between drill holes at distances beyond the area of influence of the assay values is an average of the assay values surrounding the area unless geologic considerations dictate otherwise. Computing the average of assays surrounding an area usually requires some form of weighting or interpolation (linear, exponential, two-dimensional, vector) based on distance for combining and averaging the assays.

Grade estimation also presents increasing problems as the percentage of the valuable portion of the material tested decreases with respect to the total. For example, sampling and ore reserve calculations are usually simpler and more reliable for coal and iron deposits than for copper and gold. In the latter, where the range of assays may be considerable, statistical evaluation is commonly used to approximate the trustworthiness of the estimator of grade of ore.

From the examples and discussion, it should be obvious that any observed factual data that can indicate areas of influence of assays in drill holes more accurately than standard geometric patterns should improve the accuracy of ore reserve calculations. Thus, in many cases, geological information should be used to modify the outlines of the blocks used in calculating the reserves.

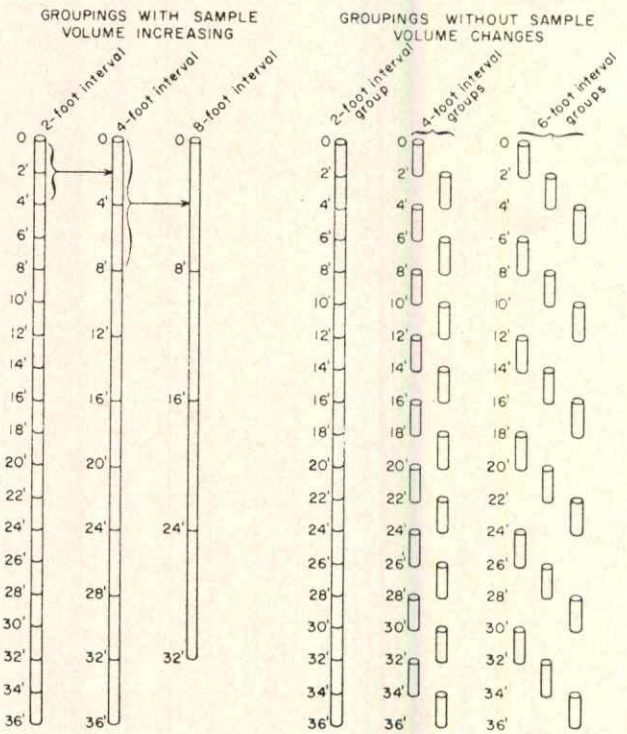

Figure 2. Assay groupings for mean-square-successive-difference test

Models Based on Mathematical-Statistical Techniques

In the past few years, statistical methods have been used intensively in estimating grade of ore (Parks, 1964, Spear, 1964, and conference Proceedings, see list of references.)

Table 2. Summary of statistical mean-square-successive-difference test results for area of influence of assay (Hazen, 1967).

Deposit and data tested	Indicated area of influence of an assay	Comments on results
Climax Molybdenum, Colorado	2 feet in one dimension and 1 foot in another dimension for a specific grade zone. May be greater for areas including more than a single grade zone.	Some inconsistencies, but most results, including correlation tests, confirm the figure. Inclusion of trend in grade of ore will increase this value for area of influence of an assay. Two-foot sample interval in one dimension was smallest interval available for testing.
Cebolla Creek titaniferous iron, Colorado	24 to 36 feet 4 to 18 feet	For 4-foot interval NX samples. For 2-foot interval special samples. The iron and titanium assays, although correlated, have different areas of influence. There is evidence of cyclical trends in area of influence along the drill holes.
San Manuel Copper, Arizona		Both sets of data are limited and results indicate greater distances should be studied. Correlation studies indicate area of influence of assay may be as large as 200 feet.
Churn-drill holes	70 to over 100 feet	
Diamond-drill holes	More than 50 feet	
Piedra Hueca Copper, Puerto Rico		There is good correlation between diamond-drill hole and crosscut assay data. Results are consistent within each crosscut, but differences between crosscuts are indicated. Drift sample preparation in sample plant reproduced results equivalent to NX drill-hole core samples.
750-EAST crosscut	16 to 20 meters (52.5 to 65.6 feet)	
650-EAST crosscut	More than 20 meters (65.6 feet)	
Butte Copper, Montana		
Vein deposit,		
Drifts	12 to 30 feet	Tests not conclusive, need more data.
Raises	8 to 32 feet	Results not uniform.
Horsetail vein,		
Crosscuts	6 feet or less	Not all results are consistent, but most tests are in agreement indicating independence of assays.
Raises	do.	
Stopes	do.	

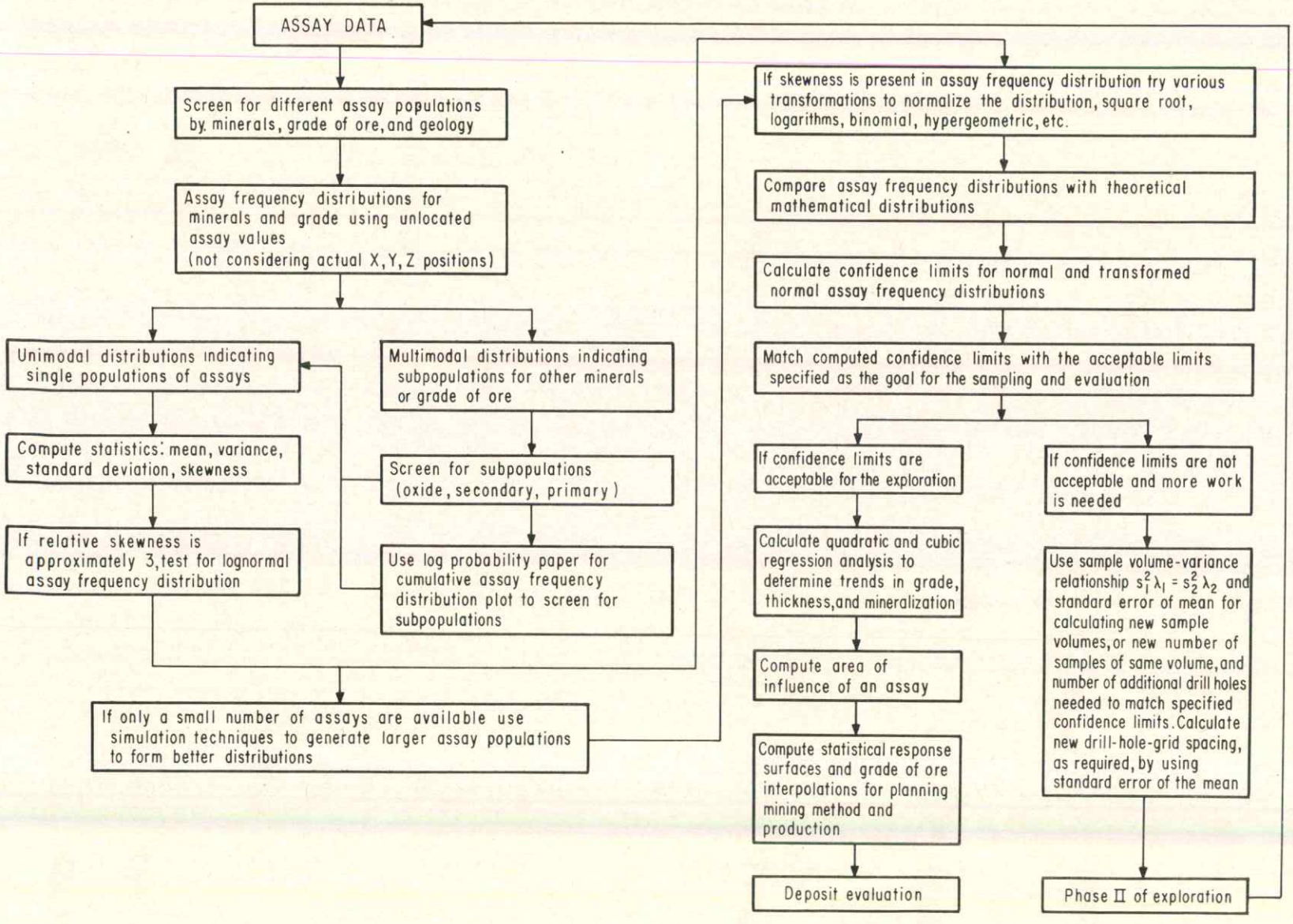

Figure 3. Flow chart of generalized procedure for statistical analysis of assay data.

techniques are available to permit computation of a confidence interval for an estimate of grade of ore when statistical methods are used (Hazen, 1958). Also, statistical techniques lend themselves to establishing a specified precision for the estimate of grade of ore before the drilling begins and then indicates the proper amount of drilling to attain this precision. This tends to minimize exploration costs and relate costs to that required for each deposit (Hewlett, 1965) and its own characteristics of mineralization.

An attempt has been made (Fig. 3) to flow chart a generalized procedure for statistical analysis of assay data. References are given in the text of this paper to provide more explanations of the techniques for those who are interested in following the development in more detail.

Assay data are usually screened to separate them into separate populations, on the basis of minerals (oxide, secondary, primary) (Hazen, 1963), grade zones (waste, leach, ore) (Hewlett, 1965), rock types (diorite, quartz monzonite, schist), alteration zones (silicified, chloritized, argillized), and so forth. This is done to simplify the analysis, to provide additional information on the grade of ore and its relationship to geological characteristics of the deposit, and to eliminate multimodal assay frequency distributions (Hewlett, 1964).

When screening has been completed, the sets of assays can be used to construct assay frequency distributions for the various minerals and grades of ore, (Fig. 4). These assay frequency distributions are made up of unlocated assays, that is, no consideration is given to either the X, Y, Z coordinate locations or the respective tonnage of ore that is represented by each individual assay.

If the assay frequency distributions are unimodal, indicating a set of assay data from a single population of data, the statistics (mean variance, standard deviation, and relative skewness of the distribution) are computed for each distribution (Hazen, 1961). If the assay frequency distributions are multimodal, indicating a mixture of minerals or grades of ore, further screening is indicated to break the data down into unimodal distributions.

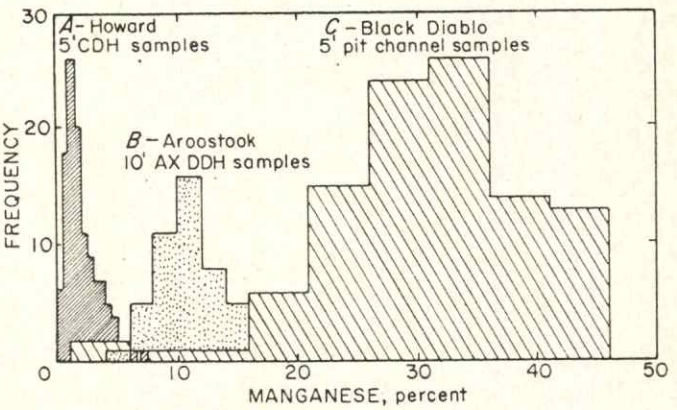

Figure 4. Positively skewed (A), Normal (B), and Negatively skewed (c) Distributions of Manganese Assays (Data for A from U.S. Bureau Mines RI 4539, data for B from U.S. Bureau Mines RI 4921, data for C from U.S. Bureau Mines RI 4713.

Often these distributions can be used as a basis for estimating tonnages involved for various cutoff grades. If the geometric area of influence of each assay (grid drilling) is the same, that is, represent equal tonnage for each assay, the percentage of assays both above and below a designated cutoff grade can be related to total tonnage both above and below that cutoff. This means that somewhere within the area drilled, because these assays are being considered as unlocated in space, the estimated tonnage below cutoff grade is present and must be removed (Hazen, 1961).

Cumulative assay frequency distributions for low-grade deposits can be plotted on log-probability paper to ascertain if more than ore population is present (oxide, secondary, primary) (Fig. 5). If the assays are distributed lognormally, and most low-grade deposits approach lognormality, these assays for different mineral

populations will plot as straight lines with different slopes. In the industrial minerals field, assays of low-grade impurities would often plot as lognormal distributions.

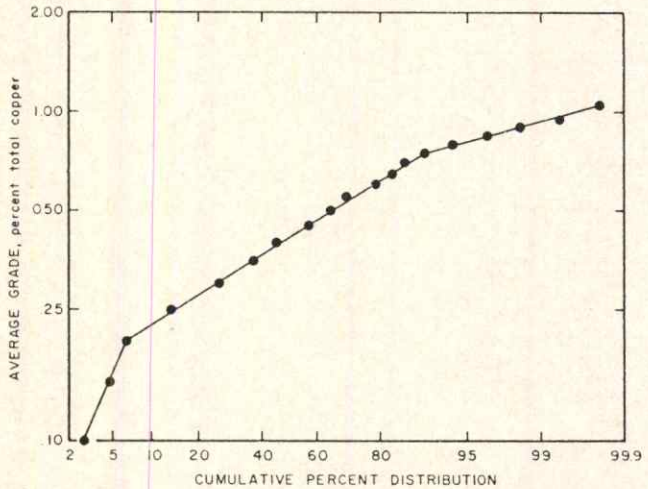

Figure 5. Log-probability plot of distributions of copper mineralization as shown by exploration assays from two deep drill holes (Hazen, 1963).

If only a small number of assays are available from the first stage of exploration, simulation techniques (Hewlett, 1964, 1964a) can be used to generate 5,000 to 10,000 additional assays having the same mean and standard deviation as the original small group that was available. The larger simulation group can be used to advantage for making predictions as to what will be found as exploration continues.

In the event that the assay frequency distributions are skewed, which is the case for virtually all low-grade deposits, some mathematical transformation of the assay values may be desirable for simplicity in analysis (Li, 1964; Miller and Kahn, 1962). Transformations are, at best, a substitute method of handling data, and the transformation does not alleviate all of the problems in the original data. In fact, there are problems introduced by using transformations. For example, log transformations do not account for maximum chemical limits for assays of minerals and occasionally high and/or low values fall outside these chemical limits when the transformed data are converted back to the original assay base.

Assay frequency distributions are often tested for comparison of fit with theoretical mathematical distributions. If the fit is adequate (confirmed by various tests such as chi square) (Hazen, 1958), the mathematical distribution can be used as a model for the assay distribution.

Confidence limits can be established for the assay data (Hazen, 1961). The limits will be symmetrical about the mean or average grade of ore for normal distributions, but will be unequal for skewed distributions and when transformed data are being converted back to the original assay base.

When the confidence limits have been calculated for a set of exploration data, it is customary to match these calculated limits with the confidence limits originally specified as acceptable for the job before the exploration was started.

If the calculated confidence limits are not acceptable, that is, they are wider than the limits originally specified, then more exploration (drilling) is required to reduce the calculated confidence limits to an acceptable size. The sample volume-variance relationship[1/] can be used to compute new sample volumes when it is desirable to change sample volume (for example, AX core size to NX core size or 2-foot to 5-foot sample interval lengths) to reduce the variance and thus increase the precision of the sampling (reduce the value for the standard error of the mean) (Hazen, 1961).

1/ $s_1^2\lambda = s_2^2\lambda_2$, where s_1^2 is the variance and λ_1 is the sample volume of one series of samples and s_2^2 is the variance and λ_2 is the sample volume of a second set of samples from the same deposit area.

It has been shown by statistical application in sampling ore deposits that the sample volume is critical when improvement in the precision of estimate of grade of ore is desired (Becker and Hazen, 1961). Increasing sample volume tends to reduce the variability between assay values and thus increases the precision in the estimate of grade of ore. As a word of caution, sample volume is not necessarily the total volume used for the sample, it is the amount of sample material pulverized for working up the final sample for assay. Thus, in driving a 5- by 7-foot drift or crosscut for sampling purposes, the sample volume is not the volume produced by the 5- by 7-foot cross-sectional area times the round length which might be sent through a sample plant. The true sample volume which reflects the statistical variance is the amount of material cut out in the sample plant and pulverized for assay purposes.

The standard error of the mean (Hazen, 1961) can be used to calculate the number of additional samples and drill holes needed to complete the drilling to the specified confidence limits. Once the new calculated value is established, this sets the requirements for the second stage of the exploration project.

When the confidence limits calculated for the exploration data are satisfactory by matching the limits specified for the job, then various statistical techniques can be utilized for developing additional information concerning the deposit. In using these techniques, the assay data are related to their X, Y, Z coordinate position and are considered as "located" data; that is, located in space with respect to each other. The assay data can be punched on Hollerith cards and electronic digital computer programs, such as quadratic and cubic regression, can be used to test for trends in the mineralization, thickness of ore, grade of ore, and so forth.

Figure 6 is an example of quadratic regression showing assay value in percent bone phosphate of lime for a 40-acre plot of land in the Florida Phosphate deposits (Berkenkotter, 1964). Figure 7 shows thickness of phosphate matrix bed, and Figure 8 shows the product of assay and thickness in feet percent, for the same 40-acre plot of ground.

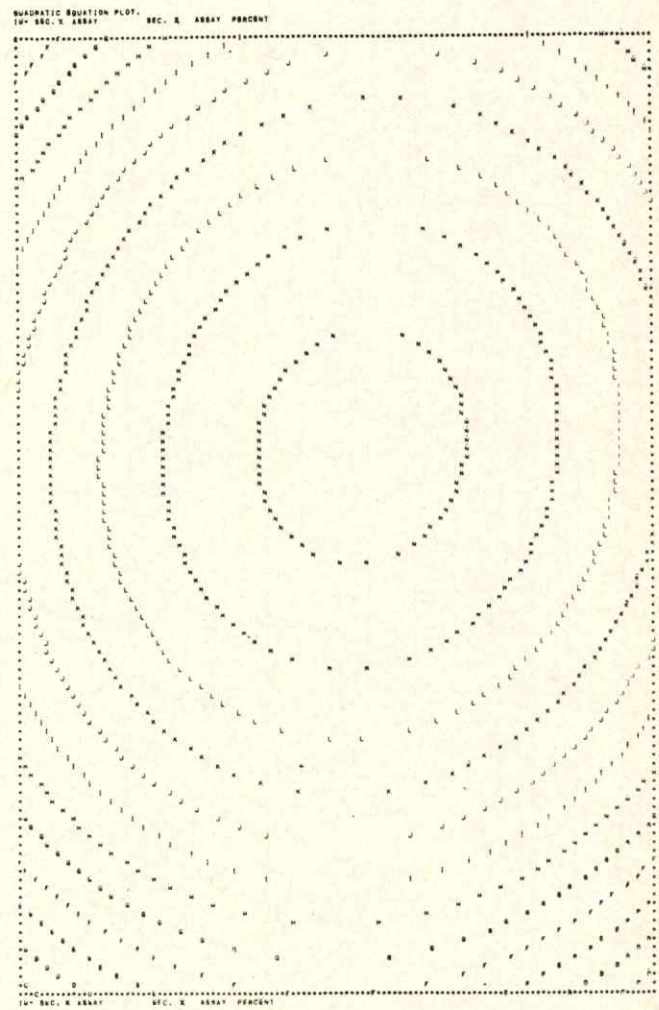

Figure 6. Quadratic regression showing assay values in percent bone phosphate of lime for a 40-acre plot of land in the Florida Phosphate Deposits (Berkenkotter, 1964).

Statistical response surface fitting techniques (Hewlett, 1964b) can be used effectively for guiding exploration, for evaluating grade and tonnage, and for determining pit limits for open pit mining.

Figure 9 shows a statistical surface fit depicting contours of equal elevation, in fact, of bottom

elevation of a matrix bed from a 40-acre plot of land in the Florida Phosphate deposits.

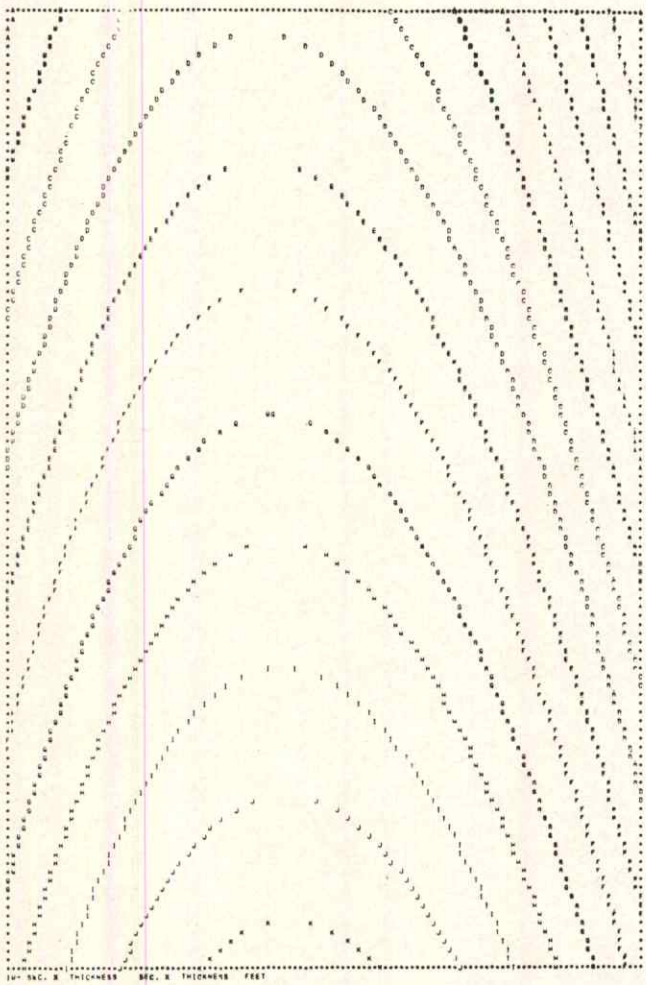

Figure 7. Quadratic regression showing thickness of phosphate matrix bed for the same 40-acre plot of land in the Florida Phosphate Deposits (Berkenkotter, 1964).

Figure 10 is a statistical response surface showing thickness contours at the plus 35 percent Al_2O_3 cutoff grade for a high alumina clay deposit in Georgia. Figure 11 is a statistical response surface showing the thickness contours at the less than 1.00 percent Fe_2O_3 cutoff grade for the same high alumina clay deposit in Georgia. These two surfaces can be overlain and form the basis for a mine development plan. If cross sections are drawn for mine planning and delimiting ore blocks, the mean-square-successive-difference test and correlation techniques can be used to compute the area of influence of an assay (Hazen, 1967) for projecting grade of ore values in the sections.

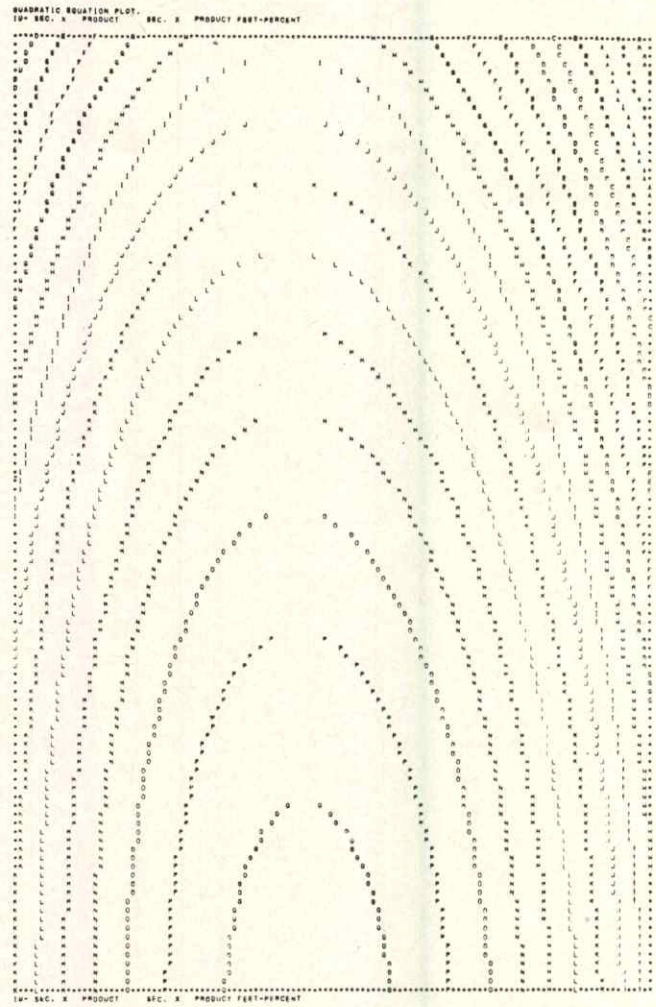

Figure 8. Quadratic regression showing product of assay and thickness in feet percent for the same 40-acre plot of land in the Florida Phosphate Deposits (Berkenkotter, 1964).

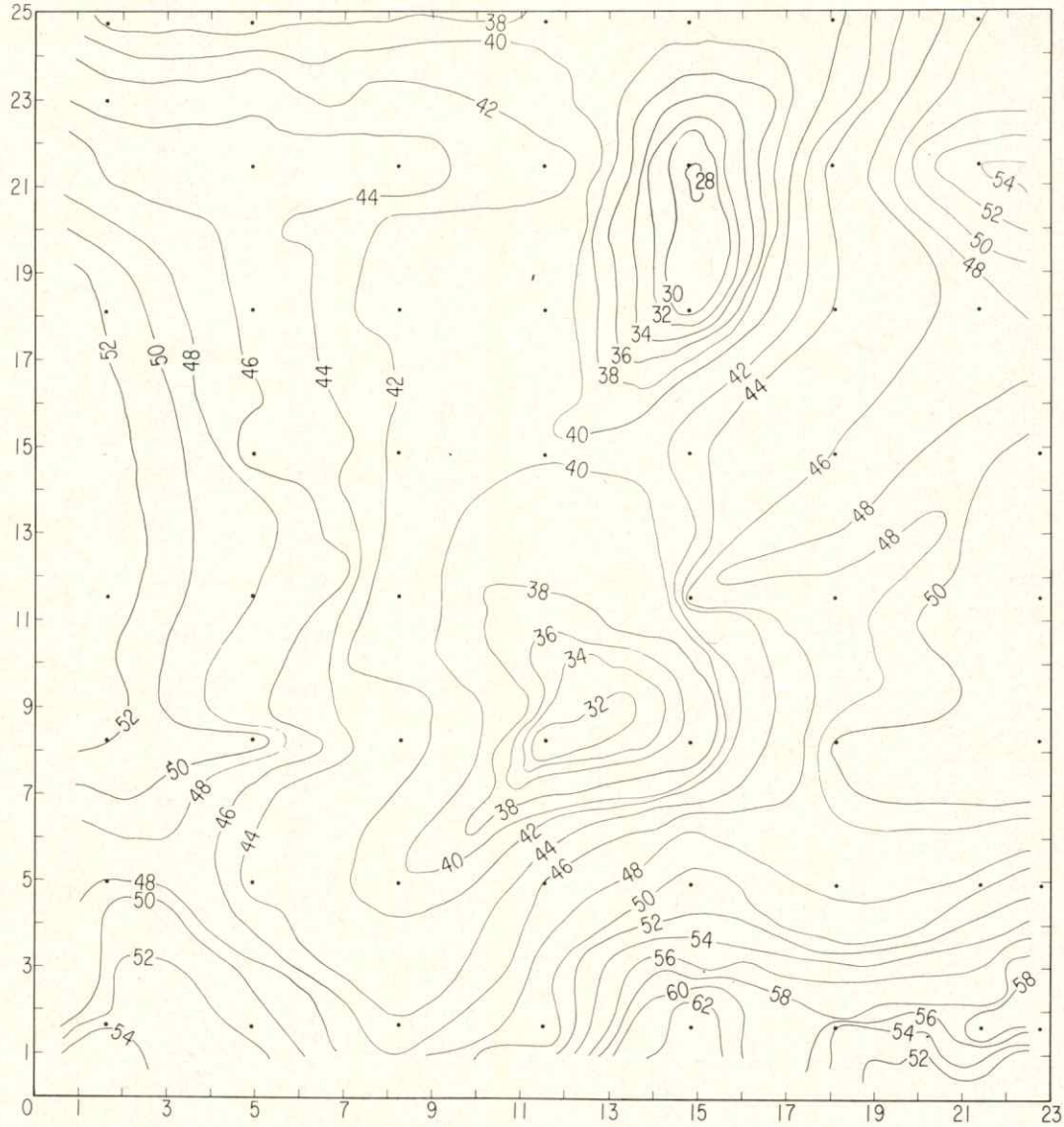

Figure 9. Statistical response surface showing contours of equal elevation, in feet, depicting elevation of bottom of the matrix bed from a 40-acre plot of land in the Florida Phosphate Deposits.

CONCLUSIONS

Geometric methods for estimating grade and tonnage of ore, although simple to use, are not realistic models for complex ore bodies. They have been developed primarily for calculating tonnage rather than grade of ore.

Although they do not solve all of the fundamental problems in accurately estimating grade and tonnage of ore, use of mathematical-statistical techniques provide a better basis for developing better models which produce much more information about an ore deposit. Much of the inadequacy in using mathematical-statistical models is not in the techniques, but it is in the lack of measurement of pertinent data during exploration. Much work remains to be done in analyzing and testing exploration data to determine the kinds of measurement data that are essential for accurate estimation of ore grade for all minerals whether they be metals or nonmetals.

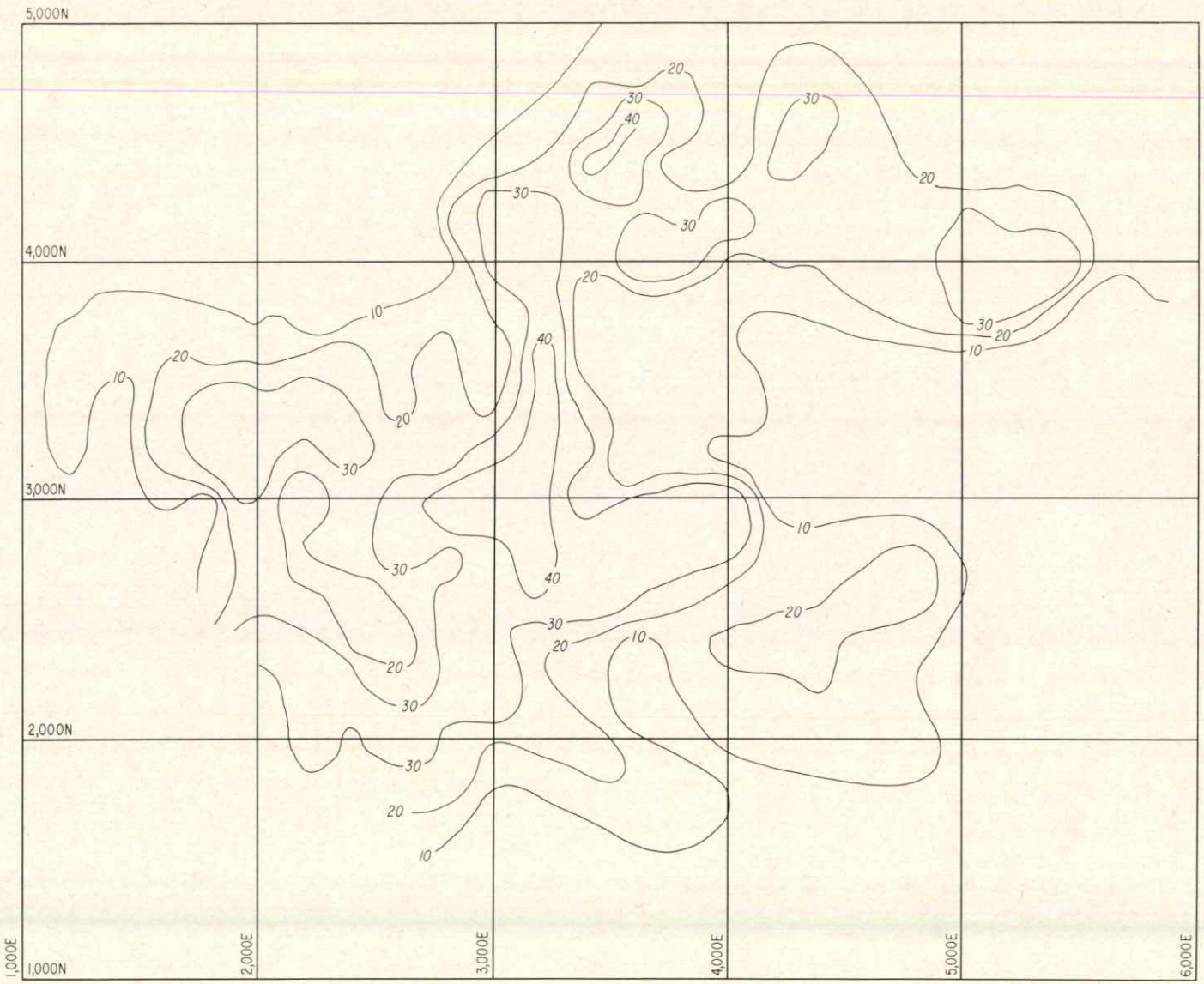

Figure 10. Statistical response surface fitted to show thickness contours at + 35 percent Al_2O_3 cutoff.

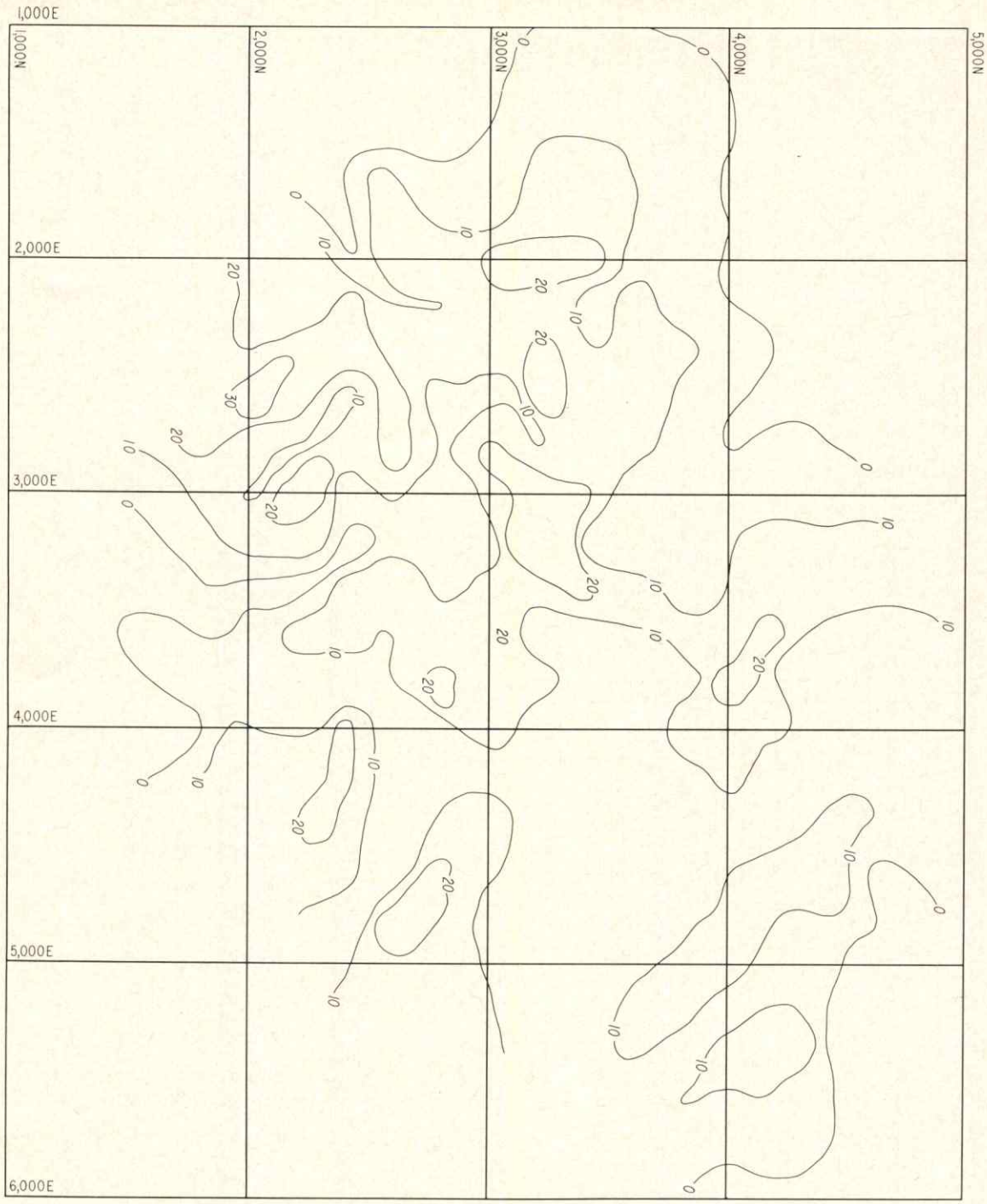

Figure 11. Statistical response surface fitted to show thickness contours at less than 1.00 percent Fe_2O_3 cutoff.

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A MATERIAL PRODUCERS APPROACH TO WORKABLE ZONING ORDINANCES

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ABSTRACT

County-wide zoning in Kansas is relatively new, and most counties have not yet adopted it. In an effort to try and get workable zoning ordinances which would not hamper the producer, this company has set up a uniform procedure to follow:

1. Counties are contacted to determine their present zoning status.

2. Counties are contacted on a regular basis to keep track of zoning progress.

3. A suggested set of regulations pertaining to the aggregate industry was drawn up. These suggestions are so written as to be easily modified to fit most any ordinance with little changes.

4. Initial meetings of new zoning boards are attended by company personnel.

5. Company representative follows through and checks new ordinances as they are published, to look for any last minute changes.

By following these basic procedures we have been able to avoid the unexpected surprise of a new ordinance.

INTRODUCTION

County wide zoning in Kansas is relatively new, although some counties with large metropolitan populations have had some form of zoning for several years. The majority of the counties however, have seen little or no activity until recently.

For example, in the area in which we operate there were only three counties zoned prior to 1965 and only four more with three-mile or limited township zoning. Since 1965 there have been three county-wide ordinances adopted, two will be adopted before the end of April 1967 and ten more have zoning plans in progress. Four counties have indicated there is no activity at present.

In general, we feel that in the cases where zoning was established or proposed that the boards were not specifically trying to write zoning detrimental to our industry but rather, they were writing from the standpoint of being poorly informed as to the nature of our industry. Witness the number of times we have been placed in heavy industry classification, when the sand or stone nearest to this zoned area might be eight or ten miles distant.

Irregardless of the reasons for placing us in whatever category we have been placed, we are at a disadvantage because of the unique nature of our industry, every ton of material we remove from a deposit puts us that much closer to being finished.

DISCUSSION

To follow progress of zoning

more closely the Kansas Limestone Association formed a committee whose job is to coordinate the action of the members of the association with regards to zoning activity.

The following program was presented to the association by the committee and approved:

1. All the producers in the association were to list their areas of interest so no counties with potential zoning problems would be overlooked.

2. A letter was to be sent to the County Engineer of each county of interest to determine the present zoning status of the county and to find out what was being considered for the future. After determining the present zoning situation, the counties would be contacted on a regular basis to keep track of progress on proposed new zoning or changes in the old.

3. A suggested set of regulations pertaining to the aggregate industry was to be drawn up. These suggestions were to be written so they could be easily modified to fit nearly any ordinance with little change. Suggestions were mainly in the area of special permits (conditional uses), non-conforming, abandonment, and general operating conditions (including the restoration).

4. Members were asked to keep track of any zoning activity in their area and to send information to the chairman of the association committee, who would then contact all members in the area affected and determine the course of action to be taken.

   If new zoning is being formed, members attend initial planning meetings. If an ordinance is to be modified, a copy of the proposed modification is obtained by the zoning chairman and if the change affects our industry, the meetings are attended.

   When new ordinances are proposed, members attend the meetings and make suggestions where applicable. After an ordinance is written, the committee examines it to see how the proposed suggestions have been handled. Before the zoning is published in its final form, the committee chairman goes over it to see that there have been no adverse last-minute changes.

By following the above described procedures, we have been able to learn of new zoning regulations in time to do something about them, and have been successful in bringing about constructive changes.

The association goal is to establish a set of suggestions which can be incorporated into the various zoning regulations as they are being written. When all the new ordinances are finished, it is hoped that some of the suggestions can then be amended to earlier regulations to update and improve them.

When the committee first learns of a new zoning ordinance in the planning stage, a letter is sent to the board offering to supply them with the following information at no cost:

1. List of leases and property owned by limestone producers in the area under consideration.

2. Reserves at the present locations and estimated length of life of production.

3. List of potential properties in the area suitable for quarrying.

4. List of stone deposits which because of some physical or chemical characteristic make them unique.

5. Offers of help in writing the section dealing with mineral extraction.

We have thought about sending a similar letter to the major planning consultants who write the ordinances. The main purpose of such a letter, of course, is to aid the board members and planners in their job by making accurate information available to them. Too many times planners have made assumptions about reserves etc. which led to undesirable restrictions in their regulations, which could have been avoided had accurate information been available to them.

Each zoning ordinance must be examined by itself. But as mentioned earlier, there are certain sections in addition to those specifically dealing with the aggregate industry which must, in many cases, be altered. Some of these are as follows:

Non-Conforming Use

This category generally allows no more than 25% expansion, which arbitrarily puts a limit on a deposit which is far less than what is actually workable. There have been court decisions, such as the one cited below, which uphold our position that the entire property under lease or ownership at the time of becoming non-conforming should continue so. (Sup. Ct. of Ill. County of DuPage vs. Elmhurst-Chicago Stone Company., 18 Ill. 2d 479, 165 N.E. 2d 310 Sup. Ct. 1960) "We think that in cases of diminishing assets the enterprise is using all the land which contains the particular assets and which constitutes an integral part of the operation, notwithstanding the fact that a particular portion may not yet be under actual excavation. It is in the very nature of such business that reserve areas be maintained which are left vacant or devoted to incidental uses until they are needed."

We have proposed the following section on non-conforming use dealing with the extractive industry: "Property acquired or leased for the purpose of extracting crushed stone, sand, gravel or other materials therefrom and which property is a part of a larger tract held for quarry purposes even though it may be divided by a public road and which property is held for such purposes on the date of enactment of this resolution shall be considered in use for such extraction whether or not such extraction as actually commenced. The extraction, including the erection of any necessary buildings or structures or uses of storage area shall be allowed to commence and continue although such buildings, structures, storage areas for such use do not conform to the regulations of the zone in which said property is located. Provided, however, that if the use of such property for the above stated purpose has been discontinued for a period of two (2) years then the use of such property shall be in accordance with the provisions of the district in which it is located."

This section has recently been adopted in Shawnee County, Kansas.

In conjunction with this type of wording we also supply to the county a list of all leases in effect at the date of enactment of the ordinance. There are now three counties which have substantially adopted this proposal with very little modification. It is workable and it is beneficial in that the quarry operations are permitted to continue and the location of all operating quarries are a matter of public record.

Special Permits (Conditional Use)

Our industry is a temporary use and therefore, except where non-conforming, we must be faced with being placed in this category. Rather than have restrictive conditions on restoration etc. written in the ordinance which attempt to cover all areas the same, it is better to make each area stand alone, particularly with respect to restoration. Therefore, under the special permit request we have proposed a list of things to be considered in applying for the permit:

1. Access routes.
2. Prevailing wind direction.
3. Blasting and removal plan.
4. Reclamation (draining and grading).
5. General plan of operation.

Under four we have proposed the following wordage: "The condition of the property upon the termination of use for production, storage and sale of sand, gravel, stone or other materials. In the event there is a landowner and lessee and they are in agreement concerning the condition after use of land for production and sale of material, this agreement shall be considered sufficient showing. In no event will the operating company be required to meet a standard higher than the condition which would prevail if the land could be seeded and mowed with normal farm equipment. The standard of being able to seed and mow with normal farm equipment will in no event be applied to areas where this would not be possible in the natural condition."

If these various factors listed above are included here, they can be kept out of the special sections dealing with explosive storage and reclamation etc. which is going to be a continually more important problem. By putting some mention of reclamation in this section each proposed quarry area can be judged by itself. One county proposed leveling all holes to as near natural condition as possible, but some areas of the same county have two feet of overburden and sixteen feet of rock while others have twenty feet of overburden and four foot of rock.

Abandonment or Discontinuance

This section generally allows abandonment or discontinuance for a period of six months before the property loses its non-conforming status. We have tried to have the discontinuance extended to at least two years, and have used the following wording: "If a non-conforming use is voluntarily discontinued for a period of two (2) years or more, such discontinuance shall be considered legal abandonment of the non-conforming use." This precludes the possibility of losing the non-conforming usage if, for example, use is not permitted due to involuntary stoppage such as some type of litigation.

It has been found that by looking critically at our operations to see them as they appear to others and then applying the program outlined in this paper, we have been successful in gaining progress towards more beneficial zoning regulations for all concerned.

POTENTIAL POZZOLANIC MATERIALS

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ABSTRACT

Pozzolans comprise a variety of mineral materials that can be used to obtain a fixation of calcium hydroxide to form cementitious compounds. The classes most commonly used in the United States have been volcanic glasses, opal or opaline rocks, clay minerals, and fly ash.

The substitution of pozzolan for a portion of the cement in concrete has many advantages for special uses of concrete such as low cost, increased plasticity, reduced segregation and permeability, improved resistance to sulfate water, greater tensile strength, and reduced expansion and cracking. Some disadvantages are slower rate of strength development, increased shrinkage, and some adverse affects of freezing. The only effective means of identifying good pozzolanic material is by several expensive physical tests; however, optical tests usually can be used to screen out unsatisfactory material. A recent Bureau of Mines program led to comprehensive tests of 276 samples.

Prospective use of pozzolan must be evaluated according to desired results. Thus far, industry has been slow to adopt the pozzolanic materials, but new applications are being investigated. In general, natural pozzolans are not being extensively exploited because of restricted uses and the competition with pozzolanic fly ash. For the foreseeable future, fly ash will comprise most of the pozzolan used because of its abundance and low cost.

INTRODUCTION

The Mineral Resource Offices of the Bureau of Mines at Minneapolis, Minn., Bartlesville, Okla., Denver, Colo., San Francisco, Calif., and Spokane, Wash., began a study of natural pozzolanic materials in 1964 with the object of determining source materials and the extent of commercial usage. Because fly ash research has and is being done at other Bureau of Mines centers, it was not included in our resource study. We found, however, that we could not study pozzolanic materials without considering this powerplant ash.

Definition

Pozzolan is defined as siliceous or siliceous and aluminous material which, in itself, possesses little or no cementitious value; but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties.

Calcium hydroxide, $Ca(OH)_2$, is formed during the hydration of portland cement, and pozzolans combine with this hydrated lime to form a stable strength-producing cementitious material. The ability to combine with the lime of the hydrating portland cement, in large measure, determines the suitability of a material as pozzolan.

History

The use of pozzolanic materials for masonry and concrete construction dates back to ancient Rome. The name pozzolan was derived from the locality, Pozzuoli near Naples in Italy, where a consolidated volcanic ash or tuff occurs that was used by the Roman builders in making remarkably seawater-resistant concrete.

The invention of portland cement replaced most of the pozzolanic cements because of a faster setting

time and better early strength. In the past 50 years, however, pozzolans have again come under investigation for the advantageous properties which include cost reduction, heat reduction, decreased permeability, alkali aggregate expansion control, increased chemical resistance, reduced concrete drying shrinkage, and increased long-term strength.

POZZOLANIC MATERIALS

The processes by which pozzolanic materials affect concrete are not fully understood. Both chemical and physical characteristics are involved. Chemically, pozzolan reacts with the calcium hydroxide of the lime in cement during hydration to form stable silicates. This reaction proceeds slowly and, consequently, maximum strength is not reached as soon as in ordinary concrete. Any excess of alkalies in cement can combine with the pozzolan, and thereby are not available for later delayed adverse reaction with concrete aggregate.

The physical properties of pozzolans affecting behavior of concrete include particle size and shape, specific gravity, porosity, and moisture-absorbing capacity. Porous, angular, or excessively fine particles usually require the most water, whereas low water requirements are preferred. The additional water used, results in more shrinkage, lower strength, and decreased resistance to freezing. The nonporous spherical particles of fly ash generally require less water than the natural pozzolans. The specific gravity of most pozzolans is 10 to 25 percent lower than that of portland cement (2.3 to 2.8 compared to 3.1) and thus the pozzolans have a greater volume and a lower overall weight.

The chemical and physical characteristics of pozzolans can govern their ultimate use. For example, a canal-lining concrete subjected to intermittent wetting would feature a different quality of the pozzolan than a monolithic concrete dam involving constant saturation.

The Bureau of Reclamation and the Corps of Engineers have been the two largest users of pozzolan and each agency has established their own specifications. Smaller consumers usually adopt specifications estab-lsihed by the American Society for Testing and Materials (ASTM).

Pozzolan Sources

Pozzolan normally is classified according to mineralogic composition, especially as to active compounds of silica, alumina, and iron oxide that react chemically with cement. The Bureau of Reclamation has rated these active minerals according to the following classifications:

Natural pozzolan:

Activity type:

1.....Volcanic glass

2.....Opal

3.....Clay minerals

a.... Kaolinite-type clays

b.... Montmorillonite-type clays

c.... Illite-type clays

d.... Mixed clays with altered vermiculite

e.... Palygorskite (attapulgite)

4.....Zeolite

5.....Hydrated aluminum oxides

Industrial waste products:

Fly ash

Ground brick

Spent oil shale

The classes of material most commonly used in the United States as pozzolans have been volcanic glasses, opal or opaline rocks, and fly ash. The other classes have been tested but have not been extensively used.

Volcanic glasses include the

amorphous silica and aluminum glasses which occur in such rock types as pumice, pumicites, pumice stone, obsidian, scoria, tuff, and andesite. Andesite may become an effective pozzolan when the amorphous silica content is greater than the crystalline silica. The pozzolanic activity of the volcanic glasses results from their special state of instability and is enhanced by a system of small ducts generated during rapid cooling by the release of gases originally dissolved in the liquid magma; thus, increasing the surface area subject to chemical attack.

Opal is an amorphous hydrous silica containing up to 10 percent water. It is associated with many igneous, sedimentary, and metamorphic rock types. Opal forms in environments where dissolved silica can be deposited rapidly at low temperatures from solutions; opal is particularly susceptible to chemical activity and possesses pozzolan characteristics. The opaline rocks include tuffs, opaline shales, and diatomaceous earth.

Clays suitable for use as pozzolan fall into the following groups:

Kaolinite-type clays include the minerals kaolinite, dickite, and nacrite. These clays, being relatively stable chemically, are rather ineffective as pozzolan in their raw state. Calcination at temperatures between 1,000° and 1,800° F, however, enhances the pozzolan activity greatly. The clay dehydrates at about 630° F, and at temperatures between 900° and 1,200° F the clay undergoes a collapse of the crystal lattice that results in an amorphous, siliceous, and aluminum substance possessing increased pozzolanic properties.

Montmorillonite-type clays consist of the minerals montmorillonite, beidellite, nontronite, hectorite, and saponite. One of the important montmorillonite clays occurring in western United States is bentonite. The pozzolanic activity of montmorillonite clays is dependent upon calcination to temperatures between 1,000° and 1,800° F resulting in the crystal structure modification or collapse.

Illite-type clays--illite and glauconite--are considered transitional minerals between montmorillonite and the well-crystallized muscovite and biotite micas. The pozzolanic activity is only slightly improved by calcination at temperatures of 800° to 1,800° F, but better activity results when crystal structure is destroyed by calcination above 1,800° F.

Vermiculite is mixed with various clays having pozzolanic properties. Vermiculite is a complex hydrous silicate formed by the alteration of biotite mica; its structure is similar to the micas except that water molecules appear between the unit layers. Vermiculite swells upon heating; dehydration of the vermiculite occurs below 400°F, and decomposition of the structure occurs above 1,560° F. The optimum calcination temperature of the mixed clays and vermiculite class is dependent upon the varying proportions of the clay ingredients.

Palygorskite is a magnesium-rich hydrated silicate of aluminum formed by alteration of magnesium-rich volcanic ash or crystalline rocks. The mineral dehydrates when heated to about 570° F and contracts rapidly between the temperature range of 750° to 1,430° F. Between 1,300° and 1,500° F maximum pozzolanic properties are induced.

Zeolites are also an active group of hydrous silicates of aluminum with sodium and calcium as the important bases. They require close calcination control. The limited occurrences do not indicate appreciable use of zeolites as a pozzolan.

Hydrated oxides of aluminum, principally bauxite, upon calcination between 400° and 900° F, can be pozzolanic.

Artificial pozzolans include fly ash from coal-burning plants, ground brick, and spent oil shale. Of these, only fly ash has been widely used; the potential of the others is uncertain.

Fly ash is formed as the pulverized coal, blown into the furnace, passes through the high-temperature zone. Carbon burns off leaving a residue which is carried in suspension to lower temperature zones of the furnace and is fused to fly ash. The particles are usually spherical, smooth-surfaced, and glassy. Carbon content and fineness of the particles are closely related, high carbon ash

being normally accompanied by a high degree of fineness. The fineness of the ash appears to have more influence on pozzolanic strength developed, however, than does the combustible content, providing the combustible content is below 10 percent.

Work by the Bureau of Mines

Mineral investigators of the Bureau of Mines in the field offices examined and sampled what they considered pozzolanic materials in their respective areas. Criteria for sampling included that the material be in one of the activity groups, that a large occurrence of the material must be indicated, and that favorability for sampling be given to deposits near railroads or potential market centers.

The sampling programs were carefully planned. Familiarity with the area geology, use of commercial experience, and consultations with State and Federal Geological Survey offices and their respective reports were all helpful. No limit was placed on the number of samples taken for petrographic examination of active ingredients; however, only the material containing in excess of 50 percent and in most cases 70 percent active ingredients was further chemically analyzed and tested for the physical properties.

The Bureau of Mines made arrangements to use the laboratory of the Bureau of Reclamation, to have their experts train two Bureau of Mines technicians, and to consult on the work. During a 2-year program, comprehensive testing was done on 276 samples. Such tests are time consuming and costly, averaging about $66 per day to operate the laboratory when performing tests at the rate of 1-7/8 days per sample.

Initial preparations of 7- to 8-pound samples for physical testing consisted of oven drying, grinding, and air-tight storing. Some samples were calcined. Fine grinding was by ball mill and all samples were size tested by screening wet through a 44-micron sieve.

Tests were made for (1) fineness, (2) specific gravity, (3) compressive strength with portland cement, (4) compressive strength in lime, (5) water requirements, (6) change of drying shrinkage, (7) soundness or autoclave expansion, and (8) reactivity with cement alkalies. Optional testing on some samples was for air entrainment, mortar expansion, and uniformity.

Samples meeting specifications in all critical tests will be reported in a forthcoming publication. Data on samples collected, whether or not they were given physical testing, will be in the files of Mineral Resource Area Offices according to sample location within the respective areas. All Mineral Resource Offices reported large resources of natural pozzolanic materials.

Current Applications

Most of the notable uses of pozzolans in the United States have been in the construction of mass concrete structures such as dams, hydraulic structures of all kinds, and other structures exposed to water.

It is also used in pumped intrusion-grouting, auger packed-in-place and mixed-in-place piling, municipal sanitation projects, oil well cement, concrete pipe and block, soil stabilization, and masonry cement.

Mass Concrete - Pozzolan has been used in the United States principally as an additive for portland cement in large mass-concrete dams. This is because the advantageous properties derived from the use of a pozzolan have particular significance in this type of construction, while the deterring effects are of less consequence. The advantages include cost reduction, heat generation reduction, decreased permeability, alkali aggregate expansion control, and to a lesser extent increased chemical resistance.

The extremely large quantities involved in mass concrete construction generally allow a substantial cost reduction by the replacement of a portion of the portland cement by a lesser expensive pozzolan material. The cost of the pozzolans used in the Bureau of Reclamation structures have ranged from approximately 50 to

100 percent of the cost of an equal weight of portland cement. Reclamation saved more than $3,500,000 by using pozzolan in Hungry Horse, Glen Canyon, Flaming Gorge, and Yellow Tail dams. Temperature control is a primary factor in mass concrete construction. Excessive early temperature rise in mass concrete may result in cracking. One method of control is through the use of pozzolans which produce a slower heat of hydration than does an equal amount of portland cement. In general, pozzolans will produce only 40 to 50 percent of the high temperature rise as an equal weight of Type II portland cement (moderate low heat and moderate sulfate resisting).

Concrete containing pozzolan is more impermeable than similar concrete that has equal cement content but contains no pozzolan. Water tightness is of particular importance in reducing uplift pressures in a dam.

The alkali aggregate expansion control owes its significance to the relative reactivity of the available aggregate. Chemical resistance is likewise relevant depending upon local conditions.

The chief disadvantages imparted by using a pozzolan, are lower strength and lower freeze-thaw resistance at early ages. These factors are of less significance in mass concrete than most other types of concrete construction. The slow strength development factor is modified by the fact that the initial difference in strength between a pozzolan portland cement concrete and a concrete with straight portland cement, becomes less as the age of the concrete increases, and at later ages concretes containing pozzolans usually develop higher strengths. This is particularly suitable for dam construction because the full water load seldom is placed against the dam until at least a year after the concrete is placed. While under field-curing conditions, the use of pozzolans usually reduces the resistance of the concrete to freezing and thawing. Under prolonged moist curing most pozzolans have a beneficial effect on the durability of concrete when compared with the durability of similar concrete containing portland cement only. In mass construction, the interior concrete is, of course, not affected by freezing and thawing, and the above benefits or liabilities would be realized by the exterior concrete only.

Concrete Pipe

Pozzolan is used in the manufacture of concrete pipe only when it is specified. Usually the mix design for concrete pipe to be used in sanitary service is different from that for concrete pipe to be used for storm drains. Concrete pipe for sanitary projects may contain pozzolan, or may be made from concrete using a Type V cement (sulfate resisting) instead of the customary Type II cement. It is common practice in northern California for specifying agencies to require a 15-percent replacement of cement Type II by pozzolan for concrete pipe for sanitary projects. However, much concrete pipe for sanitary projects is made with Type V cement without pozzolan. An exception to this is concrete pipe made for the California Department of Water Resources, which requires pozzolan in all types.

The use of pozzolan in concrete pipes results in a less permeable concrete and thus is less susceptible to the deleterious effects of leaching and more resistant to attack by weakly acid waters.

Cement Mortar Linings

Pozzolan is used in cement mortar linings of potable water transmission and distribution lines for the better workability and adhesive properties it imparts to the mortar. It is not used to inhibit the reaction that might be caused by reactive aggregates or because of the relative impermeability it provides.

Cement mortar lining is applied to the interior of steel or concrete pipe by a machine which centrifugally casts the mortar against the inner walls and mechanically trowels a finished surface. It may be applied in place to new steel pipe or to recondition and repair existing concrete

pipeline systems that have been in service for periods as long as 20 to 40 years.

Usually, pozzolan replaces 12 to 20 percent of the cement in the mortar mix. This percentage may be specified by the contracting agency, but more often the percentage is designated by the contractor, who recommends a mix in response to a general specification. This recommendation then is approved by the contracting agency.

Oil-Well Cementing

Pozzolanic materials have been used as admixtures with oil-well cements for several years. Fly ash, volcanic cinder, volcanic ash, and calcined opaline shale have been mixed with an appropriate oil-well cement,[2/] commonly in a 1-to-1 ratio.

A mixture of hydrated lime and pozzolanic material with appropriate set control additives is used for cementing deep wells where moderate or high temperatures (140° to 400° F) prevail. The quantity of hydrated lime in the mixture usually is 15 percent of the weight of the pozzolanic material.

Under conditions of high temperature and pressure, this 15-percent mixture has greater compressive strength and longer thickening time than ordinary oil-well cement slurries and oil-well cement-pozzolanic material slurries. Many cements lose their early strength because of the high temperatures generated with prolonged curing times. The strength of pozzolan-lime mixture not only does not retrogress, but the mixture develops greater strength with curing. The longer thickening time is particularly desirable at high temperatures because the hazard of premature setting is substantially reduced. This mixture also results in a lighter weight slurry and thus minimizes the pressure on a highly permeable formation.

Future increased use of natural pozzolanic materials is greatly dependent upon acceptance by the construction industry. More research is needed as to the beneficial properties of pozzolanic materials. In this, fly ash producers, by necessity are making progress. The most likely places for consistent uses for natural pozzolan to develop are in highly populated and industrial areas such as California where fly ash is not economically available.

[2/] There are seven classes of oil-well cements: A, B, C, D, E, F, and G. Each is intended for different service or well conditions.

SOME POTENTIAL NONMETALLIC MINERAL RESOURCES IN MISSOURI[1]

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ABSTRACT

Nonmetallic mineral resources available in Missouri that have been little publicized include naturally occurring materials, and industrial wastes and byproducts. Among the more important are: mine and mill tailings; byproduct sulphuric acid and phosphates; shales and clays having bloating, absorptive, and binding qualities; and fly ash. Of less importance are: impure fire clays, kaolinite clay deposits, and quartzite. Distribution and description of these mineral resources, including chemical and physical data where available, are given.

INTRODUCTION

In Missouri, a number of nonmetallic raw materials with potential value are not utilized at present or utilized only to a limited extent. Eight of these raw material resources are discussed. Location with respect to markets, technologic factors, acceptance, and demand are partly responsible for the present lack of interest. In the course of time new or expanded uses for some of these materials will be developed and it is the intent of this paper to encourage such development.

Much of the data included under the commodity headings have been taken from Survey publications, unpublished manuscripts on file, and from inquiries to mining and producing companies. The authors wish to acknowledge the following for the information they so freely furnished: Messrs. Elmer A. Jones and Paul A. Gerdemann, St. Joseph Lead Company; Messrs. Robert G. Peets and John A. Emery, Meramec Mining Company; Messrs. Clarence C. Houk and Ernest R. Achterberg, Baroid Division National Lead Company; Messrs. Robert D. Griffey and P. R. Dessieux, Chas. Pfizer & Co., Inc.; Mr. Patrick D. Harrington, Union Electric Company; Mr. Robert J. Weiss, Walter Handy Co., Inc.; Mr. William M. Huff, Central Electric Power Coop; Mr. D. C. Davis, Associated Electric Coop.

MINE AND MILL TAILINGS

Mine and mill tailings have been accumulating in Missouri for over 100 years and total reserves of potentially marketable material are estimated at 150 million tons. During the past 50 years, sales have ranged between 1 and 3 million tons annually. Value of sales during the past decade has ranged between $1.0 and $1.5 million per year. "Chat" produced in the Tri-State zinc-lead district of southwestern Missouri was the most important commercially for many years. "Chat" is the term commonly used in Missouri for the coarser-sized tailings produced by gravity milling. In recent years, the largest sales of tailings have been from the Southeast Missouri Lead district. By 1970, four new mining projects in the southeast will be in full operation. Statewide production of useable tailings, mostly dolomite fines, is expected to approach 12 million tons per year by that time.

Tailings are presently being produced in lead-zinc, barite, and iron mining. Rock types consist of dolomite in the Southeast Missouri Lead district; chert in the Missouri Tri-

[1]Publication approved by the State Geologist, Missouri Geological Survey and Water Resources.

State and in the Washington County barite district; and felsite or "traprock" in the Precambrian iron district of southeastern Missouri. The location and characteristics of these mine tailing accumulations are given in Figure 1 and Table 1.

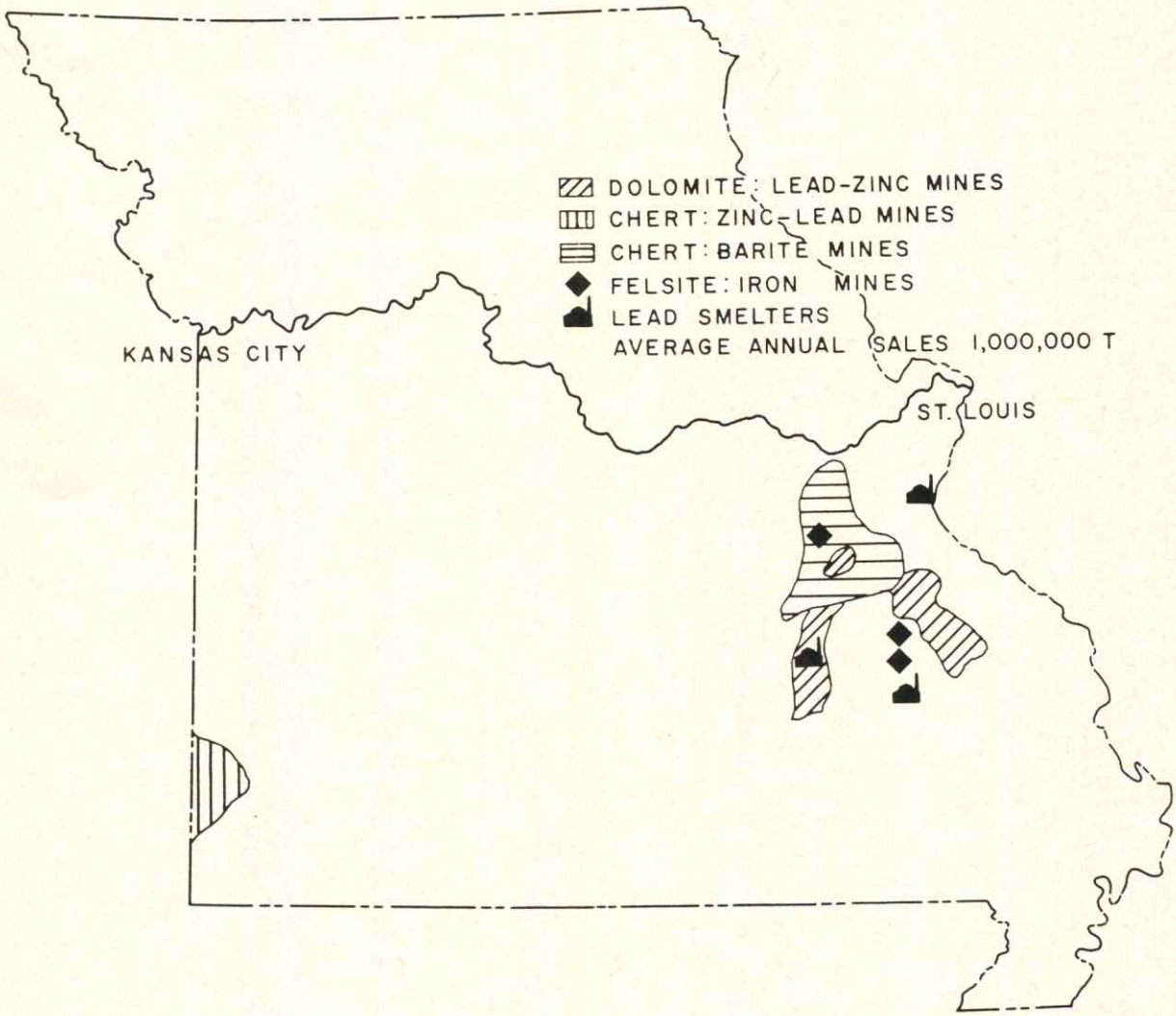


Figure 1. Types of mine and mill tailings in Missouri.

Dolomite: The Southeast Missouri Lead district comprises the Lead belt, centered in Flat River, the Indian Creek mine in Washington County, and the newly developing Viburnum trend area west of the St. Francois Mountains. Both coarse dolomite tailings (up to ½-inch) from gravity milling and fines (-35 mesh) produced by froth flotation are present in the Lead belt. However, flotation has been used exclusively since 1960, so all the tailings now being produced in the district are fines. Gravity tailings or chats account for an estimated 15 million-ton reserve in the Lead belt. Reserves of dolomite fines in that area approach 80 million tons, while those at the Indian Creek and Viburnum mines together are estimated at about 15 million tons. These reserves and all of the present production are controlled by the St. Joseph Lead Company. Current rate of production of tailings at Flat River is 3 million tons per year; at Indian Creek, nearly one-half million tons; at Viburnum and the new Fletcher mine combined, another 3 million tons

Table 1. Characteristics of mine and mill tailings in Missouri

Rock Type	Estimated Annual Production (s.t.)	Estimated Existing Accumulations (s.t.)	Size Range	Average Size	Composition
Dolomite SE Missouri Lead District Flotation Milling	Up to 10 million by 1970	100 million	35 mesh to 0	200 mesh	CaO 28% Al_2O_3 2.6% MgO 17% K_2O 0.8% CO_2 41% S 0.5% Fe 3% SiO_2 4% Base Metals 1.1% Insol. 7%
Gravity Milling	-0-	15 million	¼" and less	20 mesh	
Chert Missouri Tri-State District Gravity Milling	-0-	1 million ±	½" and less	¼" to ½"	Predominant SiO_2; some carbonates, iron oxide, Pb & Zn sulfides.
Chert Washington County Barite District Gravity Milling (1) Gravel	1.5 million	Minor amounts	Mostly under 1"	¼"	Predominant SiO_2; some carbonates, limonite, Al_2O_3.
(2) Fines	3.5 million	Slime pond; multi-millions	< 16 mesh	325 mesh	Pseudolateritic clays: hydrous iron-aluminum silicates; quartz, dolomite, limonite.
Felsite Porphyry Preθ Iron District SE Missouri Magnetic & Flotation	1.2 million by 1970 (mostly fines)	< 1 million	2 sizes: (1) ¼" to 5/8" (2) < 35 mesh	(1) 3/8" (2) <200 mesh	SiO_2 70% Al_2O_3 12% $Na_2O + K_2O$ 8%
Gravity Milling	-0-	Several million	3/4" and less	¼" to ½"	SiO_2 58% MgO 6% CaO 6% Fe_2O_3 21% $Na_2O + K_2O$ < 1% Al_2O_3 8%

annually. Three new mines now under development along the Viburnum trend are expected to yield an additional 4 million tons of dolomite tailings per year to St. Joe's present 6½ million annual total.

Over one-half million tons of tailings per year are now being sold, mainly from reserves in the Lead belt. Receipts from the sales total about $500,000 per year. The bulk of this material is fines shipped by rail to southern states for use as agricultural limestone. Appreciable amounts of the chats are sold each year for aggregate, railroad ballast, and flux. The roughly one-half million tons annual sales rate is about 10 percent of the nearly 10 million-ton annual rate of production predicted for 1970 and thereafter. It is hoped that sales can be expanded in existing uses, and that new uses, such as in mineral fillers and in the chemical industry, can be developed.

Chert: Chats in the Missouri part of the Tri-State district around Joplin are composed of chert and jasperoid, gangue minerals of the once important zinc-lead ores. The resulting gravity tailings are hard, brittle, and siliceous. Many of the larger chat piles are now depleted, having been sold, mostly for railroad ballast. In recent years, the main market has been for sandblasting, and for grinding and polishing. Other important uses are as roofing chat and granules, aggregates, and for rock wool manufacture. There has been no mining of consequence in the Missouri part of the Tri-State for 10 years, so no new supplies of tailings are being produced.

The coarse tailings produced in concentrating the residual barite ores in the Washington County Barite district consist mostly of minus 1-inch gravel rejected by the jigs in the washer plants. This material consists of chert and quartz druse with minor limonite. Small amounts are marketed each year, mostly for roadstone and sometimes for railroad ballast. The majority of the tailings are used in the mining operations for roads and tailing pond dams and readily available reserves are negligible.

About 70 percent of the tailings each year accumulate as slimes in the tailing ponds. This amounts to about 3.5 million tons at the present rate of production. The fines are mostly red clay with unrecovered barite fines. The only reported use has been for brickmaing a number of years ago.

Felsite: The diamond symbols in Figure 1 designate the three important iron mines in the Precambrian iron district of southeastern Missouri. The tailings are composed of felsite, usually rhyolite porphyry of volcanic origin. The Meramec Mining Company Pea Ridge mine, the northernmost among the three, produces about one-half million tons a year of waste material, the fines averaging about 325 mesh. Perhaps 10 percent of the tailings comprises the magnetic cobbing reject, ranging between 1/4-inch and 5/8-inch in size. No appreciable sales of the two tailing products have been reported.

Next south is the Hanna Mining Company Iron Mountain mine permanently closed down in mid-1966. The felsite tailings have been sold to a local operator for many years, and are marketed as traprock, mainly for aggregate and railroad ballast usage. The mine area and equipment have been leased to this operator. There are several years reserves of the tailings in stockpiles. These gravity tailings are 3/4-inch and less in size. Annual sales have often exceeded one quarter million tons.

The third iron mine is a joint venture of Hanna Mining Company and Granite City Steel Company called Pilot Knob Pellet Company. It is scheduled to go into production in early 1968, and will produce about 800,000 tons per year of felsite tailings averaging around 100 mesh in size; top size being about 35 mesh.

The Pea Ridge and Pilot Knob mines together will soon produce about 1.2 million tons per year of dominantly fine tailings. This felsitic material is very dense, hard rock composed mainly of feldspars. Some possible uses of the fines might be as abrasives, mineral fillers, fine aggregates, and for making pressed bricks. The coarser material is suitable for aggregates and railroad ballast.

MILL AND SMELTER BYPRODUCTS

Phosphates: The mineral apatite, a potential source of phosphate fertilizer, is present in the Precambrian iron deposits at Iron Mountain and Pea Ridge in southeastern Missouri. At the Hanna Mining Company Iron Mountain mine, the apatite was not recovered and this mine was closed in 1966. Meramec Mining Company is recovering apatite from the Pea Ridge ore prior to pelletizing. The resident manager reports that present production of apatite concentrate is about 5,000 tons per month averaging 15 percent phosphorous. This is equivalent to from 70 to 75 percent tricalcium phosphate.

Meramec Mining is also investigating the possibility of recovering monazite which is present in small quantities in the apatite concentrate. The mineral monazite is a potential source of cerium, thorium, and yttrium.

Sulphuric Acid: Byproduct sulphuric acid plants utilizing sintering plant gases have been announced by the St. Joseph Lead Company for its smelter at Herculaneum, Jefferson County, and by Missouri Lead Operating Company for its smelter now under construction near Bixby, Iron County. The estimated production of sulphuric acid from these plants is 100,000 tons per year at the Herculaneum smelter and 40,000 to 50,000 tons per year at the Bixby smelter. Construction of the acid plant at Herculaneum is scheduled to begin in late 1967. The acid plant is included in present construction at the Missouri Lead Operating smelter which is scheduled for completion in 1968. Marketing plans have not been announced by either company.

The American Smelting and Refining Company is constructing a lead smelter at Glover in Iron County. No plans for a sulphuric acid plant have been announced but if installed, it would have a potential capacity of about 30,000 to 45,000 tons of H_2SO_4 per year. Smelter locations are shown on Figure 1.

EXPANDABLE SHALES

A number of shales in the Pennsylvanian, Devonian, and Ordovician Systems in Missouri have natural bloating qualities which make them suitable for the production of expanded lightweight aggregate (Larson, 1947; Herold and others, 1958). Sample locations of the more favorable units tested are shown in Figure 2. Three of the shale units have been used commercially. At present, the Carter-Waters plant at New Market is the only producer of expanded lightweight shale aggregate in the State.

Results of standard firing tests made in an oxidizing atmosphere and quick firing tests in a reducing atmosphere are presented in Table 2. Two samples, the Pleasanton (7) and the Lagonda (9), which failed to react favorably under either firing condition gave excellent results when ferric oxide was intimately mixed with the shale. All other samples treated with ferric oxide showed good to excellent bloating quality when fired in a reducing atmosphere.

Seventeen units show the most promise for future exploitation. Twelve are in the Pennsylvanian, three in the Devonian, and two in the Ordovician.

Pennsylvanian (Units 1 thru 12 - Figure 2, Table 2): Pennsylvanian strata are widely distributed throughout the western and north central parts of Missouri and include the largest number of shale units that are of current or potential value for the production of expanded lightweight aggregate. Outliers of this strata are also present in eastern Missouri. From the standpoint of thickness and distribution, the Pleasanton (6 & 7), Weston (3), and Lawrence (2) are the most favorable. The Pleasanton has an extensive outcrop belt which is essentially the Missourian-Desmoinesian Series boundary. Thickness ranges from 40 to 70 feet. There is production at present from equivalent strata in southern Iowa and western Illinois. The main outcrop area of the Weston and Lawrence shales are between St. Joseph and Kansas City, Missouri where the thickness of each ranges between 50 and 100 feet. The Weston is used in the Carter-Waters New Market plant and the product is marketed under the brand name of Haydite. The Wea

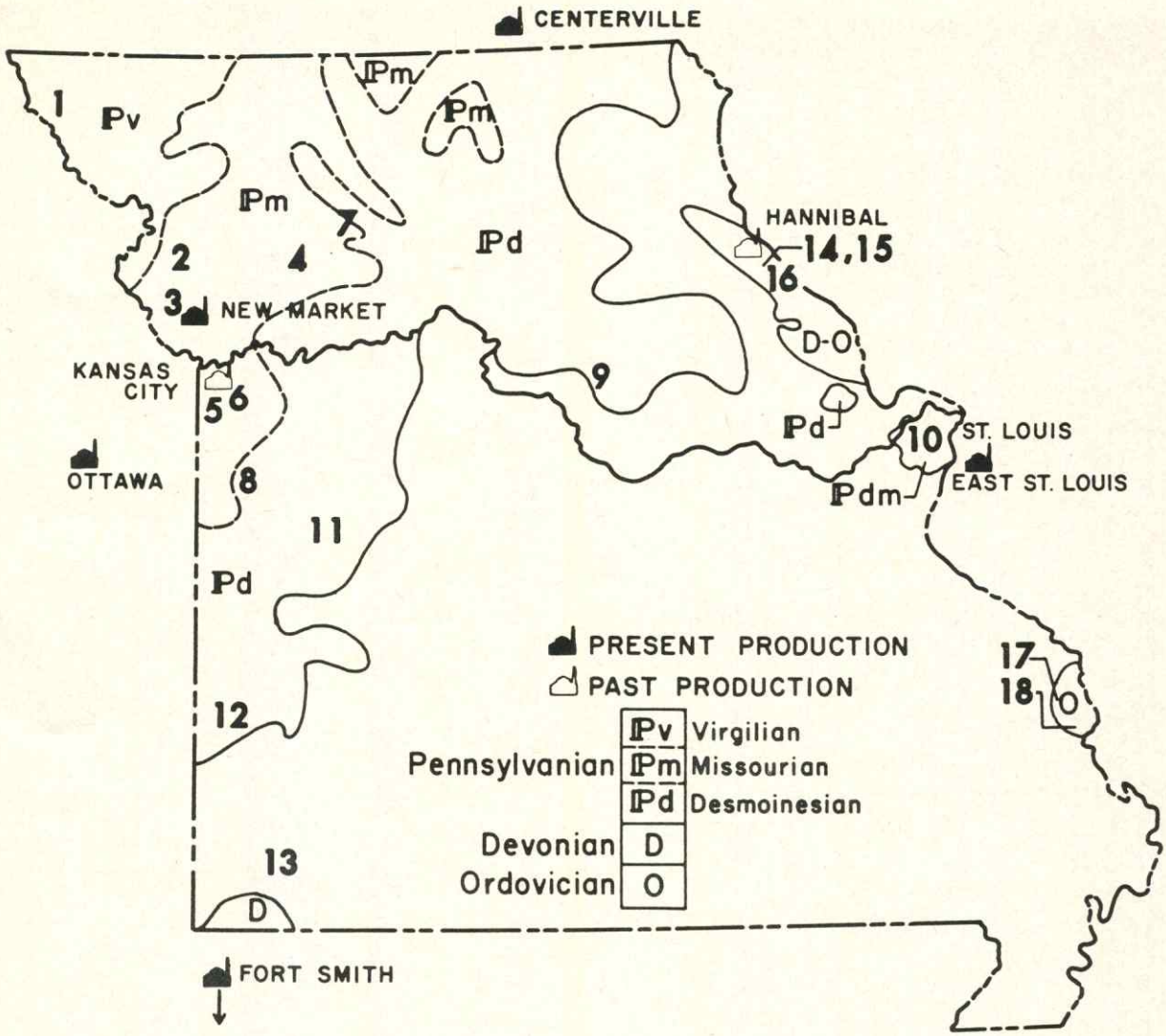


Figure 2. Expandable shale plants and sample locations.

shale, 20 to 25 feet thick in the Kansas City area, was used at a former Carter-Waters plant in that city. The Lagonda shale (9 & 10) has potential importance in eastern Missouri if an acceptable product can be produced economically with the use of additives. However, to date, only sample (12) among several industrial tests and five laboratory tests showed promise.

Devonian (Units 13 thru 16 - Figure 2, Table 2): Three Devonian formations, the Chattanooga, Saverton, and Grassy Creek, have shown excellent bloating quality and pore structure in both standard and quick firing tests. Outcrops of the Chattanooga Shale in the state are restricted to the southwest corner where the formation attains a maximum thickness of about 30 feet. The Grassy Creek-Saverton are present in Missouri only in the northeastern part. The two formations are essentially coextensive in their distribution. The combined maximum thickness of the two units is approximately 70 feet and is restricted to a limited area. Both units thin to a combined thickness of less than 10 feet in a south and southwestward direction. During World War I, lightweight aggregate was produced from the two formations at the Atlas Cement Company plant (now Universal Atlas Cement Division of U. S. Steel Corp.) south of Hannibal.

Table 2. Bloating quality of shale samples tested for expandable aggregate data from Larson (1948) and Herold & others (1958).

Map No.	Units	Thickness Sampled	Firing Tests Standard	Quick	Remarks
1.	Harveyville	13'	Poor	Good	
2.	Lawrence	52'	Good	Poor	Excellent with additive (Fe_2O_3)
3.	Weston	30'	Good	Excellent	Commercial Production
4.	Chanute	13'	Fair	Fair	Excellent with additive (Fe_2O_3)
5.	Wea		Good		Commercial Production
6.	Pleasanton	43'	Good		
7.	Pleasanton	60'	Poor	None	Excellent with additive (Fe_2O_3)
8.	Holdenville	35'	Poor	Excellent	
9.	Lagonda	39'	Poor	None	Excellent with additive (Fe_2O_3)
10.	Lagonda	30'	Fair	Good	Excellent with additive (Fe_2O_3)
11.	Tebo	22'	Poor	Good	
12.	Rowe	15'		Good	Excellent with additive (Fe_2O_3)
13.	Chattanooga	6'	Excellent	Excellent	
14.	Saverton	11'	Excellent	Excellent	Commercial Production
15.	Grassy Creek	9'	Excellent	Excellent	Commercial Production
16.	Grassy Creek-Maquoketa	39'	Good	Good	Good with additive (Fe_2O_3)
17.	Orchard Creek	18'	Poor	Fair	
18.	Maquoketa	12'	Excellent	Excellent	

Ordovician (Units 16 thru 18 - Figure 2, Table 2): The Orchard Creek Shale in Missouri is restricted to the southeast where it is separated from the underlying Maquoketa by from 5 to 25 feet of sandstone. Maximum thickness of the Orchard Creek is about 50 feet. Outcrops of the Maquoketa Shale in Missouri are present in much of the area bordering the Mississippi River. However, thick shale units are generally restricted to the northeast and southeast parts of the state where the formation thickness ranges upwards to 125 feet and 50 feet, respectively. In some areas, the shale is interbedded with thin limestones. Firing tests were made on samples collected from the upper part of the formation.

At present, the overall consumption of expanded lightweight aggregate in Missouri is not great except in the St. Louis and Kansas City areas. Raw materials are available for expansion of the industry, especially in western Missouri, when demands so dictate.

CLAYS

Widely distributed throughout the fire clay districts in east-central Missouri are impure high alumina clays that are suitable for cement manufacturing. Small deposits of impure kaolin in southeast Missouri may be worthy of future exploitation as the larger and purer deposits in other states are depleted. A non-swelling bentonitic clay in the Southeast Embayment area of the state is being produced for absorptive uses and is under investigation for use as a binder in iron ore pelletizing. The areas of fire clay, kaolinitic, and bentonitic clays in Missouri are outlined in Figure 3. The ranges of chemical composition of these clays are given in Tables 3, 4, and 5.

Fire Clay: Deposits of fire clay being exploited in the state are present in two main areas in east-central Missouri and have been designated the Northern and Southern Fire Clay districts by McQueen (1943). In the past, fire clay was also mined in the St. Louis area.

Throughout the Southern district and bordering the Northern district on the south and east are numerous pits containing large tonnages of clay unsuitable for refractory use and alum production, but which would provide a high alumina raw material for the cement industry. These clays could be a future source of alumina if and when the alkali or acid extraction processes become economical. However, a major drawback is the small size of individual deposits.

The fire clay classification used in Missouri, which is based on visual appearance, is shown in Table 3. In addition to those listed, there are intermediate types such as burley diaspore, burley flint, semi-flint, and semi-plastic. The discrepancy between the general range of alumina given for the clay type and the analyzed sample is the result of visual error.

The principal impurities in fire clay which make it unsuitable for refractory products and alum are silica, iron, the alkali and alkaline earth metals. The maxima shown in Table 3 are approximately the average highs for the impure clays.

In the Northern district, much of the area is underlain by bedded deposits of plastic and semi-plastic clay. Flint and semi-flint clays are present as fillings in sinkholes and depressions in the marginal areas along the southern and eastern part of this district. In the Southern district all of the clay is present as filled sink deposits. Clay types range from plastic to diaspore but flint and semi-flint are the principal types in the district. Essentially all of the known diaspore and most of the burley clay deposits have been mined and the bulk of current production from this district is flint and semi-flint clay.

The sinkhole deposits are quite variable in size and individual pits range from less than 100 feet to more than 500 feet in diameter, with depths of 25 to more than 100 feet. The majority are small and the average pit will contain from 5,000 to 15,000 tons. Overburden is thin, a few feet to upwards of 25 feet, and consists of soil, residium, and alluvial gravels.

Small tonnages of clay have been and are being shipped to cement plants

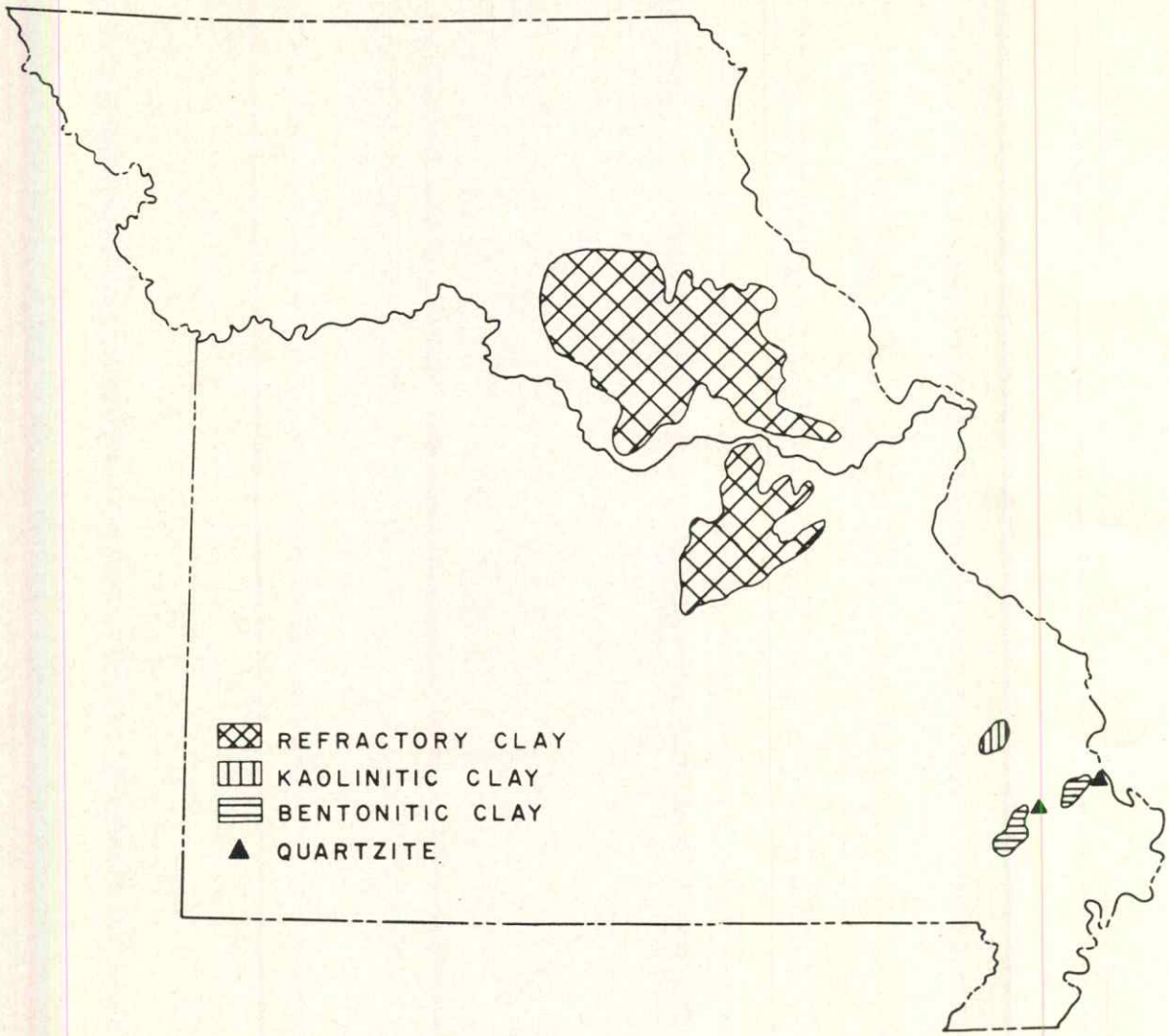


Figure 3. Distribution of clay types and "quartzite" locations.

both in Missouri and out-of-state. The bulk of this clay is presently obtained from waste-piles at mined pits. A number of small producers have been active in the clay districts for many years and could be depended upon as suppliers. It would not be economically feasible for the consumer to attempt mining or reclamation of individual pits. The main factor influencing the limited use of these clays at present is transportation costs.

Kaolin: Deposits of an impure atypical kaolin clay are present in shallow depressions and small sinkholes, ranging upwards to 100 feet in depth, over a wide area of the southeast Missouri Ozarks (Wheeler, 1896; Tennissen, 1960). The area of the larger deposits, outlined in Figure 3 and which were mined in the late 1800's is in Bollinger and Cape Girardeau Counties. The majority of samples analyzed, Table 4, have a low alumina content and contain a high percentage of quartz. Quartz sand grains, chert fragments and iron oxide staining are the major impurities. Staining, commonly red and yellow, appears to be present in most deposits; however in some, the maroon to red staining is apparently due to organic material and the clay burns white. Essentially all deposits would require washing and beneficiation to remove

Table 3. Classification of Missouri fire clays and range of chemical constituents.

DIASPORE	65+	PERCENT Al_2O_3
BURLEY	45 to 60	" "
FLINT	37 to 45	" "
PLASTIC	30 to 37	" "

	BURLEY (6)*		SEMI-FLINT & FLINT (35)		SEMI-PLASTIC & PLASTIC (14)	
Al_2O_3	41.0 to 59.0%		31.0 to 40.0%		25.0 to 38.0%	
SiO_2	22.0	41.0	37.0	48.0	40.0	55.0
Fe_2O_3	0.3	1.5	0.3	4.0	1.5	3.5
CaO	0.2	0.7	0.0	1.0	0.0	0.6
MgO	0.1	1.6	0.0	1.0	0.3	1.7
Na_2O	0.1	2.1	0.0	1.2	0.0	0.7
K_2O	0.4	1.6	0.1	1.3	0.2	3.0
TiO_2	1.5	3.0	0.1	2.9	1.4	2.5

*Number in parenthesis refers to the number of sample analyzed.

excessive amounts of quartz sand.

The clay is generally plastic, open-burning, and shows little shrinkage on firing or drying. Green and fired strengths are low.

Drawbacks to the development and exploitation of these deposits are the high percentage of contaminants, irregular shape, small size, and scattered distribution. Future use in ceramic ware, as extenders, additives, and fillers may be expected as the larger, better quality deposits in other areas are depleted.

Bentonitic Clay: Initial interest in the Tertiary Porters Creek Clay in the northern Mississippi Embayment area for use as a fuller's earth began in the early 1920's when Sinclair Oil and Standard Oil began production of the clay at Olmstead, Illinois. Reports on the clay during the period 1920 to 1935 were by Lamar (1928) and Grim (1933) on the Illinois deposits and by Farra, Grenfell and Allen (1935) on the Missouri clay. In recent years, interest has been rejuvenated because of the absorptive property and potential use of the clay as a binder in iron ore pelletizing. At present two plants, one at Olmstead, Illinois, and the other at Oran, Missouri, are mining and calcining the clay for "kitty litter", floor sweep, carriers, and filler material.

In 1961, about 4 years before the Pea Ridge iron mine went into production, the St. Joseph Lead Company began investigating the possibilities of using the Porters Creek clay as a pellet binder. In early 1967 St. Joe formed the Missouri Clay Products Company, Inc., a wholly owned subsid iary, to mine, process, and market the clay for pellet binding and other uses. Production will be from Stoddard County, Missouri. Publication of Illinois State Geological Survey Industrial Min-

Table 4. Chemical range of 13 samples of kaolin clay from Bollinger County, Missouri (Tennissen, 1960).

	RANGE	AVERAGE
KAOLIN	30 to 60%	45%
SILICA	40 to 70%	55%

SiO_2	39.0 to 88.0%		CaO	0.0 to 1.0%	
Al_2O_3	5.0	42.0	MgO	Tr	0.7
Fe_2O_3	0.0	2.0	Na_2O	0.0	0.6
TiO_2	Tr	1.5	K_2O	0.1	1.1
	Loss on Ignition	2.0 to 14.0%			

eral Notes No. 22 (Jackmann and others, 1965) brought the possibility of using the Porters Creek clay as an iron ore pellet binder to wider public attention.

The Porters Creek Clay is the uppermost Paleocene formation present in Missouri. Although the formation underlies much of the northern Mississippi Embayment area of southeastern Missouri, outcrops are restricted to a topographic high, known as Crowley's Ridge, in Scott and Stoddard Counties (Figure 3). In Scott County, the eastern area, the Porters Creek underlies 10 to 15 square miles and has a maximum thickness of about 50 feet. In the western outcrop area, Stoddard County, 30 to 40 square miles are underlain by outcrop and near surface deposits with a maximum thickness of 200 feet. Overburden consists of loess, gravels, sand, and sandy clay. In the subsurface to the south and southeast of the outcrop, thicknesses of over 400 feet have been recorded in wells. Although thick sections of Porters Creek Clay are within 40 to 60 feet of the surface in the floodplain area adjacent to the east side of Crowley's Ridge, the problem of water from the overlying alluvium would be most difficult if not impossible to overcome.

The Porters Creek is composed essentially of the clay mineral montmorillonite and is probably best classified as a non-swelling bentonite or bentonitic clay. Its origin has been referred to as altered volcanic ash (Allen, 1935) and more recently as selective deposition (Pryor and Glass, 1961). Freshly exposed clay is dark gray to black but after relatively short periods of exposure the clay will dry to a light gray or cream color. Frequently the upper few feet is bleached to a light gray color and is often higher in alumina and lower in silica than the dark gray to black clay. The clay is micaceous and contains a small percentage of glauconite, quartz sand, and amorphous silica. Small to large nodules of impure iron carbonate are locally abundant. Fresh samples of the clay contain from 20 to nearly 60 percent water and will average about 30 percent.

Rough measurements of the bulk density of loosely packed Porters Creek clay gave a range of from 39 to 52 pounds per cubic foot, air dried; and from 35 to 49 pounds per cubic foot, oven dried. Approximations of oil retention using commercial grade kerosene and granules in the -14+28 sieve range gave values from 20 to 40 percent. The range of chemical constituents in the clay is

shown in Table 5. Tests by Larson (1947) on Porters Creek samples from Stoddard County showed the clay to vitrify into a moderately strong, hard product with a specific gravity of from 1.27 to 1.41. The firing range was between 1450° and 1900° F. Porosity ranged between 40 and 47 percent for the fired product. Although a sample of Porters Creek clay tested by Herold and others (1958) showed no bloating quality, an earlier test on the clay produced an expanded product with a specific gravity of less than one (1.0). However the size and shapes of the pores were quite irregular.

Future exploitation of the Porters Creek clay in Missouri for absorbtive uses and pellet binder will probably depend on the percentage of the market that can be accomodated by the present operations at Olmstead, Illinois, Oran, Missouri, and the St. Joseph Lead Company operation near Aquilla, Missouri. The possibility of producing a lightweight aggregate product would depend on demand, transportation rates, and competition from expanded shale. The clay has been used at the Marquette Cement Company plant some 10 to 15 miles to the north of the outcrop belt but use as a cement raw material would be limited by haulage distance.

QUARTZITE

A Cretaceous quartzite, or more specifically an orthoquartzite, crops out along the eastern flank of Crowley's Ridge in Scott and Stoddard Counties, southeast Missouri (Figure 3). The quartzite is in the McNairy Formation and is informally termed the "Commerce quartzite". The degree of induration varies locally and the quartzite grades laterally into friable, micaceous, quartz sandstone.

In the northeastern outcrop area - Scott County - thickness of the quartzite is some 2 to 10 feet and extends along the Mississippi River bluff for about 2 miles north of the town of Commerce. In northern Stoddard County, the main outcrop extends along the east-facing bluff of Crowley's Ridge for a distance of nearly a mile in the vicinity of Bell City. The quartzite is in two beds having an aggregate thickness of 12 to 35 feet. The quartzite beds are separated by a soft sandstone. Boulders of quartzite are found in areas adjacent to the outcrops in both Scott and Stoddard Counties. The subsurface extent of the quartzite for areas adjacent to the outcrop is unknown.

Chemical analysis of the quartzite from the Scott County area gave

Table 5. Range of Chemical constituents in the Porters Creek clay.

	SCOTT COUNTY		STODDARD COUNTY	
SiO_2	63.0 to 69.0%		55.0 to 67.0%	
Al_2O_3	13.0	15.0	14.0	20.0
Fe_2O_3	4.0	5.5	3.5	7.0
TiO_2	0.5	0.6	0.5	1.1
CaO	0.7	1.1	0.7	1.5
MgO	1.7	1.1	0.7	3.0
Na_2O	0.1	0.5	0.0	1.2
K_2O	0.9	1.5	0.8	1.4
Loss on Ignition	8.0	13.5	6.0	8.5

the following: SiO_2 - 99.5%; Al_2O_3 - 0.24%; and Fe_2O_3 - 0.12%. The weathered surface generally shows ferruginous staining.

Should drilling show an appreciable reserve of high-purity quartzite in these areas, the "Commerce quartzite" could become an important resource of lump quartzite for such products as ferrosilicon and silicon carbide.

FLY ASH

With the increasing interest in the research and utilization of coal fired boiler wastes during the past 10 to 15 years, it has become evident that fly ash and bottom ash should be considered among the industrial mineral resources of the state. Two supporting examples of large tonnage uses in recent years are the utilization of fly ash in the raw mix at Missouri Portland Cement Company's Joppa, Illinois plant and by River Cement Company at Selma, Missouri. An estimated 120,000 tons of fly ash is used annually by these plants. Other uses of fly ash and bottom ash in Missouri include concrete admixture, asphalt filler, bituminous surfacing aggregate, base, fill, and ice control.

Figure 4 shows the location of major coal fired steam generating electric plants in Missouri and lists the approximate annual tonnages of fly ash and bottom ash being collected at each. Only two companies presently market fly ash - Union Electric from their Meramec plant in St. Louis County and Kansas City Power and Light from the Montrose plant. Marketing of the K.C.P. & L. ash is handled by the Walter N. Handy Company, Inc., Springfield, Missouri. Bottom ash is marketed in central Missouri by Central Electric Power Cooperative. Associated Electric Cooperative is not presently equipped to handle its ash commercially and the bulk is being wasted in ponds as a fly ash-bottom ash slurry. Only a small amount of ash is being stockpiled for potential future sales.

A recent report by Waters and Kenworthy (1967) describes a method of extracting germanium and gallium from fly ash. The Bevier and Herrin (No. 6) coal seams, used extensively by Missouri power plants, are reportedly rich in these metals. Sulphur recovery is also being investigated.

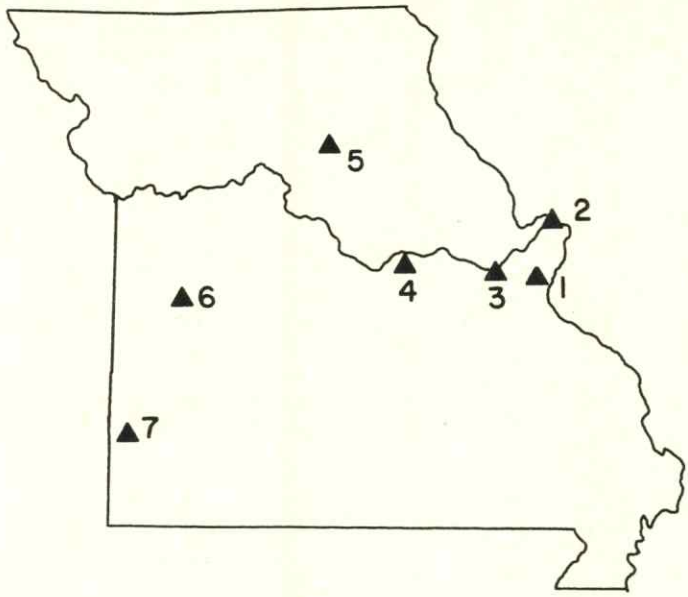
The geographic distribution of existing and proposed power plants in the state is such that fly ash and bottom ash is available to the major market areas in Missouri and adjoining states. Although the economic justification is not apparent at present, the future possibilities for the production of sintered lightweight aggregate and ash brick utilizing fly ash is especially promising in the metropolitan areas.

SUMMARY

Over 150 million tons of mine and mill tailings and several million tons of fly and bottom ash are now available in the state. An estimated 12 million tons of tailings and 1½ million tons of ash will be produced annually in the near future.

Apatite and monazite are recovered in beneficiating Precambrian iron ores at the Pea Ridge mine. Meramec Mining Company is conducting studies to determine if marketable byproducts can be produced from them. Phosphate fertilizer and the exotic metals cerium, thorium, and yttrium are the commodities in question. Beginning in 1968, up to 150,000 tons per year of byproduct sulfuric acid are expected to be produced at two of the state's three large lead smelters.

Expandable shales are present in areas adjacent to barge and rail transportation, and not far from the large metropolitan areas in the state. Other clays and shales are available for cement manufacturing, ceramics, and for absorptive, binder, and miscellaneous uses. Further investigation is required to determine if a Cretaceous quartzite in the southeast Embayment area has possibilities as a raw material for the manufacture of silicon carbide and ferrosilicon.



COMPANY	APPROXIMATE ANNUAL PRODUCTION OF ASH	
	FLY ASH	BOTTOM ASH
UNION ELECTRIC		
1. MERAMEC	180,000 T/Y	60,000 T/Y
*2. PORTAGE DES SIOUX	---	300,000 T/Y
*3. LABADIE	300,000 T/Y	---
CENTRAL ELECTRIC POWER COOP.		
4. CHAMOIS	5,000 T/Y	15,000 T/Y
ASSOCIATED ELECTRIC COOP.		
5. THOMAS HILL	1,000 T/Y	39,000 T/Y
KANSAS CITY POWER & LIGHT		
6. MONTROSE	800 T/D	200 T/D
EMPIRE DISTRICT ELECTRIC		
*7. ASBURY (OPOLIS)	45,000 T/Y	135,000 T/Y

*UNDER CONSTRUCTION

Figure 4. Major steam generating plants in Missouri.

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A FEASIBILITY STUDY FOR THE PRODUCTION OF FILTER AIDS FROM KANSAS VOLCANIC ASH

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ABSTRACT

Volcanic ash, although a little-used Kansas resource, is available in numerous locations with estimated reserves of more than 20 million tons. Total production to date is estimated at 2 million tons, the major use being as an abrasive in scouring compounds and soaps; additional uses include ceramic glazes, an additive in cement, and a filler and stabilizer in hot mix asphalt for paving. This report on volcanic ash as a filter aid is one of the results of a search for new or different uses and applications of Kansas mineral commodities.

When the small particles of Pearlette ash are rapidly heated to their softening temperature in a gas flame, occluded gases expand them into minute, thin-walled spheres which are solidified by sudden cooling. This expanded volcanic ash, after it has been crushed and classified, has desirable filter aid properties and is comparable to expanded perlite and diatomite.

This report encompasses basic product development, market evaluation, analysis of costs and price structure, and measures of profitability. This report is, therefore, a feasibility study of the use of processed Kansas volcanic ash as a filter aid, a summary of laboratory studies to determine product characteristics, a market analysis relating to demand and market penetration, cost estimates and capital investment for producing volcanic ash filter aids, and a profitability analysis.

INTRODUCTION

Volcanic ash is a little-used Kansas resource, but it is available in forty counties with estimated reserves of more than 20 million tons. It was first produced in Kansas in the early 1900's, but not until the early 1920's did it become important as an abrasive material. Total production to date is estimated at more than 2 million tons, the major use being as an abrasive in scouring compounds and soaps; additional uses include ceramic glazes, an additive in cement, and a filler and stabilizer in hot mix asphalt for paving. Unrecorded tonnages have also been used in construction of black-top (macadam) roads. From 1916 through 1944, Kansas ranked first among the states in volcanic ash production; peak production was about 52,000 tons in 1923. Since 1945, production has steadily declined, primarily because materials other than volcanic ash are now being used for abrasives. There were three producers of volcanic ash in Kansas in 1965. Two produced the ash for road construction and the other for use as a Chinchilla dusting powder.

Kansas volcanic ash is a white to light-pearly gray material, consisting predominantly of small particles or shards of volcanic rock glass. The ash presumably came from volcanoes located near the Rocky Mountains in the region west or southwest of Kansas. The ash was thrown into the air by explosive volcanic eruptions and was carried over Kansas by winds. The ash falls are of limited areal extent and range in thickness from a few inches to more than 30 feet. Western Kansas ash deposits of value for filter aid production are all of Pliocene or Pleistocene age.

This report on volcanic ash as a filter aid is one of the results of a search for new or different uses and applications of Kansas mineral commodities being carried on by the State Geological Survey of Kansas. This

search encompasses basic product development, market evaluation, analysis of costs and price structure, and measures of profitability. Our investigations show that processed Kansas volcanic ash possesses properties similar to those of a class of other industrial minerals currently used as filter aids. This is, therefore, a feasibility study of the use of processed Kansas volcanic ash as a filter aid, a summary of laboratory studies to determine product characteristics, a market analysis relating to demand and market penetration, cost estimates and capital investment for producing volcanic ash filter aids, and a profitability analysis.

TECHNICAL DATA ON BLOATED VOLCANIC ASH AS A FILTER AID

When small particles of Kansas Pearlette ash are rapidly heated to their softening temperature in a gas flame, occluded gases expand them into minute, thin-walled spheres which are solidified by sudden cooling. This expanded volcanic ash, after it has been crushed and classified, has desirable filter aid properties and is comparable to expanded perlite and diatomite.

A filter aid is a material used to clarify or remove finely divided substances from liquids. Ideally, a filter aid will form an extremely fine-filter surface which will retain all solids, prevent contact between the solids and the filter septum, and allow many filtering cycles. To perform these functions, filter aid materials should be: (1) inert and insoluble -- they must not react with the liquids or solids, (2) incompressible -- the filter aid cake must be able to maintain high permeability under the pressure differentials developed in the filter, (3) irregularly shaped, porous and small -- the cake must have many tiny flow channels that are small enough to provide optimum flow.

Filter aids are generally classified on the basis of their flow rate in a standardized test filtration using a raw sugar liquor. The filter aid is evaluated on the flow rate it permits and the degree of clarity achieved in the filtrate.

Flow of a liquid through a filter is a function of the viscosity of the liquid and obstruction to flow. Obstructions include the resistance of the filter cake, the filter medium, and piping and mechanical features of the filter. The resistance of the filter cake depends upon whether the cake is loose or compacted, coarse or fine, and granular or gelatinous.

Filter aids are used for clarification in processing sugars, syrups, beer, wine and distilled liquors, fruit juices, beverages of all types, mineral, vegetable and animal oils, fats and waxes, varnishes and lacquers, lubricating oils, dry-cleaning fluids, water sewage trade wastes and metallurgical slimes and solutions.

Test Procedures and Results

Pearlette volcanic ash was bloated, crushed by passing it between a solid plate and a wooden roller, classified using standard screens into +80-mesh, -80 to +100-mesh, -100+200-mesh, -200 to +235-mesh, and -325-mesh sizes. For testing purposes, uncrushed composite, crushed composite, and uncrushed-mixed with minus 100-mesh fractions were also prepared.

Pre-coating characteristics and resistivity values for prepared Kansas volcanic ash fractions, as well as for some commercial diatomite filter aids, were determined at the Sanitary Engineering Department, Iowa State University, Ames, under the direction of Dr. E. R. Bauman.

Filter aids with acceptable resistivity properties can be made from bloated, crushed volcanic ash which has been classified to the -100+325 mesh size. It was noted that prepared ash samples coarser than 200 mesh had a tendency to float in the liquor. Undoubtedly, the floating particles consisted of bloated ash bubbles that had not been broken in the crushing process.

Tests were conducted to measure liquid-flow rates and degree of filtrate clarity in actual filtering operations. Three water suspensions or solutions were used. A one percent suspension of Kentucky #4 ball clay in water, a one percent suspension of iron oxide (Fe_2O_3) in water, and a raw sugar solution with a specific

gravity of 1.25 were filtered utilizing prepared volcanic ash, diatomite, and perlite dispersed within the suspension or solutions as filter aids. Various concentrations were used, and for the -325 mesh bloated and crushed volcanic ash, maximum effectiveness for a clay suspension and a sugar solution was achieved using 0.75 percent of filter aid. Effectiveness increased with increasing filter aid for the iron oxide suspension.

An American Optical Colorimeter Model 10131 was used to provide a relative measure of clarity of all filtrate samples. Samples of the filtrates from the clay and iron suspensions were compared with distilled water. Relative clarity is based on the amount of light passed by filtrates as compared with distilled water; higher figures indicate greater clarity. The standard comparison in the raw sugar determination is the unfiltered raw sugar solution. The filtrate was compared with the standard, higher readings indicating a clearer filtrate.

Crushed expanded volcanic ash of proper size performs well as a filter aid. Its measured ability to regulate flow rates and clarify suspensions and solutions is comparable to commercial expanded perlite and diatomite. The size gradation and maximum size affect filtration characteristics. It is essential that small expanded ash bubbles be broken during crushing to prevent the filter aid from floating in the suspensions.

MARKETS AND MARKET TRENDS

A demand or market analysis seeks out and measures the forces that determine sales. There are at least two purposes of such an analysis: (1) forecasting sales, and (2) manipulating demand. In this study of filter aids both aspects are covered, but emphasis is on manipulating demand, for it is this information that can be used for formulating sales policy and sales strategy. Using demand studies in an active rather than a passing way, better equips a company to select the course of action which will maximize sales. Such studies can be particularly helpful in matching salesmen and sales effort with potential sales in various industries and territories as well as formulating price policy and evaluating packaging design, value of merchandising, technical assistance, etc.

The geographical area encompassed by this study of filter aid markets is generally the four-state area of Kansas, Nebraska, Missouri, and Iowa. Visits were made to the metropolitan areas of Wichita, Topeka, and Kansas City, Kansas, St. Louis, St. Joseph, and Kansas City, Missouri, Omaha, Nebraska and Des Moines, Iowa.

Survey Method and Scope

Because of the competitive nature of the filter aid business, and the type of information being requested, the survey was conducted primarily by personal contact with the suppliers and users.

The survey included comprehensive coverage of dry cleaning and swimming pool suppliers, with representative surveying of companies involved in:

Beer brewing
Corn processing
Soybean processing
Petroleum refining
Chemical processing
Oleomargarine manufacturing
Other food processing and industrial users

In all cases an attempt was made to obtain annual sales or usage in tons, freight cost, sales price, brand and grade of filter aid. Other information, such as customer satisfaction and brand allegiance, was volunteered without solicitation.

Filter Aid Use and Demand

The two major types of filter aids currently in use are produced from diatomite and perlite. The demand in 1961 for these two major types of filter aids in the United States was estimated at 365,000 tons ("In the Bag: Filter Aid Growth," Chemical Week: August 12, 1961). Of this, diatomite accounted for approximately 86 percent. Projected filter aid demands for 1970, based on a constant per capita use and on value added by manufacture ratios, are 457,

340 tons and 490,000 tons, respectively.

Discussion of Filter Sales by Industry

Dry Cleaning -- Sales are characterized by very strong brand allegiance and customer satisfaction with diatomite filter aids. Premature entry of the perlite processors into the filter aid field, forced by a major strike in the diatomite field in 1952, resulted in a distaste for perlite filter aids by the dry cleaning business. The nature of the dry cleaning business demands a high degree of clarity of the filtrate; flow rate is a secondary consideration. Assuming that volcanic ash filter aid characteristics are technically comparable with those of diatomite, a small part of the market could be captured.

Swimming Pool Industry

Swimming pool suppliers were contacted because of the rapid growth of the number of swimming pools and the increasing use of filter aids in filtration. Because of: (1) expanding market, (2) low brand allegiance, and (3) desired high-flow characteristics, a large percent of the swimming pool market should be capturable.

Beer Brewing Industry

Five breweries were contacted. Of these, all used diatomite filter aids. Three breweries had tried perlite, but only one found it satisfactory as a filter aid and this particular brewery still prefers to use diatomite. Filtration requirements in the beer brewing industry are such that if any new type of filter aid is to penetrate this market, it must maintain a high degree of clarity and either equal diatomite in flow rate while maintaining an appreciable price advantage or exceed diatomite in flow characteristics while equaling or possibly maintaining a price advantage.

Other Industrial and Food Processing Users

Sales penetration in this group will depend primarily upon the characteristics of the filtration requirements. Perlite filter aids have been able to penetrate approximately 30 percent of the market as surveyed in the four-state area of Kansas, Nebraska, Missouri, and Iowa.

F.O.B. Price and Freight Costs

F.O.B. price listing for filter aids vary with the grade and intended use. Examples are:

Dry Cleaning	$59.50
Beer Brewing	$65.00 - $70.00
Swimming Pools	$72.00
Other	$30.00 - $150.00

Freight costs in this area range from $20.00 to $26.00 per ton for diatomite and about half of this amount for perlite. Freight costs account for a sizeable portion of the cost to the user and can be attributed to their West Coast origin. If a filter aid were produced in Kansas, the producer would have an appreciable freight advantage in those areas east of the Rocky Mountains.

Summary

Predictions in this analysis of probable immediate market penetration by volcanic ash as a filter aid of 372 tons for Kansas and 1,395 for the four-state area, and estimates of probable market share in 1970 after five years of operation of 876 tons for Kansas and 3,107 tons for the four-state area of Iowa, Kansas, Missouri, and Nebraska may seem optimistic. It must be remembered, however, that these figures were based upon several important assumptions. Penetration into the swimming pool markets is considered the most probable followed in order by other industrial and food processing, beer brewing, and the dry cleaning market.

Whatever the market, an enterprise contemplating a business venture involved in the production and sale of a filter aid made from volcanic ash must package its product in 40, 50 or 100 pound bags, maintain good quality control and realize the value of merchandising. Advertising, tech-

nical assistance, and the accurate matching of salesmen and sales effort with potential sales will be of continuing prime importance.

ESTIMATED PLANT AND PRODUCT COSTS

The next logical consideration in deriving the over-all profitability of volcanic ash as a filter aid is the determination of estimated plant costs. Once plant costs have been determined, an estimate of product costs can be made.

Plant Costs

In the absence of basic small-scale, continuous-flow pilot plant experience in producing volcanic ash filter aids, plant size, choice of equipment and estimated costs of a commercial operation can be subject to considerable error. Recently a large plant to produce diatomite filter aids was built at a cost of about $70.00 per annual ton of product at capacity production. A plant designed to produce volcanic ash filter aids requires, for the most part, similar basic processing steps and equipment. Therefore, we assume that a volcanic ash filter aid plant could be built at a comparable cost.

Two plant cost estimates have been made, one based on a direct cost per annual ton (Aries and Newton, 1955) and the other using a 0.6 scaling factor (Chilton, 1960a). These estimates were then weighted by probabilities to give an expected value as a final estimate.

Final estimates of plant costs were found to be approximately $180,000 for a 1000-ton annual capacity plant and approximately $320,000 for a 2000-ton annual capacity plant.

Product Costs

The essential processing steps required to produce a filter aid from volcanic ash are: (1) extraction of the raw material, (2) transportation to and in-plant storage of this raw material, (3) screening, drying, and delivery to expanding furnace, (4) pyro-processing to expand the ash, (5) collection and crushing of the expanded ash, (6) classification of the expanded and crushed ash, (7) packaging, (8) storage of the packaged product, and (9) loading and shipping of the product.

For the purposes of this estimate, maximum plant capacity was assumed to be 2,000 tons of product annually on a one shift basis. Market estimation indicates that this tonnage should be entirely absorbed at some period during an estimated plant life of 15 years; additional capacity could be gained by a more than one shift operation.

General Data

Annual product output at capacity, tons	2,000
Estimated working days/year	250
Daily production, tons	8
Working day, hours	8
Unit weight of raw ash, lbs/ft^3	66
Unit weight of expanded ash, lbs/ft^3	5
Cubic feet of expanded ash	3,200
Unit weight of product, lbs/ft^3	10
Cubic feet of product per day	1,600
Estimated plant cost	$300,000

A PROFITABILITY MEASURE APPLIED TO THE VOLCANIC ASH FILTER AID PROJECT

The quantifiable measure used for economic evaluation of a manufacturing project is the expected profit. The ratio relating profit to investment in some manner is known as rate of return on investment. A number of such ratios are commonly used and the one selected for this analysis is known as the interest rate of return, profitability index, discounted cash flow, or internal rate of return. Briefly, it calculates the interest rate at which the company's outstanding investment is repaid by proceeds from a project. A company can value a project in terms of a project's life. Any money netted by the project in excess of this constant annual "interest rate of return" is credited against project investment. Interest rate of return is set so investment is reduced by zero at the end of the project's life. This interest rate on the unreturned balance is an excellent measure of net

effective project profitability.

CONCLUSIONS

Markets

The demand for filter aids in Kansas, Missouri, Nebraska, and Iowa correlates more accurately with the value added in manufacturing than with population. Thus demand for filter aids should increase gradually in proportion to the increase of value added in manufacturing.

Penetration into the market of a new filter aid made from volcanic ash will be slow and somewhat difficult initially. The quality of a volcanic ash filter aid must be equal to and preferably greater than present perlite types. Technical knowledge of the product and its application is absolutely necessary for this type of commodity to sell effectively.

Sales of Kansas volcanic ash filter aid should initially be 700 to 900 tons annually with growth to 3,000 tons over a 5-year period. This is based on a four-state market area of Kansas, Missouri, Nebraska, and Iowa.

Plant Costs

A facility to produce filter aids from volcanic ash will require specialized equipment, namely furnace and crusher. The classification and collection equipment for the product must be efficient and effective to insure proper quality control. These facts suggest that a filter aid plant for processing volcanic ash will require a sizeable investment, most likely in the range of 150 to 200 dollars per annual ton of product.

Product Costs

Product costs are based on a plant that would produce filter aids only. The final cost per ton for this product, based on present knowledge, will very likely be in the 40 to 50 dollar per ton bracket.

Profitability

Sixty dollars per ton f.o.b., place of manufacture, was arbitrarily selected for a selling price. This represents a fairly frequent quoted price in the trade; and, furthermore, suggests that user savings are possible through freight differentials.

At this stage of development, a project to produce volcanic ash filter aids would be a fair to high risk. On the other hand, the interest rate of return estimated from sales realization and necessary investment would be extremely low, namely 3 to 5 percent. Considering the risk involved it should be 16 to 25 percent.

An increase in sales realization, if this could be obtained by increasing tonnage produced and sold rather than increasing sales price, and a reduced capital investment, would shift the profitability to a more favorable range.

Generally speaking, penetration into the swimming pool market is considered favorable because of the expanding market and weak brand allegiance. In the dry cleaning and beer brewing industries, market penetration should prove to be more difficult as a result of the high clarity and rate of flow requirements, as well as strong customer satisfaction and strong brand allegiance. Market capture into other fields of food processing and industrial uses will depend upon the characteristics desired in the filter aid.

This particular analysis applies to the situation under which a small isolated industry might be established. Obviously, the analysis would not be applicable to a manufacturing facility which is part of a multi-production organization, the latter having laboratory facilities, sales and merchandising channels and some overlapping management.

As indicated previously, a market area consisting of the four states, i.e., Kansas, Missouri, Nebraska, and Iowa, was used to calculate a potential total market. It is entirely reasonable to contemplate a substantially larger market embracing states east of the Mississippi River. A filter aid manufactured in Kansas should have a shipping cost advantage to this area compared with products from Texas and the Mountain and Western states.

This analysis is based on the use of expanded ash solely for a fil-

ter aid. Some other market for this product, based on its lightness of weight, color, texture, and insulating properties should exist. If so, then a market could be expanded into these areas.

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