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Symposium held April 6-7, 1967.

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COLORADO SCHOOL OF MINES OIL SHALE SYMPOSIUM

JOHN A. LOVE

I welcome the opportunity to discuss with this distinguished group a subject which is of such paramount importance to our nation and to the State of Colorado.

At no time in the past has there been more unanimity among the private and public sectors of our economy that the oil shale of Colorado, Utah, and Wyoming will be needed to supplement our growing national energy requirements. The years of preparation and the millions of dollars which you and the organizations you represent have spent in research and other activities are about to bear fruit.

We in Colorado welcome you and are prepared to assist in every way possible in the development and growth of the oil shale, nahcolite, and dawsonite industries.

Substantial research efforts by both private industry and the federal government over the past 20 years have resulted in the development of a large body of technology in mining, retorting, and refining of oil shale and its products. Whatever the problem, you have been resourceful in finding the solution. Today, we have a proven mining system available, with others under consideration and study. Today, we have not one, but at least four above-ground retorting processes at various stages of development. Today, we have improving technology for converting shale oil to useful end-products. In summary, today we have a body of experience available to produce shale oil as a supplement to other existing sources of domestic liquid fuels.

It may be well to point out here that what we have been calling the "Oil Shale Industry" may turn out to be a very different one—a multiple-minerals industry. The United States is the world's largest consumer of aluminum and an importer of 90 percent of its requirements. Needless to say, the occurrence in Colorado of substantial deposits which can be developed as a source of aluminum would be of great significance to our nation's economy as well as to the oil shale industry.

The answer to those who ask, "Is there a need for shale oil?", is *Yes!*—unless we are prepared to accept, within the next decade, the alternatives of (1) reliance on external sources of energy vulnerable to the changes and pressures of international political and military developments; (2) alteration

Governor, State of Colorado

of our industrial and transportation base to accommodate less convenient fuel sources; or (3) the uncertainties of substitute energy sources.

In 1966, the United States imported approximately two and one-half million barrels of oil, the bulk of which came from Venezuela and the Middle Eastern countries. While it is important that we continue our friendly relationships with these countries, both economic and strategic considerations require that we not rely entirely on these sources.

In September 1963, President Kennedy requested the heads of nine federal departments to undertake a comprehensive study of "the development and utilization of our total energy resources to aid in determining the most effective allocation of our research and development resources." This interdepartmental study resulted in a report entitled, *Energy R & D and National Progress*, known as the Cambel Report. In a summary memorandum of this report produced by the interdepartmental Steering Committee in 1966, we note that the cumulative projection of energy requirements for the period 1960 to 2000 is estimated at 3.2 quintillion BTU's. The requirement for liquid hydrocarbons (petroleum products) is 1.4 quintillion BTU's, or 46 percent of the total. Yet, for the same report, known reserves of crude oil and natural gas liquids recoverable by primary and secondary recovery methods under present economic and technological conditions are equal to only .3 quintillion BTU's, or 2 percent of the requirement for this forty-year period.

Of course, no one questions that we will continue to add to our petroleum stocks by continued exploration for and development of conventional resources. The only questions are, at what cost and at what rate?

Oil shale, as a source of these liquid hydrocarbons, must compete with new discoveries of petroleum, tar sands, and coal to meet these increased demands. Liquid fuels, in spite of their convenience and acceptance in our present society, must compete with other energy sources—coal, gas, hydroelectric, nuclear and solar. We are fortunate to have so many alternatives. In my opinion, all will be needed, all will be developed—and this will be done without dislocation of our economy, unless we delay too long; and in this connection, I would urge that the Department of Interior note with care the measures adopted by the Canadian government to encourage the development of the tar sands industries.

It is a paradox that our government has spent billions of dollars in the development of other energy resources, while at the same time pursuing a policy of frustration and delay in dealing with the oil shale industry.

One of the most encouraging developments of the last year has been Secretary Udall's recently announced Five-Point Program because it reflects an increased awareness on the part of the present administration of the im-

portance of oil shale and associated minerals to the nation's economy and the need for action in encouraging rather than discouraging their development.

We are not only pleased by the various elements of the program itself, but are gratified by the stated objectives of the program which the Secretary enumerated in his testimony before the Senate Committee on Interior and Insular Affairs on February 21 of this year. In emphasizing certain goals, Mr. Udall made several significant statements of policy which evidence a sound, overall philosophy. I quote as follows.

1. "The central core of this effort to get oil shale into the mainstream of the American economy is aimed directly at development of the resource itself. . . ."

2. "Our objective is to get the broadest kind of industrial participation, either through a number of individual companies or through joint venturers. . . ."

3. "Heavy emphasis will also be placed on maximum recovery and development of all the minerals present—sodium and aluminum as well as oil shale. . . ."

4. "We will take particular care to secure and evaluate the voices of the three states involved, since we are acutely aware that they have a deep interest in the subject and that their cooperation is essential to the adoption of total conservation measures.' "

In connection with the last stated objective, you will be interested to know that on May 4, 1967, I, together with the Governors of our sister states Wyoming and Utah, plan to meet with Secretary Udall to discuss other measures in addition to his Five-Point Program which will aid in forwarding oil shale, nahcolite, and dawsonite development.

Before turning to these additional measures, I would like to comment in passing on one phase of the Secretary's research program and two aspects of Interior's recent handling of these resources.

While we are always interested in scientific research in areas calculated to stimulate the economy of Colorado and to preserve its natural beauties, we would caution against too much reliance on the successful outcome of experiments in in situ production through atomic explosions. It is never sound to rely solely or primarily on one line of attack, particularly an experimental one, to the detriment of established techniques. We do not believe that attention to this in situ effort should be permitted to divert energies from large-scale development by underground or other mining techniques already known to be feasible. The effect of such an explosion upon nahcolite and the aluminum compounds creates additional complexities to the problem of sustaining combustion of underground solids. In this con-

nection. I can think of no more suitable project for the Colorado School of Mines Research Foundation facilities at Anvil Points than an interim, scaled-up experiment in in situ production to bridge the gap between the bench experiments of the Bureau of Mines at Laramie and the proposed Bronco experiment.

There is another subject to which I, as a lawyer as well as the Governor of one of the nation's great mining states, must direct your attention. During the past several months Department of Interior officials have devoted considerable time and space to their views of the responsibilities of the Department in the administration of mining laws. There is no question of the role of department officials as trustees of the nation's resources, but I would add that these fiduciary obligations also extend to that portion of the public which is entitled to rely upon the assumption that proper administration of the mining laws must have as its objective the carrying out of Congressional intent.

The rights and obligations of the Government and mining claimants have long been defined by statute and court interpretation. The policies behind the mining laws have stood for more than 95 years. The intent of Congress to vest in the prospector who made a valuable discovery and perfected his claim through appropriate location procedures an interest in real estate which is taxable and inheritable and as fully transferrable as any other interest in real estate, is beyond question. It is apparently the view of some individuals in the Department that these laws and the policies behind them are now anachronisms: and that an executive agency has the right, without the sanction of Congress, to place upon these laws which have been well understood by the industry and by the public, new interpretations tending to vest in the Federal Government the role of prosecutor rather than administrator. Such a view, I submit, is inimical to the development of our country and inconsistent with our basic concepts of government.

While I recognize that changes in the mining laws are inevitable, and even desirable, and look forward to the recommendations of the Public Land Law Review Commission for future action in this area, I cannot agree that it is the function of the Department of Interior to legislate. If there is dissatisfaction with the laws under which the Department is charged, then the forum is Congress and there should be presented to that body reasons for and suggested changes in the laws now governing these matters. It is only when we recognize and respect the separate prerogatives of the Legislative, the Judicial, and the Administrative branches of Government that we can go forward to meaningful and constructive solutions of the complex problems which confront us.

The Department complains that a vast area of land which should be available for leasing under the Leasing Act of 1920 has now been cluttered with unpatented dawsonite mining claims. These claims now confront the Government with gigantic expenditures of time and effort to test their validity. While I recognize the magnitude of the problem and sympathize with the Department of Interior, let us place the responsibility where it belongs. It was the Department of Interior which first learned of the existence of dawsonite and which first released to the public information which led to the staking of the claims in question—a result highly predictable in view of the conduct of the American public in past similar situations. Had the Department acted promptly in anticipation of what was likely to result from its own disclosures, it could have, by a timely withdrawal of these lands and a prompt classification of the minerals discovered, prevented a tremendous expenditure of effort and avoided the confusion now confronting both government and industry.

It is not my intent here to engage in destructive criticism by these comments, but rather to point out that the public is entitled to prompt and responsive administrative action and that undue delay tends to increase rather than diminish the complexities of the Department's problems.

There are at least four steps, in addition to those proposed by Secretary Udall, which could and should be taken to get oil shale into the mainstream of our economy. Two require action by the Federal Government.

1. *Depletion Allowance.*

The Treasury Department should eliminate the discriminatory tax treatment against oil shale which now exists because of administrative interpretations of those portions of the Internal Revenue Code dealing with the depletion allowance.

The Internal Revenue Service has taken the position that under the Federal Tax Law the depletion rate applicable to oil shale is limited to 15 percent. The Treasury Department has indicated it will apply the rate to the value of mined and crushed shale rock rather than to the value of the first oil produced at the retort. Approximately one-half the costs of production of the initial oil product are those costs related to mining and crushing. Thus, the value of the mined and crushed rock would be approximately half the value of the oil. Applying the 15 percent rate to the crushed material, therefore has the anomalous result of reducing the depletion allowance for oil shale to 15 percent of one-half the value of the extracted crude oil. If the proposed depletion treatment of oil shale as a petroleum source is compared to the treatment of conventional petroleum, or if shale oil that is mined and retorted

is compared to shale oil produced by in situ retorting techniques, the inequity of such a program becomes apparent.

The questionable, if not unreasonable, situation, which I have pointed out, is clear to the executive departments concerned. Corrective measures can and should be undertaken now by the proper policy revisions. The time for a reformed and progressive policy has arrived. Shale oil should be given an opportunity to compete in the marketplace. Competitive discrimination in the tax laws against one type of petroleum production ought to be promptly eliminated.

2. *Oil Import Regulations.*

As a second and very important step, the Federal Government should clarify its policy dealing with the qualification of shale crude oil as a refinery input for purposes of import quota allocation. The present import regulations are unclear as to whether domestic shale crude oil will be treated as a qualified refinery input like all other domestic crude production. The uncertainties created by such hazy regulatory language should be removed. The primary objective of the import quota system to maintain a vigorous domestic petroleum industry would be seriously jeopardized without the necessary corrective action.

There are two other areas which can and should be appropriately dealt with primarily at the state level. Your state government is not only aware of these important problem areas but is prepared to move ahead with constructive programs in each one.

1. *Water Resources.*

First, the State of Colorado, in cooperation with the Federal Government, can contribute meaningfully to the development of oil shale in water resource planning and development. I have noted with dismay the Secretary's latest plan for the Colorado River Basin, which defers the West Divide Project and others important to Colorado. We intend to press for an immediate authorization of the West Divide Project. In the White River Basin the feasibility report on the Yellow Jacket Project is now almost completed. This would be a major project to provide industrial water supplies in that area. Under a cooperative venture with the United States Geological Survey, we are now bringing to completion a survey of the ground water resources of the Piceance Basin.

I have asked the legislature for an appropriation, part of which will be used to fund a study of water resource development specifically designed to meet the needs of the oil shale, nahcolite, and dawsonite industries and to devise a plan for the supply of water for the development of these resources through the Colorado River Water Conservation District, or such other local

quasi-municipal authority as may be appropriate, in cooperation with the Bureau of Reclamation and private industries.

2. *Conservation.*

Second, the imminent development of an industry on privately owned and federally held lands in Colorado requires immediate attention to and planning for resource conservation and the abatement and prevention of air and water pollution. Colorado has taken a position of strong leadership in these fields and we will continue to discharge our responsibilities at the local level where the problems are and where the people affected reside.

Sound conservation practices require that maximum economic value be recovered from the shale and that the residue be left in such condition that it will not be a nuisance to those who reside in the area or who depend on the water from the streams that flow through the area for life and livelihood. This applies whether the shale is processed in a surface plant or by in situ operations and whether underground or strip mining is involved.

There is a community of interest in the problem of spent shale disposal between the land holders, both private and federal, and the citizens of the State. If we work together in solving these problems, I am confident that criteria and methods acceptable to all concerned will be quickly found.

In this connection, I am prepared to request a substantial appropriation from the State Legislature to be used for studying the problems and for developing proposals for research projects in the field of spent shale disposal. With this seed money available, we will be able to identify the problem areas; to determine what research programs are necessary; and to prepare detailed proposals for such programs.

In conducting the research and development programs which will stem from these proposals, we would expect and will seek the support of both industry and the Federal Government. I note with interest that the Department of Interior, in the proposed oil shale resource development program announced in February of this year, estimates that 3.5 million will have to be expended over a 10-year period in research on the "Impact of an Oil Shale Industry on the Environment." Our great private and state universities, with their affiliated institutions for the conduct of research and development, are eminently qualified for conducting research relating to spent shale disposal, prevention of stream and air pollution from this source, and other attendant problems.

In closing, I will summarize by saying that if we at state and federal administrative levels will address ourselves promptly to eliminating the iniquities of federal depletion policy and the uncertainties of import regulations, to assuring ourselves of an adequate and orderly water supply and

to the conserving of our resources, I am confident that industry is prepared to furnish the technology and capital necessary to press to fruition the promise of oil shale and its associated minerals.

THE OIL SHALE INDUSTRY'S WATER PROBLEMS

NORTHCUTT ELY

I have been invited to talk to you today about the water supply problems which will confront the oil shale industry as it develops in the states of Colorado, Utah, and Wyoming. The invitation came to me because these three states are in the Colorado River Basin, and the problem of finding a water supply will bring this new industry into contact with the mysteries of several compacts, statutes, and treaties. These have the effect of restricting the quantity of water available for consumptive use in those states to a substantially smaller quantity than that physically available. This interstate problem is the one to which I shall give primary attention today. But first let us put the problem in perspective against its background.

Many of us, myself included, had not realized the magnitude of the future water demands of the oil shale industry until Raymond D. Sloan of Humble Oil and Refining Company made a speech on this subject at a meeting of the Colorado River Water Users Association in Las Vegas in December 1965. A little later, C. E. Reistle, Jr., Chairman of the Board of Humble, in a speech to the American Institute of Mining, Metallurgical and Petroleum Engineers,¹ and Mr. Sloan, in another paper,² stated the supply and demand equation for shale oil quite graphically. As this equation really controls the potential demand for water for this new industry, let me take just a moment to review this forecast.

On the demand side, the energy requirements of the United States are increasing at a rate which doubles them every 20 to 25 years. On the supply side, natural gas and petroleum are currently supplying 70 percent of our energy, compared with 55 percent in 1950. The United States is consuming 11 million barrels of petroleum products per day, and this is expected to increase to 18 million barrels daily by 1980. To meet this demand, the oil industry must develop reserves on the order of 89 billion barrels by 1985. This is almost three times the existing known domestic reserve of 31 billion barrels. If we do not succeed in this, we will become primarily dependent on importations. This total of required reserves, to be achieved in less than 20 years, represents more liquid energy than the United States has consumed in the past 100 years. Even after taking into account various offsetting factors, such as the likelihood of increases in drilling costs and

Ely and Duncan, Washington, D.C.

the law of diminishing returns on discovering significant new oil and gas fields, and, on the other hand, the probability that nuclear energy and other new sources will supply an increasing share of the total demand, the conclusion nevertheless appears inescapable: Synthetic liquid fuels will become a major domestic source of energy well within two decades.

In this frame of reference, the statistics of the domestic oil shale reserves are impressive indeed. The Nation's oil shale covers about 16,500 square miles in northwestern Colorado, the Uinta Basin in northeastern Utah, and the Green River Basin of southwestern Wyoming. Let us put to one side the estimates of total oil content in place, which are astronomical. Let us restrict the estimate to the richer portion of the shales in Colorado, which average 25 gallons of oil per ton. Let us further restrict the estimates to take into account only the presently known technology of mining, retorting, and upgrading. The estimate of the recoverable reserve in Colorado, restricted in this fashion, is 280 billion barrels of oil. This is nearly 10 times our presently known domestic reserve of liquid petroleum.

Getting the oil out of the shale at prices competitive with other sources of energy is another matter. I can contribute nothing on that subject to this audience, compared with what I shall learn from you. But I accept as a premise the forecast of the experts that we can expect production of oil from shale at competitive costs on a large scale in the early 1970's, and that this will amount to at least 2 million barrels daily in the 1980's. This will be about 10 percent of the total domestic oil production projected for that time.

The resulting water problems, as is generally the case, fall into two categories, quantity and quality.

As to quantity, Mr. Sloan has estimated that the production of two million barrels of oil a day from oil shale will require the consumption of about 1.2 times that amount of water in processing, retorting, and upgrading. This works out to about 112,000 acre-feet per year. If the oil is refined locally, this requirement will increase to 200,000 acre-feet annually. If in situ methods of retorting were used, this total quantity might be more than doubled. And these are only the direct uses of the industry. In addition, the population and related activities which will grow up around the new industry will consume large quantities of water. Assuming an associated population of 500,000 to 1 million, as much as 200,000 acre-feet annually of indirect uses must be added. We are thus dealing with a total water requirement of the general order of 500,000 acre-feet, stated in terms of consumptive use. Considerably more water than this must be diverted, since consumptive use, by definition, is the difference between the quantity diverted and the quantity returned to the stream. This demand will mature well before the turn of the century. It will, therefore, coincide with the predicted onset of

basin-wide water shortages, to which I will refer in a moment. This time of troubles is forecast for about the last decade of the present century.

Moreover, the question of quality is involved. The return flow of effluent from oil shale operations must necessarily be of much lower quality than the water diverted. This pollution can reach serious proportions if atomic blasting is used in preparation for in situ retorting. Many of the aquifers in this area carry a high sodium content, I am told, and this might be rendered radioactive. It is being suggested that the alumina content of the oil shale rocks, carried as dawsonite, and the sodium content, found as nahcolite, be mined and processed in some sort of combination with the recovery of the oil from the shale. Some of the proposed processes for the recovery of associated minerals involve leaching, thus adding to the water contamination problem. The states of the Colorado River Basin have agreed on an apportionment of the water among them in terms of quantity, as I will explain in a moment, but they are still struggling to arrive at an agreement on the allocation of the pollution absorption capability of the Colorado River system. The Secretary of the Interior has final authority to prescribe water quality standards, under recent legislation.

The quality of the water which is now being diverted from the Colorado River for use in Los Angeles, San Diego, and other Lower Basin cities carries more than 700 parts per million of salts, which is 200 parts worse than the Public Health Service standards for drinking water. This is destined to grow to 1,000 parts per million, we are told, quite aside from any consideration of the adverse impact of the oil shale industry on water quality. In addition, we have been having quality problems with Mexico. That nation is increasingly restless about the quality of water reaching it for irrigation in the delta. This has reached a salt concentration approaching 2,000 parts per million, has leveled off now at about 1,400, but is destined to become worse as more water is consumed upstream without reduction in the total weight of the solid content returned to the stream.

I now turn to the problem of quantity and the limitations on supply imposed by the various interstate and international agreements. I have said that the oil shale industry, with its dependent population and associated new industries, can be expected to consume roughly a half million acre-feet of water a year, on a conservative forecast. This will require a diversion of a greater quantity, perhaps a total of 750,000, assuming that a third of the quantity diverted returns to the stream. The finding of water for a new demand of this magnitude in this particular area presents some fascinating, although by no means insuperable, problems.

It is quite probable that most companies seeking a water supply for oil shale development regard this as simply a problem of either appropriating

water under the laws of Colorado, Utah, or Wyoming, or of buying existing water rights. This, of course, is the first and essential step, to acquire water rights which are recognized by the laws of the state in which the water is to be used, but the problem is not quite that simple.

The great hazard to the availability of an adequate supply of water for oil shale development rests in the mortgages which the states of origin of this water have assumed in their various interstate compacts and which the United States has assumed in its treaty with Mexico. These have the effect of drastically limiting the quantity of water ultimately available for use in Colorado, New Mexico, Utah, and Wyoming.

The most extreme example of this interstate problem is Colorado. This deserves particular examination in view of the fact that the richest of the oil shale reserves appear to be in the Piceance Basin, which is within the watershed of the White River in that state. This is one of the five streams originating in the State of Colorado which flow into the river of that name and on down to the Lower Basin and Mexico.

Colorado's over-all situation is this: Over 11,000,000 acre-feet annually of the water supply of the Colorado River System originates in the state of Colorado. But about 8 million acre-feet of this apparently abundant supply must ultimately flow out of the state in discharge of compact and treaty commitments to downstream users. Some of these obligations are stated in fixed quantities of acre-feet, some in percentages. The effect, when these percentage commitments are reckoned against the total water supply predicted by most experts, is that less than 3,000,000 acre-feet, less than 25 percent of the 11 million which the state produces, can be permanently used in Colorado. More than 75 percent must ultimately flow out of the state. This burden is expected to fully mature well before the end of this century, at about the time when the new oil shale industry's demand for water is itself maturing on a large scale. Let us see how this has come about.

Three commitments limit the use of water in the four Upper Basin States. In chronological order these are the Colorado River Compact, to which these States and the Lower Basin States of Arizona, California, and Nevada are parties, the Mexican Water Treaty, and the Upper Colorado River Basin Compact. Collectively, they are referred to as the "law of the River," along with several Supreme Court opinions.

The Colorado River Compact was signed in 1922. It is an agreement allocating rights and obligations between the Upper Basin and Lower Basin as blocks. The division point between the two basins is Lee's Ferry, in northeastern Arizona. The Compact does not allocate water to individual states. It purports—I use that word for reasons which will appear—to apportion to the Upper Basin and to the Lower Basin, each, the consumptive

use of 7.5 million acre-feet annually. It permits the Lower Basin to increase its use by an additional one million. The uses so apportioned or allocated include, by definition, the uses of the waters of the tributaries. Mexico was to be supplied first out of the water surplus to those required to satisfy these quantities of consumptive use. If that surplus was insufficient, each basin was to contribute one-half of the deficiency. The four Upper States promised not to deplete the flow at Lee's Ferry below an aggregate of 75 million acre-feet in each ten year period and agreed to add to this their half of the Mexican deficiency, if any. It is thus apparent that the negotiators thought that the resource, after supplying the Mexican obligation (which at that time was not yet fixed), could support 16 million acre-feet of consumptive use in the United States. Just how much of this was expected to be satisfied from Lower Basin tributaries was never very clear, and the subject has been greatly clouded by later Supreme Court opinions.

In 1922 the Compact negotiators assumed that the flow at Lee's Ferry would average in a state of nature at least 18 million acre-feet. But we now know that the average of the so-called virgin flow at Lee's Ferry, the supply which would be available in the absence of all Upper Basin depletions, has averaged not over 15 million for the 60-year period for which records or estimates are now available. For the 45-year period since the Compact was signed, it is about 14 million. For the most recent 30 years, it is not much over 13 million.

Compare these statistics with the Compact's arithmetic. Subtract the Upper Basin's Lee's Ferry mortgage of 75 million acre-feet per decade, equated to 7.5 million per year, from any one of the three supply figures that I have just given. If the whole supply is only 13 million, the Upper Basin residue is 5.5: if 14 million, it is 6.5; if 15 million, it is 7.5. The Upper Basin States have recently agreed among themselves, based on a joint hydrologic investigation, that the residue that they can depend on is an intermediate figure of about 6.2 million acre-feet,³ available for the four Upper States, exclusive of Arizona's small share. This includes reservoir evaporation of about 700,000 acre-feet, leaving a net supply available for consumptive use of about 5.5 million acre-feet, measured at site of use.

However, this assumes that the Upper Basin will not have to deliver additional water to help satisfy Mexico. The Mexican Water Treaty, ratified in 1945, obligates the United States to deliver 1.5 million acre-feet annually at the border. Evaporation losses between Lee's Ferry and the border, and unavoidable over-deliveries to Mexico, raise the Mexican burden to the equivalent at Lee's Ferry of about 1.8 million acre-feet annually. The Upper States claim, and the Lower States deny, that under the terms of the Colorado River Compact the Lower Basin tributaries can and should con-

tribute to this burden to an extent which relieves the Upper Basin of any obligation to deliver additional water at Lee's Ferry for Mexico. If the Lower Basin position were sustained, the 6.2 million acre-foot residue on which the Upper States are counting would shrink to about 5.5 million, but as 700,000 acre-feet of this must be lost in reservoir evaporation, the residue available for consumptive use would be about 4.8 million at site of use.

To digress a moment, the situation in the Lower Basin is just as bleak. If the Upper Basin contention about the Treaty burden prevails, and the whole inflow to be counted on at Lee's Ferry is only 75 million acre-feet per decade or 7.5 million per year, then only about 5 million of that can be used from the mainstream in Arizona, California, and Nevada. This is because 1.5 million must flow on to Mexico, and another million is lost in transit by evaporation over and above all contributions by Lower Basin tributaries.

Now to the last of these interstate agreements, the Upper Colorado River Basin Compact. This agreement, made in 1948, gives Arizona 50,000 acre-feet, and divides the residue, whatever it may be, on a percentage basis: Colorado 51.75 percent, New Mexico 11.25 percent, Utah 23 percent, Wyoming 14 percent.

To take Colorado as the major example, the application of its ratio of 51.75 percent to the residue available for consumption at site of use would produce a figure in the range between about 2.5 and 2.9 million acre-feet, the differences in these quantities being due entirely to the difference in legal assumptions as to the Upper Basin's Mexican Treaty obligation.

Substantially all of Colorado's dependable supply is, or soon will be, committed. The State's Water Conservation Board has tabulated Colorado's "present, authorized, and committed" projects as capable of consuming about 2.4 million acre-feet. Projects now pending in Congress would bring this up to about 2.7 million, measured at site of use. Of this, about 150,000 acre-feet can be identified with oil shale development. If no other projects were authorized, a demand of 2.7 million could be satisfied with a margin to spare of about 200,000 acre-feet, if the favorable assumption is made about the Treaty burden, but would create a deficit of about 200,000, if the Treaty question were answered adversely. Other projects not yet authorized or committed, but in various stages of planning, would add about 500,000 acre-feet to the demand, but there is no long-term supply now available for them. These include about 100,000 acre-feet earmarked for oil shale development.

Let us transpose these factors to the White River Basin, which encompasses the richest of the known oil shale reserves in the Piceance Basin.

Five major streams flow out of Colorado into other Colorado River Basin States, en route to Lee's Ferry. These, from north to south, are the Green, which receives the Yampa just before leaving Colorado; the White, which joins the Green in Utah; the Colorado; the Dolores; and the San Juan (a river which, during its passage through New Mexico, receives a half-dozen streams which originate in Colorado, then itself enters Colorado and flows a very short distance across the State's southwest corner before entering Utah).

The two Compacts, Colorado River and Upper Basin, are both silent as to which streams must bear the burden of curtailment of use in Colorado to supply Colorado's neighbors. As to the White River, figures furnished by the State show a "virgin production" of 610,000 acre-feet annually, a present consumptive use of 35,000 and "remaining State Line flow" of 575,000 acre-feet. But if the White is to bear the same proportionate burden of supplying the guaranteed flow at Lee's Ferry as Colorado's streams as a whole must bear (77 percent), then, of the White's total "virgin production" of 610,000 acre-feet, only 23 percent, or about 140,000, is permanently available for use in Colorado. Existing appropriations add up to more than that. This is aside from any local interstate contests between water users in Utah, particularly the Ute Indians, and the oil shale industry using White River water in Colorado.

The problem of how to allocate the State of Colorado's Compact burdens among that State's streams has not been thought through by anyone as yet, so far as I know. The Upper Basin Compact authorizes an interstate commission to make findings of supply and projected depletions, but this has not been done.

It will be many years before the Compact "ceiling" becomes critical. One respectable estimate by the State is the year 2000. Others say later, some say earlier. But collision is inevitable between the total demand, amplified by the oil shale industry, and the compact-restricted supply. The question is simply one of time.

This prospect has prompted Colorado to join California and Arizona in seeking importations into the Colorado from other watersheds. Legislation proposed by Chairman Aspinall of the House Interior and Insular Affairs Committee provides that whenever 2.5 million acre-feet annually is imported, this will relieve both basins of the Treaty burden. In such event, even though this importation would come into the river below Lee's Ferry, the Upper Basin supply would be relieved of about 900,000 acre-feet of the potential Treaty obligation, and Colorado's by 51.75 percent of this, or about 460,000 acre-feet. Hopefully, this will occur well before the 2000. Other features of

the bill contemplate the ultimate importation of an additional 2,000,000 acre-feet for the account of the Upper Basin, but this is a long way off.

The conclusion from this discussion of the water budget can be summarized in this way:

First, as to demand. An oil shale industry producing 2 million barrels of oil daily can be expected to require each year the diversion of about 750,000 acre-feet, for direct use plus use by the population and affiliated industries which oil shale development will add to the economy of the Upper Colorado River Basin. Of this, about 500,000 would be consumed and say 250,000 returned to the river. This return flow, as in all cases of return flow everywhere, will carry with it some degree of contamination. Such pollution could create a serious problem, locally and interstate. To the extent that it reduces the usability of the river downstream, the impairment may conceivably be characterized as an additional consumptive use, but this is in a sensitive and unsettled legal area.

Second, as to supply. The total lawfully usable supply in the Upper Basin is a good deal less than the total visible supply. This is due to interstate commitments to downstream users. The effect, particularly in Colorado, is that there is not enough uncommitted water available for use in the state of origin to supply the anticipated water requirements of the oil shale industry, and these requirements must be met in large part by the purchase of existing water rights, perhaps reducing the State's agricultural economy in some degree as a partial offset to the benefits to be derived from the new industry. The ultimate remedy, which may well come about, is the importation of several million acre-feet annually into the Colorado River Basin from other watersheds.

Third, as to timing. If the foregoing analysis of supply and demand is even approximately correct, the time of water supply troubles will be the last two decades of this century, which coincides with the anticipated period of vigorous growth of the oil shale industry. It is high time for those interested in the development of an oil shale industry to bring their needs much more actively to the attention of the Bureau of Reclamation and the States concerned. So far, oil shale water requirements have been a vague subject, recognized in words but not in figures in the planning of the region's water budget. When water projects are once built, decisions become literally set in cement and steel. The oil shale industry ought to make its needs known in the planning of the region's water supply structure, rather than in its subsequent remodeling. The reshaping of an economy which is based on already existing uses of waters is an expensive and sometimes tragic business.

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IMPACT OF DAWSONITE AND NACOLITE ON PICEANCE CREEK BASIN OIL SHALE ECONOMICS

WALTER E. HEINRICHS, JR.

ABSTRACT

Recent identification of major quantities of dawsonite and nacolite oil shale in the Green River Formation of the Piceance Creek Basin, may have crucial effect on local oil shale development. The total resource potential has been vastly increased and thus the ultimate importance of early conservative exploitation becomes even more essential.

It is incumbent upon government and industry to cooperate on ways and means to immediately initiate long range programs and begin testing various development methods. It will take the combined know-how of both groups, under a climate of healthy private enterprise incentives and competition to gain maximum public benefit. If this is not done soon, the tremendous value to our economy will soon pass and the opportunity to apply it toward improving our own living standard and that of others will be lost forever.

INTRODUCTION

Another year and here we commiserate again on the status of the oil shale industry. What progress was made during the past year? How do we stand now? What does the future portend? What facts are available and what is rank speculation? Based on some stale experience but mostly on a rather recently crammed birdseye background, and at the risk of contradiction by the more constant experts, I want to outline the salient factors as I see them.

For over a year, my company has been retained by Mr. Joe Juhan to make certain preliminary studies regarding the association of low grade soda ash and aluminum ores with the oil shale in the Piceance Basin. Other facilities and personnel at the University of Arizona contributed substantially, in particular Dr. John Anthony, who made extensive mineralogical examination of continuous drill core of the pertinent section from Mr. Juhan's well located near the center of the basin.

Seemingly the oil shale record is almost drowned in technical literature, studies, and re-studies dating back to 1920 and older. Although progress

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has been made each time, there are still important diverging opinions. Finally, now there may be more room for compromise and action.

Everyone agrees we are dealing with a resource potentially of major geo-political magnitude, but this potential will not last forever. If we are to benefit most constructively from this resource, we must move now, regardless of necessary compromise. History and common sense inevitably tie the health of society to raw material production. No better example exists than our own case since 1850, Canada since 1940, and Australia since 1960, as a more recent example.

Certainly it is unfortunate that our best decisions too often do not meet the test of mass popularity, and here, of course, is the root to much of our present ecological conflict. Policy of our Interior Department can have profound effect on these matters; however Interior is not part of Congress and should not operate on a Gallup Poll basis. Culmination of today's gravest mineral land problems are exemplified in our present oil shale situation. These are largely the result of mutual non-feasance, short sightedness, and past expediencies of both government and industry.

Surely by now this nation has the technical knowledge, leadership, and foresight to forge broad, firm, and equitable policies for the urgent needs of long-range development and orderly and increased production of our vital domestic mineral resources. Perhaps, the occurrence of other minerals besides oil will be the catalyst to help get adequate policy shaped and shale-oil development started.

RESPONSIBILITY OF GOVERNMENT AND INDUSTRY

To some, the ideal industry is totally invisible, odorless, soundless, with no waste product, and one hundred percent conserving. As yet, this is neither feasible nor practical. On the other hand, aside from simple self-preservation, we are morally committed to increasing living standards, fighting poverty, reducing our financial deficit, defending our nation, and continually taking care of the general welfare of more and more people. Obviously, this requires constantly increasing domestic production of everything. Really, we have very little choice except to do the job as wisely as possible and without needless waste and destruction.

Fortunately, ancillary factors for the establishment of a viable major new basic industry are favorable in the Piceance Basin. These include unusual compatibility with modern concepts of population and industrial dispersion, multiple use conflict, conservation, anti-pollution, and reclamation. Important agricultural potential, including timber, is minimum or nil, as would also be the effect on existing wildlife, and no exceptional scenic wonder is involved. The natural basin configuration, with proper added

safeguards, such as small dams and other minor features, will control any potential groundwater or stream pollution. Much of the water used would be recycled. Any potential air pollution certainly can also be effectively controlled.

Some worry is expressed regarding so called windfall profits. Considering the magnitude of capital required, the extreme nature of the risks involved, and the length of time until payout, this is totally unrealistic. If private enterprise competition is encouraged, then profit will only be proportional to maximum conservation and production efficiency, with market control and the real benefits going to the ultimate consumer, the public. Naturally the effects on established industries and on foreign economy and imports must be considered, but so should all the other rapidly changing domestic and international factors. As a nation we can no longer act entirely unilaterally in any field.

Much has been said. considerable funds expended, and major new tests are planned for better ways and means to recover oil from the shale. The main considerations of mining and refining methods and costs have been studied and valuable work in this continues. However, by the addition of soda ash and aluminum into the picture, a new situation exists. If maximum recovery at least cost of all potential products is to be our objective, then clearly, open cut mining is most desirable, but some doubt if it is feasible. To explore this question, let us first look at the things involved besides oil.

NACOLITE AND DAWSONITE CONSIDERATIONS

The principal sodium minerals, near the basin center, begin to appear above 1800 feet below the surface and extend intermittently to below 2600 feet. The richest zone of these, though not continuous, is about 500 feet thick and lies between 1850 feet and 2375 feet below the surface. This zone is included within the much thicker oil shale zone above and below, and all become shallower and thinner toward the basin margin. For discussion and simplicity and correlation with previous reports, we can assume a maximum overburden thickness of approximately 1000 feet on top of 2000 feet of mixed pay zone, with proportionately less thickness for each as one approaches the basin edge.

Present value ratio, per vertical column unit, of recoverable material in the maximum known 2000-foot pay section is \$9 oil, \$7 soda ash and \$2 alumina, or about \$3.50 per vertical ton of ore on a weighted average basis. Recovered and refined equivalent products, expressed also as a ratio, is 1 ton of aluminum metal to 16 tons of soda ash to 30 tons of shale oil with each of these being worth roughly \$500 at today's market. Thus the total

potential value of the basin reserves is about tripled by adding the sodium byproducts.

DEVELOPMENT, MINING METHODS AND COSTS

In proposing open cut mining, I do not mean totally to ignore other methods. Block caving is still a possibility and, of course, nuclear blasting may be justified for open cut preparation aside from the various in situ recovery considerations. Several types of very large continuous mining machines and semi-portable belt conveyors should receive careful scrutiny. Dr. Tell Ertl covered the idea in his 1965 paper, although his figures now may be too conservative.

Mining a section of ore to 3,000 feet deep will need a trench or inverted pyramid no greater than 6,000 feet wide at the surface in the basin center, and this width would decrease toward the basin edge if slopes greater than 45 degrees can be tolerated. If controlled, self-induced open caving methods can be perfected, the width may decrease even more, with a corresponding reduction in stripping and blasting costs. Once room is developed at the bottom of the pay section, then overburden and spent shale can be back-filled into the mined out areas and the surface permanently reclaimed for other future uses. The fundamental procedure is somewhat akin to placer dredge mining operations. Minimum unit rate of mining and stripping for optimum efficiency would probably not be much less than 100,000 tons per day each—from an area of about 5,000 acres per unit operation. Unitization of land holdings to fit this minimum order of magnitude scope will be most desirable, although selected portions of the basin may allow unit operations one-half or even one-quarter this size.

Initial strip ratio on first cut or pass would be in the vicinity of one to one but from then on would decrease approaching one half to one. Mining costs for ore and waste will be much less than \$0.25 per ton and waste disposal and reclamation less than \$0.10 per ton of material re-handled. Initial capital investment estimates may approach \$250 million, 40 percent for stripping and 60 percent for plant for the average operation, but this may vary somewhat depending on differing factors over the whole basin, and especially the relative stripping ratios and costs required to start production at a given unit.

These elements can only be removed from untenable risk and speculation by completely and carefully drilling, sampling and testing based on the statistics of chemistry, distribution, spacing, and representation of tests and sampling. The next stage may be to confirm these results by sinking shafts and obtaining bulk samples for pilot plant beneficiation tests. This would allow also for a more accurate appraisal of production methods and costs,

water disposal, availability, requirements, and related problems. Such programs often consume 5 years or more before any real production is achieved. Concurrently, in other areas, other approaches such as underground block-caving, room and pillar, or in situ nuclear blasting techniques should be under way if the need otherwise continues to be indicated.

CONCLUSIONS

Although other electrical power may be available at less cost, conceivably the shale oil (and some soda ash) might be utilized in aluminum reduction. Very cheap soda ash might find and develop new markets eventually, but much will depend on related transportation factors which also will affect the aluminum economics.

In any event, if most of the sorting out is done on a competitive private enterprise basis in a climate of reasonable and equal rules for all concerned, the result will be the earliest establishment of a most important and worthwhile new industry for the maximum benefit of all.

Permission for this paper was provided by Mr. Joe Juhan of Tucson, Arizona and his assistance, together with that of Mr. Irvin Nielson of Wolf Ridge Minerals, Glenwood Springs, Colorado, and Dr. John Anthony, Hawley & Hawley, assaying chemists and others of Tucson, Arizona, is acknowledged.

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POTENTIAL RESOURCES OF DAWSONITE AND NAHCOLITE IN THE PICEANCE CREEK BASIN, NORTHWEST COLORADO

ROBERT J. HITE and JOHN R. DYNI

ABSTRACT

Large quantities of dawsonite [$\text{NaAl}(\text{OH})_2\text{CO}_3$], nahcolite (NaHCO_3), halite, and other sodium minerals were discovered in a saline facies of the oil shales of the Parachute Creek Member of the Green River Formation of Eocene age during recent core drilling in the Piceance Creek basin, northwest Colorado. Although the complete distribution of dawsonitic oil shale is unknown, data from one drill hole indicate that dawsonitic aluminum in 1 square mile exceeds that in the total bauxite reserves of the United States.

In the Joe T. Juhan core hole 4-1 an interval of dawsonite-bearing oil shale is 628 feet thick and averages 10.7 percent dawsonite. In this interval, rocks nearly 300 feet thick average 2.3 percent aluminum which is extractable by dilute acid solutions. The richest zone within this 300-foot-thick interval is 18 feet thick and averages 3.9 percent acid-extractable aluminum. Data indicate that part of the extractable aluminum is from amorphous substances. In the same core hole, the dawsonite zone is nahcolite-bearing through two intervals that total 468 feet in thickness and average 15.5 percent nahcolite.

Dawsonite and nahcolite constitute potentially valuable sources of aluminum and soda ash, respectively. Alumina and soda ash may be recoverable byproducts of spent shale from oil-shale retorts. A process for recovering alumina from the spent shale by a water leach may be feasible.

INTRODUCTION

Recently, large quantities of dawsonite, nahcolite, halite, and minor amounts of other sodium minerals have been discovered in the rich oil shales of the Eocene Green River Formation in the Piceance Creek basin, northwest Colorado. This discovery is of economic importance because dawsonite, a dihydroxy sodium aluminum carbonate, and nahcolite, a sodium bicarbonate, constitute potentially valuable sources of alumina and soda ash.

This paper discusses the occurrence and distribution of these minerals

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within the enclosing matrix of oil shale, portrays the geologic and geochemical framework in which these minerals were deposited, and briefly summarizes the abundance of these minerals in terms of sodium and aluminum. Particular emphasis is placed on soda ash and alumina extraction processes which are compatible with recovery of shale oil.

The authors are indebted to Joe T. Juhan, John W. Savage, and Irvin Nielsen for allowing us to study the core which made this paper possible. We thank K. E. Stanfield of the U.S. Bureau of Mines for making available shale oil assays on some of the core.

GEOGRAPHIC SETTING

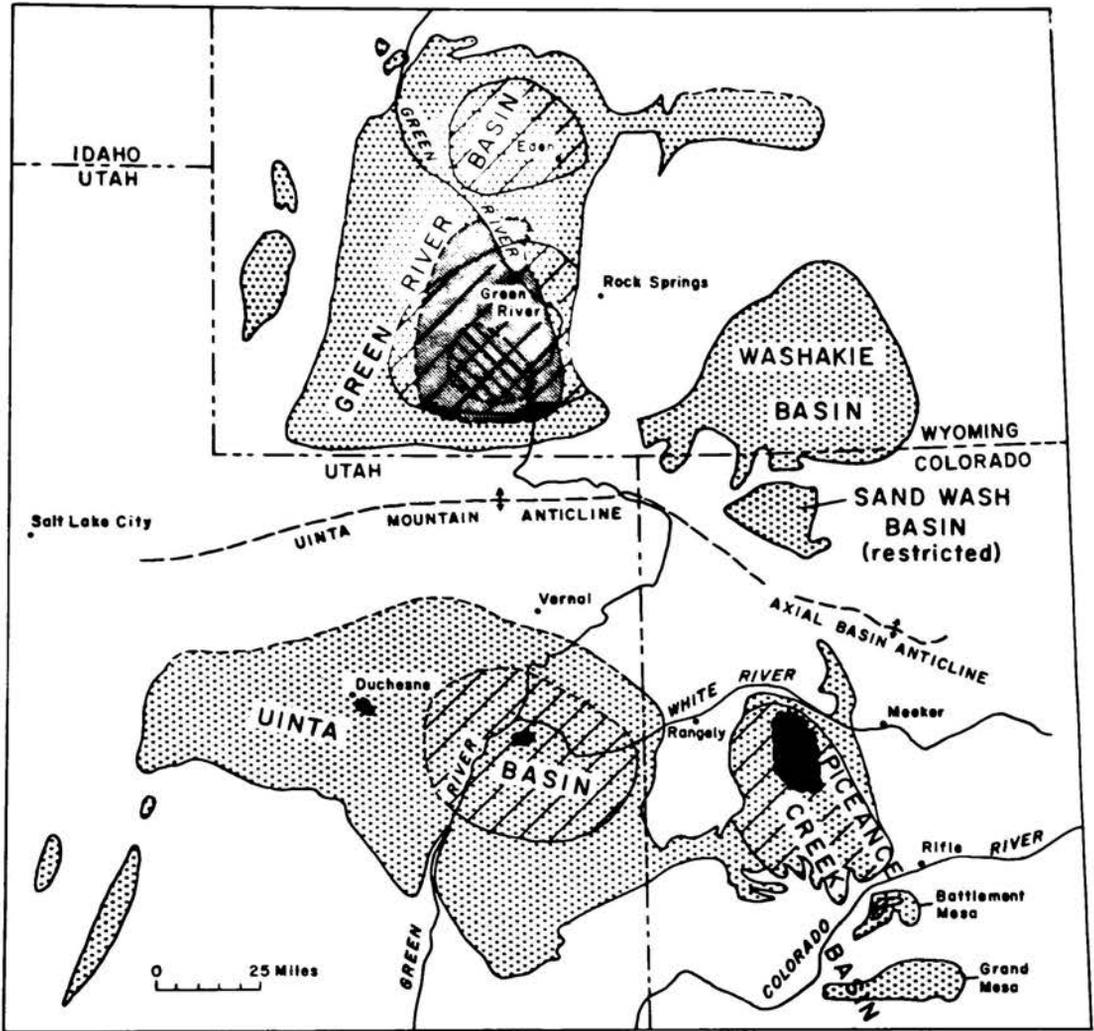
The Green River Formation is distributed through the three-state area of Wyoming, Utah, and Colorado (fig. 1). The main body of the formation was deposited in four basins: the Green River and Washakie basins in Wyoming, the Unita basin in Utah, and the Piceance Creek basin in Colorado. The Piceance Creek basin is the smallest of the four, occupying about 1,600 square miles. This basin contains the thickest and richest accumulation of oil shale in the world and the associated dawsonite and nahcolite deposits. This paper emphasizes the geology of the northern half of the Piceance Creek basin where the greatest concentration of these resources occurs.

STRATIGRAPHY

The dawsonite and nahcolite deposits of the Piceance Creek basin occur in the lacustrine Green River Formation. The formation is divided into five members (fig. 2). Starting at the base these are the Douglas Creek, Garden Gulch, Anvil Points, Parachute Creek, and Evacuation Creek Members. The lower three members consist chiefly of fine-grained clastic rocks whose maximum aggregate thickness is probably more than 1,000 feet. Near the top of this sequence (fig. 2) is a persistent basin-wide electric log datum which is informally referred to as the orange marker. It is extremely useful for subsurface mapping in the Piceance Creek basin.

The Parachute Creek Member contains the rich deposits of oil shale and associated dawsonite and nahcolite deposits. The member ranges in thickness from about 850 feet on the margins of the Piceance Creek basin to about 1,800 feet.

Dawsonite, nahcolite, halite, and other sodium minerals are commingled with oil shale and form a saline-rich zone in the lower half of the member. Near the basin depocenter the saline-rich zone attains a thickness of at least 900 feet. Near the base of the saline-rich zone are three thin but persistent nahcolite units (fig. 2) which are easily correlatable between numerous wells.



Adapted partly from Duncan and Swanson, 1965, fig. 3, and Culbertson, 1966, fig. 1.

EXPLANATION

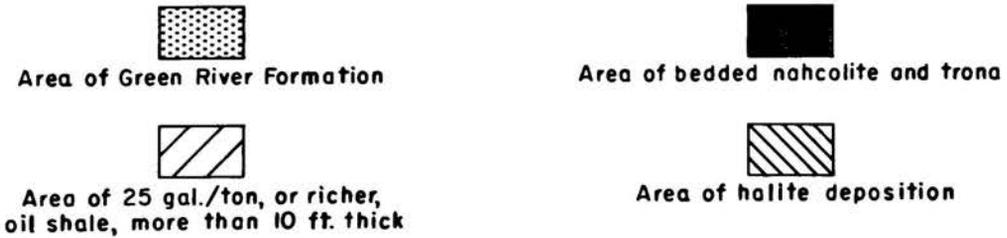


FIGURE 1.—Known distribution of bedded sodium saline minerals in the Green River Formation of Colorado, Utah, and Wyoming.

In the upper part of the zone are two intervals of halite-bearing rocks, each over 100 feet thick. The top of the saline-rich zone is a dissolution surface. Above is a leached zone of oil shale, several hundred feet thick, from which water-soluble minerals have been removed by ground water. The rocks in the leached zone are commonly broken and brecciated, and units of soft, punky, and bleached oil shale, as well as solution cavities, are common. This

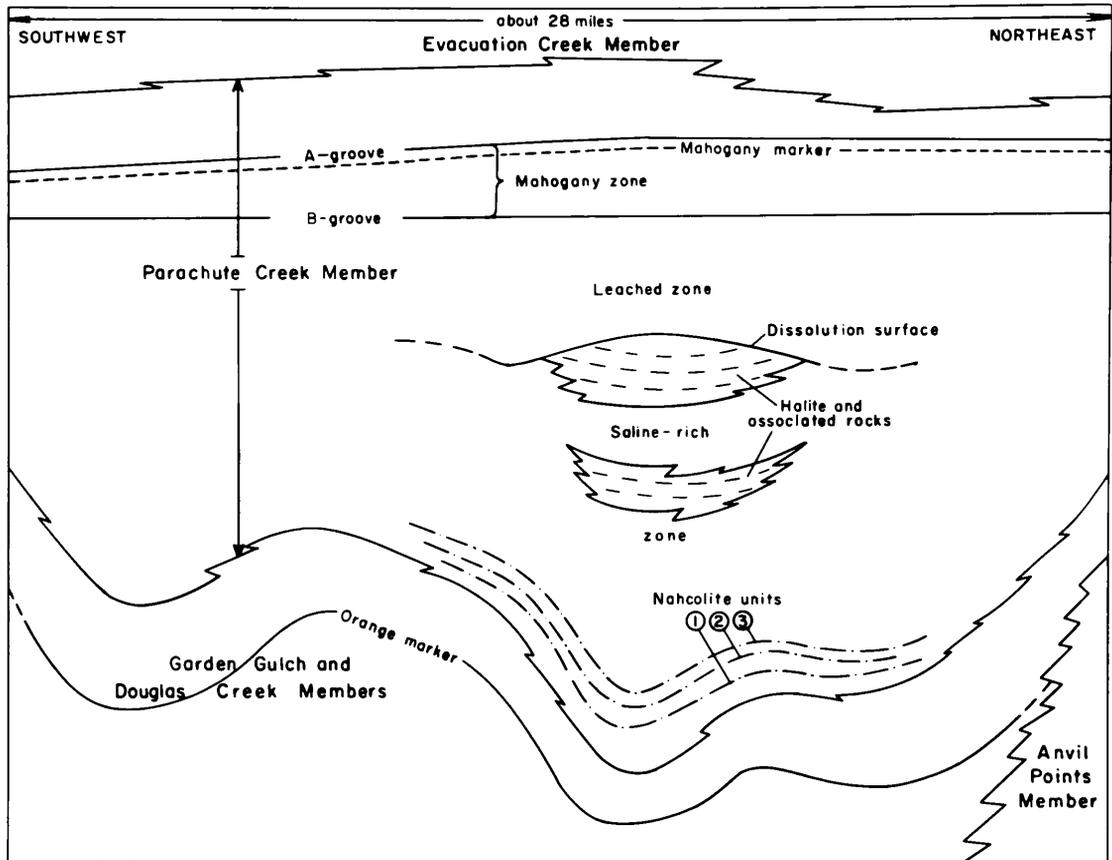


FIGURE 2.—Diagrammatic southwest-northeast stratigraphic cross section through the approximate depocenter of the Piceance Creek basin, Colorado. This figure shows the relationship of the saline-rich zone to the enclosing rocks of the Green River Formation.

zone is apparently water bearing and active removal of water-soluble minerals may still be taking place. Other important stratigraphic guides are two oil-lean tuffaceous units called the A- and B-grooves which mark the top and base of the Mahogany zone in the upper part of the Parachute Creek Member.

Overlying the Parachute Creek is the Evacuation Creek Member, which consists chiefly of tuffaceous sandstone, shale, and siltstone. It forms the top of the Green River Formation and is exposed over most of the Piceance Creek basin.

STRUCTURE

The Piceance Creek basin is both a sedimentary and structural basin which is bounded on the south by the Uncompahgre uplift, on the east by the Elk Mountain-White River uplifts, and on the north by the Uinta Mountain-Axial Basin anticlinal trend. The Douglas Creek arch on the west side of the basin is a gentle north-trending upwarp that separates the Piceance Creek basin of Colorado from the Uinta basin of Utah.

The major structural elements within the Piceance Creek basin involving the Green River Formation are three small generally northwest trending synclines and the Piceance Creek dome. The dome is a gas-producing structure. Several northwest trending faults, commonly paired to form grabens and having small displacement, cut the Piceance Creek dome and an eastward-plunging anticlinal nose just west of the dome.

An unpublished isopach map of part of the Parachute Creek Member by the junior author shows that trends of thickening coincide with the synclines suggesting pre-Parachute Creek folding. Tectonics further modified the intrabasin structure in post-Parachute Creek time forming Piceance Creek dome.

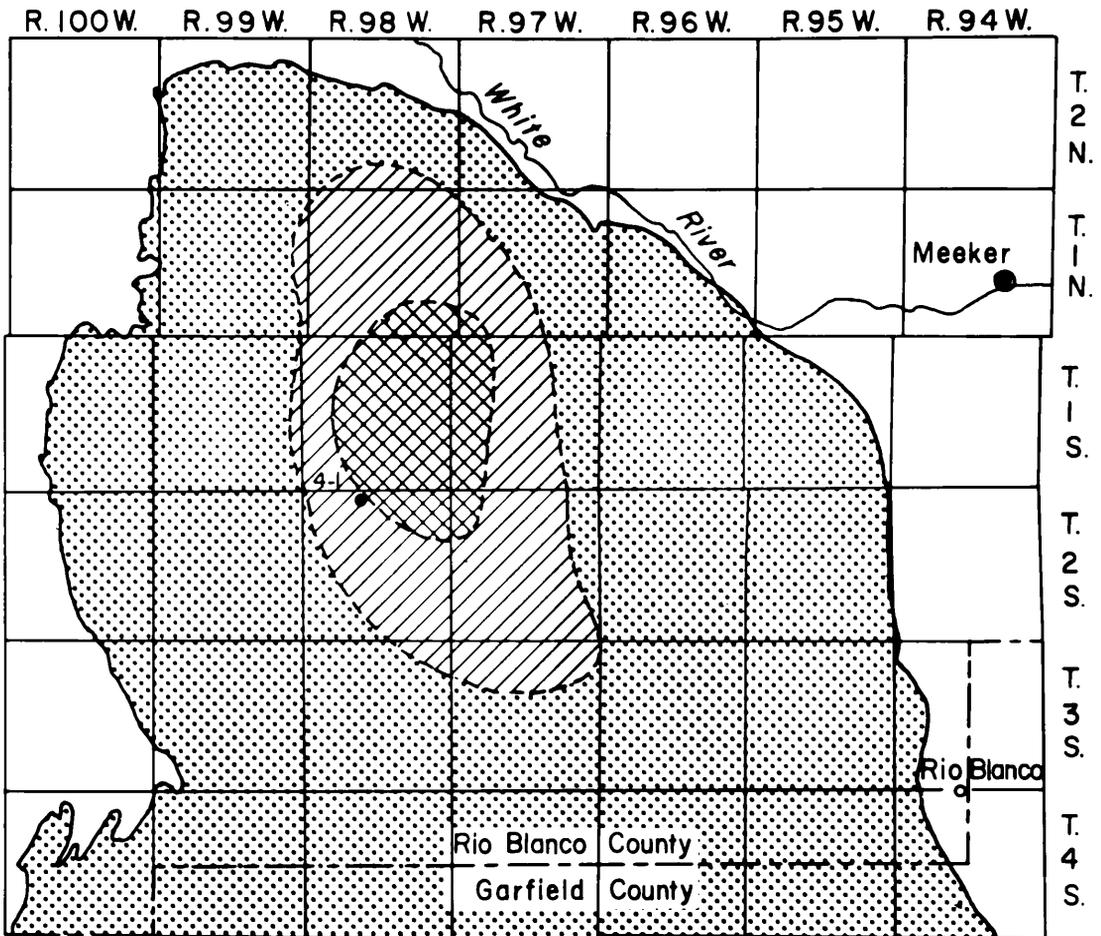
DAWSONITE AND NAHCOLITE DEPOSITS

Nahcolite was first reported in the oil shale deposits of the Piceance Creek basin, Colorado, by Ertl (1947) and Glass (1947). Dawsonite was identified in cores from the basin by Charles Milton of the U.S. Geological Survey in 1958 (Milton and Eugster, 1959). However, it was only with the recent discovery of large quantities of nahcolite and dawsonite in the basin that the potential economic importance of these minerals was realized.

The dawsonite and nahcolite deposits of the Piceance Creek basin are distributed through a tremendous volume of rich oil shale. The distribution of these deposits may be controlled by salinity gradients that existed in the lacustrine environment and caused most of the dawsonite and nahcolite to be concentrated in the deeper northern half of the Piceance Creek basin.

Dawsonite shows great vertical and areal distribution in the northern part of the basin. The thickness of oil shale continuously mineralized by dawsonite in 18 drill holes is reported (Smith and Milton, 1966) to range from zero just south of the Rio Blanco County line to 760 feet toward the center of the basin (fig. 3). In the Juhan core hole 4-1, located in the SW $\frac{1}{4}$ NE $\frac{1}{4}$ sec. 4, T. 2 S., R. 98 W., the authors found dawsonite distributed through a continuous zone 628 feet thick. The zone may be thicker but this could not be confirmed because samples in the upper part of the core hole have not yet been analyzed. In 1966, D. A. Brobst of the U.S. Geological Survey discovered that dawsonite is present discontinuously through several hundred feet of oil shale cropping out along the north side of the basin. Near the center of the basin, the top of the dawsonite zone ranges in depth from 900 to 1,900 feet below the surface.

The mineral dawsonite occurs as microscopic crystals finely disseminated through the oil shale and as thin laminae along bedding planes. Smith and Milton (1966, p. 1034) have found it in fissures and in small vugs. The mineral is also found in some of the halite and nahcolite units. Because



Adapted from Stanfield and others, 1960, fig. 3.

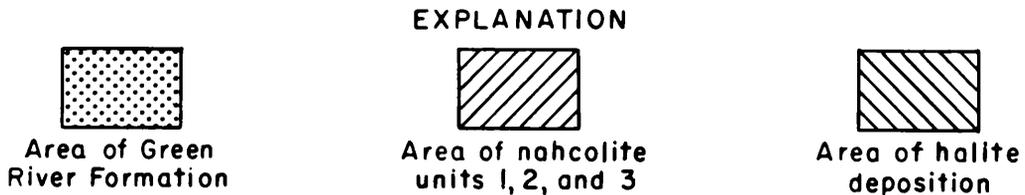


FIGURE 3.—Map of the Green River Formation in the northern part of the Piceance Creek basin, Colorado, showing the areal distribution of three nahcolite units and the area of halite deposition.

dawsonite is extremely fine grained, X-ray diffraction analysis is necessary for rapid, positive identification. Dawsonite, quartz, albite, potash feldspar, dolomite, and a little pyrite form the major fine-grained crystalline mineral constituents of the oil shale in the saline-rich zone. Clay minerals are conspicuously absent through most of the saline-rich zone.

Nahcolite is more abundant and widespread than dawsonite in the Piceance Creek basin. Like dawsonite, nahcolite becomes more abundant toward the basin depocenter. The three units of nahcolite shown on figure 2 can be traced in the subsurface over about 180 square miles (fig. 3). The units

range in thickness from about 1 to 9 feet. Disseminated forms of nahcolite have even greater distribution, but present data are too sparse to show its extent with any degree of accuracy.

Nahcolite occurs in both nonbedded and bedded forms in oil shale. Scattered through much of the saline-rich zone of the Parachute Creek Member are rosettelike and irregular aggregates of coarse-bladed crystals of brown nahcolite. These aggregates range from a few inches to a few feet in diameter. Bedded forms of nahcolite include finely crystalline layers and units of honeycomblike intergrowths of nahcolite and oil shale. Much of the nahcolite contains a high percentage of organic matter. In the two halite-bearing units shown in figure 2, thin layers of nahcolite are interbedded in cyclic fashion with halite. Other minerals associated with the halite units include wegscheiderite ($\text{Na}_2\text{CO}_3 \cdot 3\text{NaHCO}_3$), shortite ($\text{Na}_2\text{CO}_3 \cdot 2\text{CaCO}_3$), northupite ($\text{Na}_2\text{CO}_3 \cdot \text{MgCO}_3 \cdot \text{NaCl}$), searlesite ($\text{NaBSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$), and possibly trona ($\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$).

GEOCHEMISTRY

The geochemical environment of the Green River Formation in the Piceance Creek basin is far from being fully understood. A greater understanding of this environment can be gained, however, by studies of the lateral and vertical variations in distribution of the clastic, authigenic, and evaporite minerals. Although many profiles across the basin will be needed to demonstrate lateral facies, a single vertical profile near the depocenter of the basin shows many interesting relationships.

Profiles showing variations in mineral percentages, as determined by X-ray diffraction analysis, have been prepared from samples from the Juhan core hole 4-1. The core hole is located near the basin depocenter but just outside the area of halite deposition. A portion of these profiles showing the lower one-third of the saline-rich zone and part of the underlying Garden Gulch Member is illustrated on figure 4. The base of the Parachute Creek Member is at the depth of about 2,440 feet on the profiles. The three nahcolite units previously discussed are present in the hole and are labeled on the illustration. The minerals shown in the profiles include dawsonite, quartz, albite, potash feldspar, dolomite, nahcolite, and illitic clay. These minerals, plus kerogen, total almost 100 percent of the sample.

Starting at the bottom of the mineral profiles and progressing upward, several interesting relationships can be observed. Below 2,480 feet the rock-forming minerals are chiefly quartz, illitic clay, dolomite, and minor amounts of the feldspars. Dawsonite is first noted at about 2,470 feet. At this same depth albite, potash feldspar, and dolomite begin to increase as

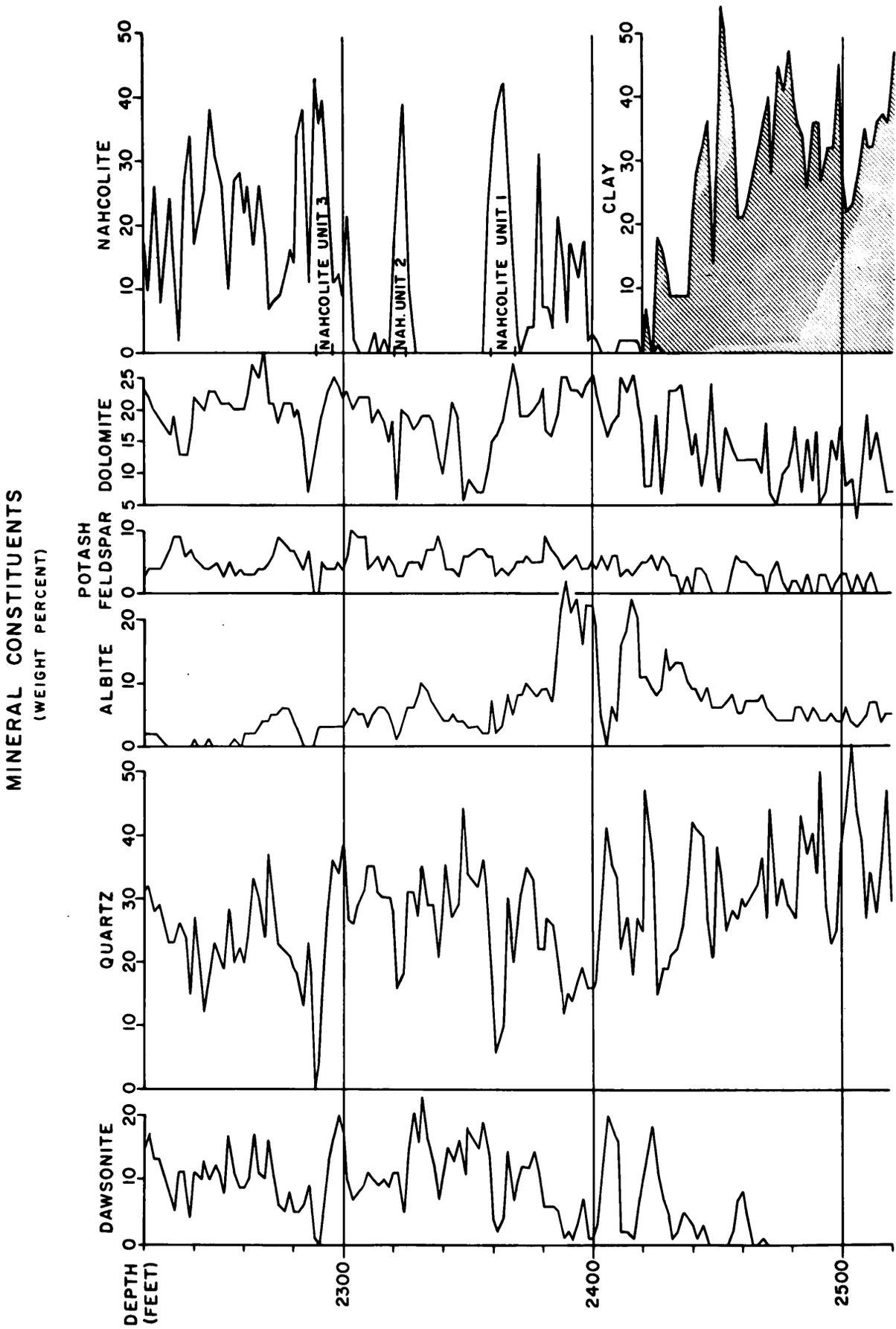


FIGURE 4.—Diagram showing variations in percentages of the major crystalline minerals through the lower one-third of the saline-rich zone and part of the underlying Carden Gulch Member. Weight percents of each mineral were determined by X-ray diffraction analysis on samples of core composited on 2-foot intervals from the Juhan core hole 4-1.

clay begins to decrease. The first trace of nahcolite at 2,420 feet coincides with the disappearance of clay. Albite reaches its maximum concentration between the depth of 2,420 to 2,380 feet where several samples contain as much as 20 percent by weight of the mineral. From this point upward albite steadily decreases in abundance and is absent or nearly so near the top of the profile. Although quartz seemingly shows an erratic distribution pattern from sample to sample, the average amount of quartz in each 100-foot-thick interval is about the same. Significantly, in single samples, the quartz content is directly proportional to the amount of dawsonite present. Thus, a sample containing a high percentage of quartz also contains a high percentage of dawsonite. The ratio of dawsonite to quartz which is nearly constant through the saline-rich zone is about 1:2.5. Albite shows an inverse relationship to quartz and dawsonite; as albite increases the amount of quartz and dawsonite decreases.

The changes in mineralogy and the mineral relationships described here reflect changes in the salinity and alkalinity of the lake waters in which these minerals formed. Salinity and alkalinity are believed to have increased steadily during deposition of the interval shown on figure 4. This line of reasoning is supported by the upward increase of nahcolite. Greater salinity is also indicated by the presence of halite in rocks in the deeper part of the basin which are lateral equivalents of the Juhan core but stratigraphically higher than the interval shown on figure 4. The disappearance of clay may be due to its reaction with a carbonate-chloride brine, or the clay minerals in contact with this brine may have flocculated around basin margins before reaching the basin center. The correlation of the dawsonite and quartz profiles, which in turn inversely correlate with albite and clay, suggests a sequence of diagenetic reactions involving the brine and these minerals. Clay or possibly tuffaceous material may have been the parent material, and diagenesis may have then produced the other minerals.

ECONOMICS

Considerable interest is being expressed by industry in the economic possibilities of extracting alumina and soda ash from the Green River oil shale. Dawsonite contains 35 weight-percent alumina, and nahcolite contains 65 weight-percent soda ash. The authors' data suggest that both commodities may be recoverable from retorted oil shale containing these minerals.

Although dawsonite constitutes only a small part of the rock, the alumina in the mineral may be extractable by dilute acid or base leaches. In the Juhan core hole about 300 feet of the dawsonite zone averages 2.3 percent aluminum which is extractable by dilute acid solutions (2.0 percent sulfuric

acid). The richest zone within this 300-foot-thick interval is 18 feet thick and averages 3.9 percent acid-extractable aluminum. Extraction using a 2 percent sodium hydroxide solution gave slightly lower results.

Of great interest is the possibility of extracting dawsonite alumina with a water leach. Differential thermal analyses of synthetic and natural samples of dawsonite show a large endothermic reaction near 400°C . At this temperature dawsonite loses its carbon dioxide and hydroxyl water and forms an amorphous substance that is not readily soluble in water.

Figure 5 shows X-ray diffraction traces of samples of dawsonite heated to temperatures ranging from 525° to $1,000^{\circ}\text{C}$. This figure shows the gradual conversion of dawsonite from an amorphous substance (sample A) to a water-soluble crystalline compound (samples C and D) that is identified as sodium aluminate. Alumina can then be precipitated from the sodium aluminate solution by conventional methods of carbonation.

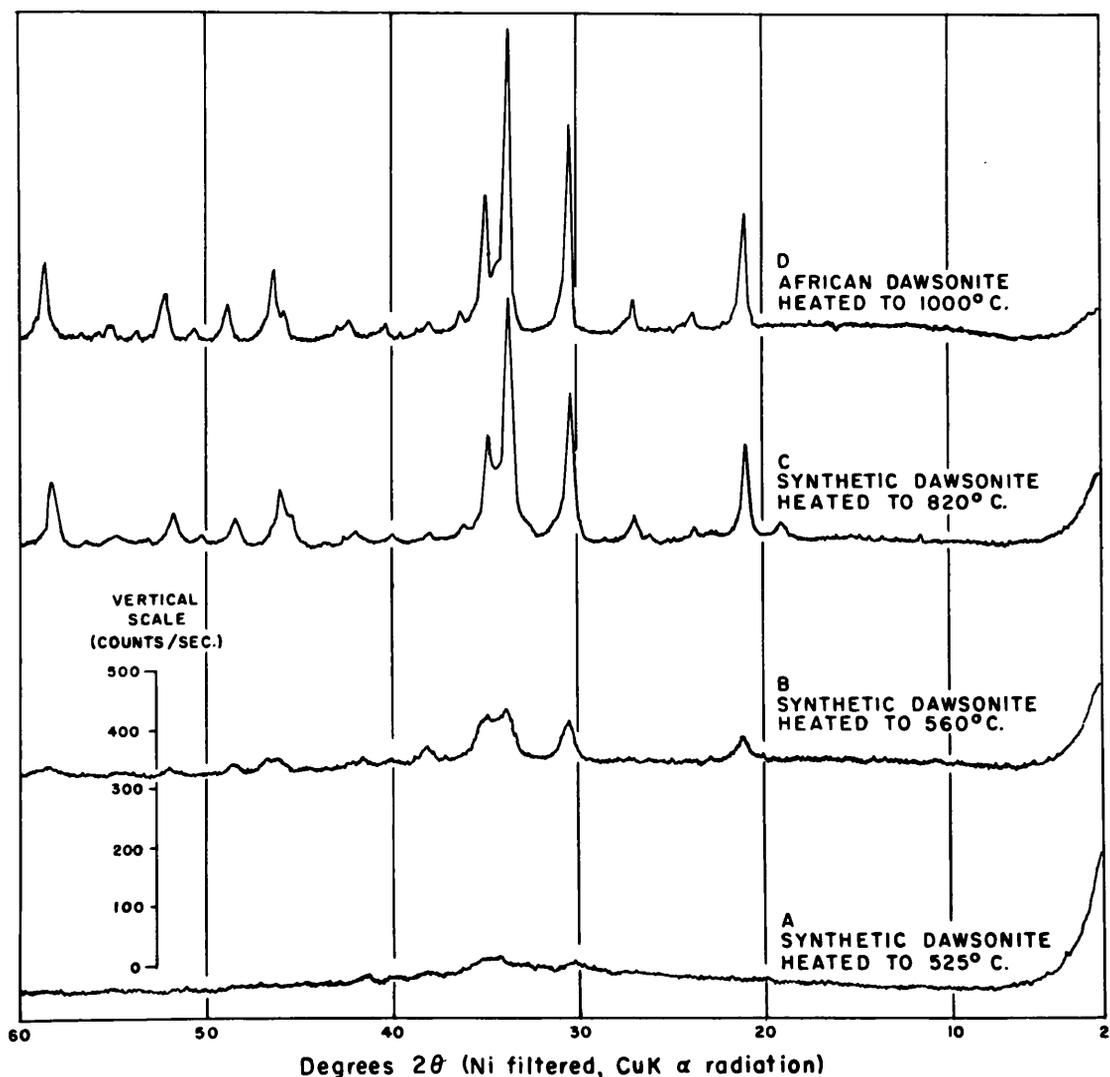


FIGURE 5.—X-ray powder diffractograms of heated samples of dawsonite.

The chemistry involved in heating a dawsonite oil-shale mixture is more complex. Evidently only part of the dawsonite in the shale converts to a water-soluble aluminum-bearing compound. However, the remaining water-insoluble aluminum may be recoverable by dilute acid or base leaches.

Figure 6 summarizes the results of firing sets of three different samples of dawsonite-bearing oil shale at temperatures ranging from 400° to 1,000°C and using distilled water, 2 percent sulfuric acid, and 2 percent sodium hydroxide leaches. The total aluminum for each sample was determined by chemical methods, and the dawsonite aluminum was calculated indirectly from X-ray diffraction data. Maximum recovery seems to be achieved in those samples which were fired to temperatures ranging from 400° to 700°C. Significantly, this is in the temperature range of some oil-shale retorts. The acid leach is the most effective, followed by the base leach, then water. Although the recovery of aluminum in the water leach is low, it seems feasible that with a better understanding of the chemistry involved in firing dawsonitic oil shale, better yields could be achieved.

One important point suggested by sample D122356 in figure 6 is that more aluminum is extracted by the acid and base leaches than can be accounted for by dawsonite alone. In this sample and others the feldspars account for about 5 to 10 percent of the total aluminum in the rock. Aside from feldspar and dawsonite no X-ray crystalline aluminum-bearing mineral was found in the oil shale. Therefore, additional extractable aluminum as amorphous substances seems to be present in the oil shale.

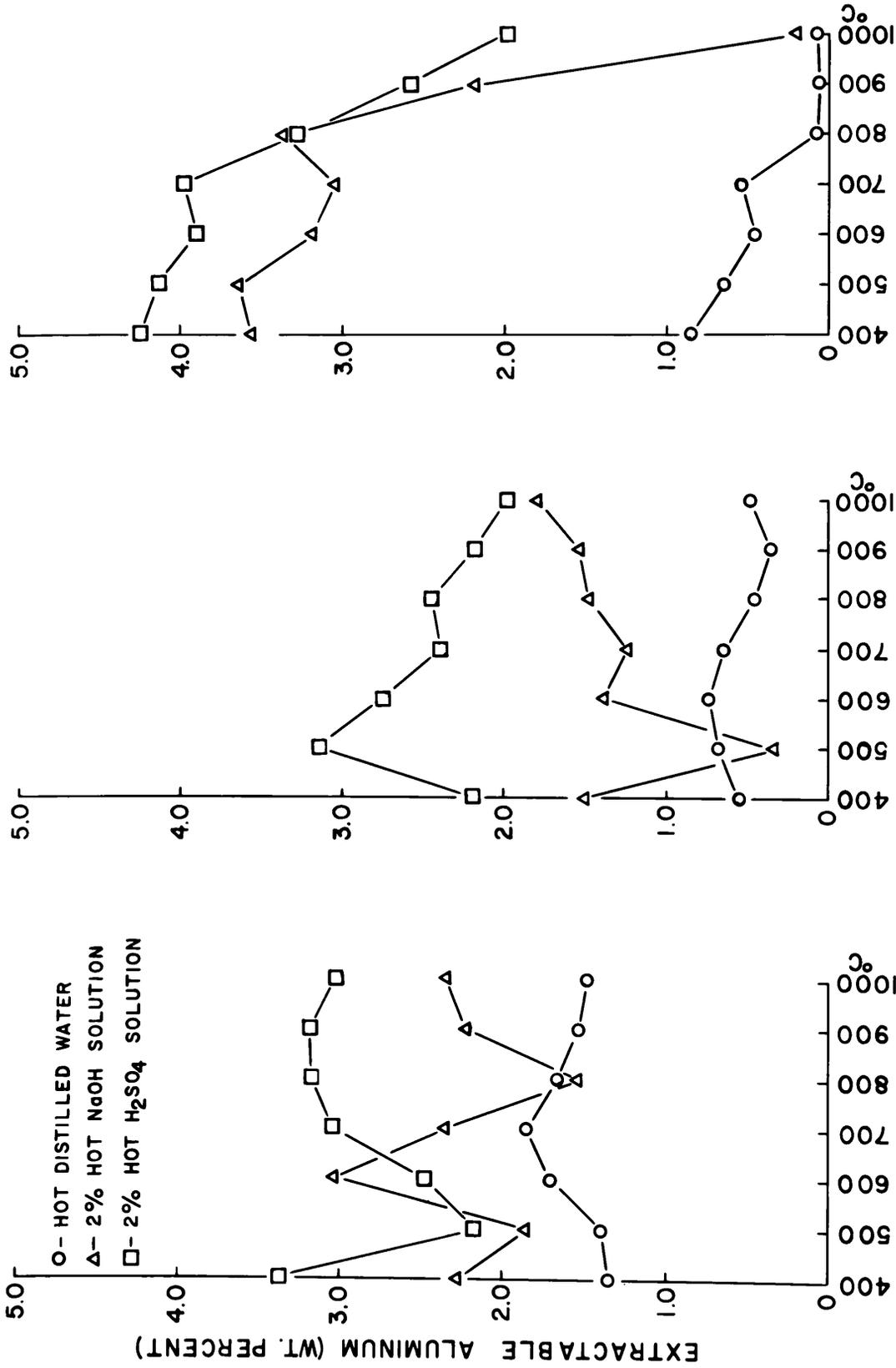
Nahcolite is water soluble and can be removed by a simple water leach either before firing or after firing when the nahcolite is converted to soda ash.

Dawsonite and nahcolite are present in rocks that already have great potential value for their shale oil content. Figure 7 summarizes the depths, thicknesses, and grades of dawsonite, nahcolite, and oil shale in the saline-rich zone of the Juhan core hole 4-1. Oil shale above this zone is not evaluated here, although it should be pointed out that large amounts of rich oil shale overlie the saline-rich zone.

In the Juhan core dawsonite averages about 11 weight-percent through a continuous interval of oil shale 628 feet thick. The rocks containing nahcolite are divided into an upper zone and a lower zone. The two zones average 15 weight-percent nahcolite.

The interval of oil shale shown in figure 7 starts at the top of the saline-rich zone and continues to the total depth of the drill hole. Shale oil assays by the U.S. Bureau of Mines indicate that this 761-foot interval averages about 31.1 gallons of shale oil per ton.

The amount of each potential resource in the Juhan core hole is calculated on the basis of 1 square mile using the thicknesses and grades shown



Sample D122342

Total Al in sample: 4.20 wt. %
 Dawsonite Al from X-ray data: 3.8 wt. %

Sample D122325

Total Al in sample: 4.50 wt. %
 Dawsonite Al from X-ray data: 2.9 wt. %

Sample D122356

Total Al in sample: 6.82 wt. %
 Dawsonite Al from X-ray data: 2.5 wt. %

FIGURE 6.—Extractable aluminum in fired samples of dawsonitic oil shale using water, dilute acid, and dilute base leaches. Aluminum analyses by L. F. Rader, Jr., H. H. Lipp, and W. D. Goss, U.S. Geological Survey; dawsonite aluminum calculated from X-ray diffraction data by R. J. Hite.

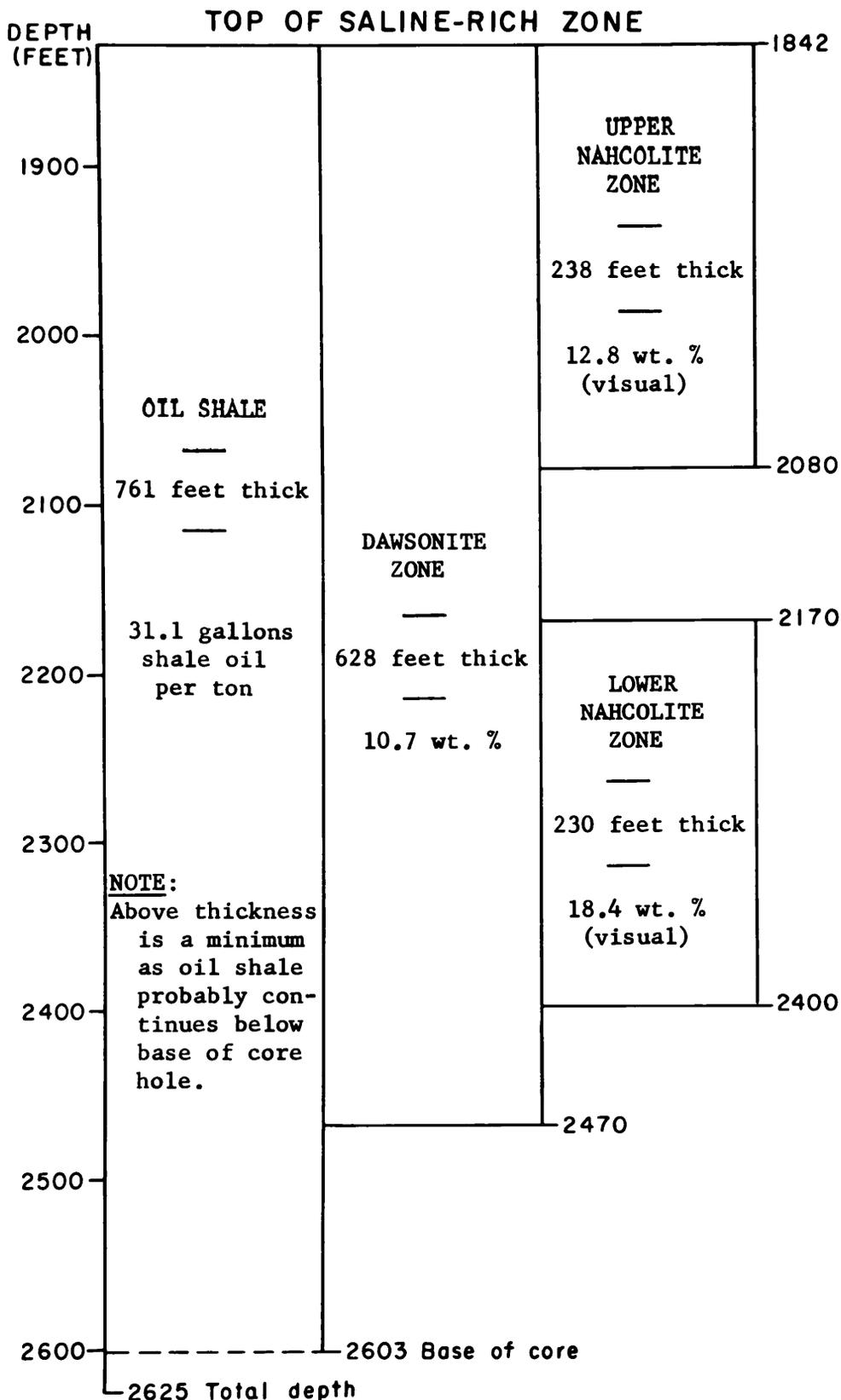


FIGURE 7.—Depths, thicknesses, and averaged grades of dawsonite, nahcolite, and oil shale in the lower part of the Juhan core hole 4-1. Grade of oil shale based on unpublished shale oil assays by the Laramie Petroleum Research Center, U.S. Bureau of Mines.

in figure 7. The shale oil amounts to nearly 1 billion barrels. About 130 million tons of nahcolite are present, or calculated as soda ash about 82 million tons.

Potential resources of alumina from dawsonite are enormous. About 42 million tons of dawsonite alumina are present in 1 square mile. The total known bauxite reserves of the United States contain about 30 million tons of alumina. Thus, just 1 square mile in the Piceance Creek basin contains about 1.5 times as much alumina as in the total bauxite reserves of the United States.

SUMMARY

In the Piceance Creek basin, dawsonite and nahcolite deposits commingled with rich oil shale form what is potentially the world's largest contiguous mineral reserve. The dawsonite and nahcolite deposits are potentially valuable for their alumina and soda ash. Although economically proven extraction processes have not been demonstrated, preliminary laboratory work by the authors suggests that the recovery of soda ash and alumina is feasible. Such processes seem compatible with oil-shale retorting. If these commodities can be recovered along with the shale oil, development of mineral industry in the Piceance Creek basin may be expedited.

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ALASKAN OIL SHALE

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and HARRY A. TOURTELOT²

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Deposits of oil shale were first reported in Alaska north of the Arctic Circle in the latter part of the 19th Century. Before this time, according to evidence near old camp sites, shale had been used for fuel in interior Alaska, as it is being used now, 1967, by the Eskimos of Anaktuvak Pass in the central part of the Brooks Range.

Fragments of oil shale were found by early explorers as far north as the basin bordering the Arctic Ocean, and during early geological investigations of the area north of the Arctic Circle oil shale was collected and identified by Collier (1906), and later by Smith and Mertie (1930) in gravel bars and outcrops in stream cuts. Other deposits, too, were described in several early reports but were erroneously identified as coal.

Detailed geologic mapping in 1950-51 by U.S. Geological Survey field parties in connection with the geologic evaluation of Naval Petroleum Reserve No. 4 delineated additional oil-shale localities. In 1964, Tailleir published a short article in U.S. Geological Survey Professional Paper 475-D giving Fischer assay results from oil-shale samples of marine oil shales collected by these Survey field parties. These samples yielded from 6.7 to 146 gallons of oil per ton of rock. In the summer of 1964, Tailleir collected oil-shale samples from 12 localities in the Southern Foothills belt of the Brooks Range, and also obtained larger samples from some of the localities previously tested. These samples were routinely assayed for oil content, were examined petrographically and mineralogically, and were analyzed chemically for major constituents and minor elements. The results of this examination were reported in an open-file report by Tourtelot and Tailleir (1965).

As a result of the analytical work of 1964 a reconnaissance project was initiated, headed by Tailleir, to attempt to determine the thickness, value, and extent of the oil-shale deposits on the Arctic Slope. This project was funded by the Office of Naval Petroleum and Oil Shale Reserves, Washington, D.C., and was logistically supported in great part by the Arctic Research Laboratory at Point Barrow.

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The area north of the Arctic Circle, and more particularly that part immediately north of the Brooks Range, a west-trending mountain range that is the northernmost mountain range in Alaska, was of principal interest.

From south to north the area is divided physiographically into the Brooks Range, a mountainous area with a maximum relief of 5,000 feet; the Southern Foothills belt, an area consisting of hills having a maximum relief of 1,500 feet; the Northern Foothills belt, consisting of more broadly rounded hills having possibly as much as 500 feet of relief; and the Arctic Slope, a flat poorly drained plain with a maximum relief of 150 feet. Most of the exposed oil shale is in the Southern Foothills belt. This area is north of timberline and its vegetation consists chiefly of arctic tundra that forms a very effective cover on the steep slopes of the hills and the adjacent gently sloping river terraces. Willows with a maximum height of 15 feet and a trunk diameter of no more than several inches are in and adjacent to the major drainages.

In the area north of the Brooks Range the weather is cold and dry, and because of the low mean annual temperature permafrost is present at depths ranging from a few inches under the tundra-covered slopes to several feet on many gravel bars.

Much of the Southern Foothills belt is structurally complex and is characterized by west-trending isoclinal folds, thrust faults, and high-angle reverse faults. The thrusting, probably post-Cretaceous in age, has resulted in a maximum horizontal displacement of 75 miles to the north.

Underlying the north slope from the Brooks Range to the Arctic Ocean are mostly marine sedimentary rocks that range in age from Devonian through Quaternary. In this sequence only rocks of Pennsylvanian age are missing. In the Southern Foothills belt, rocks range in age from Mississippian to Early Cretaceous. The Mississippian through Jurassic rocks are dominantly black shale, chert, and black organic limestone, and the overlying Cretaceous rocks are dominantly beds of sandstone, grit, and conglomerate. The oil shales are contained in the Mississippian through Lower Cretaceous rock sequence.

The Mississippian oil shale submitted for assay by Tailleux in 1964 yielded only 6.7 gallons of oil per ton; therefore, during the 1965 reconnaissance oil-shale field study, no additional Mississippian samples were taken. In rocks ranging in age from Triassic to Early Cretaceous, however, several different types of oil shale were noted and sampled. These were:

- 1) *Tasmanite*.—Tasmanite is a woody-appearing oil shale that is a lustrous dusky brown on fresh fracture and a moderate brown on weathered surface. Tasmanite is composed almost entirely of a sporelike alga and is named for its occurrence in Tasmania. Frequently the Alaskan tasmanite

contains white bands that, by unaided eye, resemble quartzite but under high magnification is identified as diagenetic silica, which occurs within each alga. The Alaskan tasmanite also contains small quantities of barite. The tasmanite ranges in thickness from a few inches to 4 feet 7 inches and yields up to 160 gallons of oil per ton at the localities sampled. At one locality a sample of tasmanite that was 4 feet 7 inches thick yielded an average of 130 gallons of oil; however, the tasmanite at that locality is bounded by claystone barren of oil, which in turn is enclosed by a thick sequence of thin-bedded varicolored chert. In comparison, the richest 1-foot bed of the Rocky Mountain area oil shale in the Eocene Green River Formation yields about 95 gallons of oil per ton, and a maximum thickness of 2,000 feet of almost pure oil shale will yield an average of 15 gallons of oil per ton. Specific gravity of the richer tasmanite is 1.2 or less and it is commonly carried by streams to places many miles from the outcrop. Tasmanite probably is the material that has been found strewn along the beach bordering the Arctic Ocean. Tasmanite becomes highly contorted when subjected to high pressures possibly because of the high percentage of a single type of organic material; at most localities it occurs as elongate blebs or pods several feet long and a foot or two thick.

2) *A type of black oil shale superficially resembling the Green River oil shale.* This shale is dark brown to black on fresh fracture and locally weathers bluish gray. Microscopically the organic matter in this black shale ranges from red to reddish-brown fibrous-appearing material to black opaque material. Commonly it is interbedded with thin-bedded black organic cherts and limestones. At one locality thin units of black shale yield more than 50 gallons of oil per ton but at some other localities black shale units up to 20 feet thick yield an average of about 15 gallons of oil per ton. Black shale at one locality is 20 feet thick, relatively free of chert, yields an average of 15 gallons of oil per ton, and contains an average of 6,300 ppb Ag and 630 ppb Hg. Another sequence of black shale, 20 feet thick, consists of about 50 percent thin-bedded black limestone and chert, yields an average of 15 gallons of oil per ton and contains 1,500 ppb silver, 120 ppb gold, and abnormally high amounts of barium, copper and zinc.

3) *A type of oil shale locally called whale-blubber rock.* This type was found east of the Naval Oil Reserve and about 20 miles southwest of the Eskimo village of Anaktuvak Pass. This deposit is greatly valued by the Eskimos in the area as a source of fuel and the location was shown to the Survey field party by the chief of the Eskimos of Anaktuvak Pass. The material is black on both fresh and weathered surface, is extremely flexible, and closely resembles a piece of hard rubber. The largest pieces of shale were found along the stream bed, and were about 4 feet by 2 feet by 2 feet—

they probably weighed 200 to 300 pounds. The pieces almost invariably were covered with thin parallel to subparallel grooves that the Eskimos claimed were animal tooth marks. An abundance of fragments of this shale was found in a dominantly black fissile marine shale slope. Trenches were dug at several likely looking spots on this slope and large pieces of the shale were unearthed but it could not be determined with any degree of certainty that any were in place. Upon assay this material yielded 85 gallons of oil per ton.

Thin slivers of tasmanite and the whale-blubber rock were easily ignited and burned readily. The other black oil shales also could be ignited but only with the help of gasoline; however, once started they burned readily for a long period of time.

Specific gravity of the oil from Alaskan oil shale ranges from 0.70 to 0.97 at 15.6°C and most of the oil flows freely at temperatures near 0°C. The specific gravity of the oil from most of the tasmanite sample is less than 0.90.

In addition to the Fischer assays of the shales sampled, six-step spectrographic analyses were made to determine the elemental composition of the shale. Content of barium is unusually high in most all samples and is as high as 7 percent in a few samples. Unusually high concentrations of other minor elements were found. Some maximum concentrations are:

B.....	0.05%	Mo.....	0.2%
Cr.....	.1%	Ni.....	0.07%
Cu.....	.05%	Sr.....	.3%
Co.....	.02%	V.....	.15%
Pb.....	.02%	Zn.....	.5%

In addition to six-step spectrographic methods, more precise chemical analyses were run for gold, silver, and mercury. Maximum quantities found were:

Gold.....	350 ppb
Silver.....	20,000 ppb
Mercury.....	2,800 ppb

Amounts above 100 ppb for gold and 300 ppb for mercury are considered anomalous.

In general, an inverse relationship exists between the organic content and trace-metal content of the shale. However, many samples of tasmanite are very high in mercury and silver. One example is the sample of 4 feet 7 inches of tasmanite that contains 530 ppb silver and 1,820 ppb mercury.

Some of the Alaskan oil shales that are rich in both oil and trace metals would in another setting ordinarily be attractive industrially. However, because of adverse weather conditions, remoteness from market, estimated high cost of mining and processing, and last but certainly not least, the thinness and limited extent of the presently known deposits, initiation of any commercial oil-shale operation in Alaska in the foreseeable future is doubtful.

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FRACTURING OIL SHALE WITH ELECTRICITY

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ABSTRACT

Laboratory studies to evaluate the use of electricity for fracturing various grades of Colorado oil shale were started in 1964. Breakdown voltage requirements ranged up to several thousand volts and varied widely from one grade of shale to another. With few exceptions, the shale samples were readily fractured at relatively low current levels.

On the basis of the encouraging results obtained in the laboratory, experiments were expanded to a small-scale field project in an abandoned oil-shale mine tunnel near Green River, Wyo. The purpose of these experiments was to study electrical characteristics of oil shale when subjected to overburden pressure. In general, these tests confirmed the laboratory experiments. Fracturing was accomplished at all electrode spacings used. The spacings varied from 3 to 129 feet.

Based upon the results obtained in the mine-tunnel experiments, a test site 7-1/2 miles west of Rock Springs, Wyo., was selected for a larger scale field experiment. Fracturing tests were conducted in four shallow wells drilled in the oil-shale formation. Some new permeable zones were created but, in general, the induced permeability between wells was not up to desired levels. In an attempt to improve the induced permeability, two conventional nitroglycerin well bore shots were detonated in one of the wells. Air-injection tests made after the detonations showed appreciable improvement.

INTRODUCTION

Before an in situ retorting process can function, it is necessary to develop techniques to increase the permeability of the oil shale formation. Induced fracturing is the best method of increasing the effective permeability of oil shale deposits, and this may be accomplished by hydraulic pressure, high explosives, high-voltage electricity, or combinations of two or more of these. This paper covers the laboratory experiments and the preliminary field tests that are being made to study high-voltage electricity as a method of fracturing oil shale. Fracturing is the first phase of the electrocarbonization process and is the phase with which this investigation is primarily concerned.

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Several investigators have studied the electrocarbonization process as applied in coal,^{1 2 3} petroleum formations,^{4 5} and oil shale,^{6 7} but none of them has reported making field tests in Green River oil shale.

LABORATORY EXPERIMENTS

PRELIMINARY STUDIES

Laboratory studies to evaluate electrical properties of various types of oil shales were started in 1964. Samples used for the preliminary tests ranged in size from 2 to 175 pounds and represented a broad spectrum of Colorado oil shales ranging from 1.5 to 58.6 gallons of oil per ton. The first tests were made to determine the breakdown voltage required to initiate a current flow of five milliamperes through the sample. In all cases, 1/4-inch stainless steel tubes spaced four inches apart were used as the electrodes. Breakdown voltages varied greatly from one sample to another, ranging from a minimum of 300 to a maximum of 15,000 volts.

FRACTURING STUDIES

Establishment of Air Communication

After it was definitely established that fracturing could be accomplished, attention was directed toward other factors related to an in situ retorting process. The first of these was the establishment of air communication between two or more holes drilled at different locations in the shale block. Experiments were made on several shale blocks, in which three holes were drilled in a line and 1/4-inch perforated steel tubes were cemented into the holes. The holes were spaced two inches apart. The two end tubes (four inches apart) served as electrodes and one end tube and the center tube served as air injection and air outlet tubes. In most cases interconnecting fractures that permitted substantial amounts of air to flow between all three holes were created. In these experiments, the entire length of the steel tubes served as the electrode, and under these conditions the fractures occurred at random along the low resistance paths chosen by the electric current.

Controlled Fracturing

In order for an in situ retorting operation to be successful, a technique must be developed to create a system of horizontal fractures vertically spaced at preselected intervals. Accurate control of positioning the horizontal fractures is essential because the combustion process may require that the vertical spacing between fractures be as little as one or two feet.



FIGURE 1. — Piece of oil shale fractured by electricity.

In February 1965, experiments were initiated to investigate the feasibility of creating a controlled system of horizontal fractures. The electrodes used in these experiments were designed to concentrate the current at a small, well-defined contact point. In the first experiments, made with oil-shale slabs weighing 150 to 300 pounds, it was found that horizontal fractures could be induced at preselected levels vertically spaced at 3-inch intervals (fig. 1).

On the basis of these results, the experiments were expanded to a larger scale involving oil-shale slabs weighing several tons. The largest slab was a rich shale (55.7 gallons of oil per ton) which weighed approximately 7 tons (fig. 2). Two 1-inch diameter holes spaced four feet apart were drilled to a depth of 36 inches. In the first test the electrode contact points were positioned in these holes so that a fracture would be created at a depth of 30 inches. Application of 10,200 volts at one ampere created a horizontal fracture at the predetermined level. In the second test the electrode contacts were raised 10 inches above the first fracture and another fracture was attempted at this level.

Subsequent dissection of the slab revealed that during this test the current had followed a preexisting vertical fracture down to the first fracture 10 inches below, and most of the activity took place in this fracture. This behavior was observed in some of the previous experiments, but unless the

current is diverted by a preexisting vertical fracture, it will usually follow a serpentine path confined to one horizontal layer (fig. 3).

In the third test the contact points were raised another three inches and current was applied at this point. Current flow was started with 3,840 volts and gradually increased to 1.0 ampere with a potential of 6,480 volts. Within 20 minutes a fracture occurred at the predetermined level and the potential suddenly dropped to 660 volts for a current flow of 1.0 ampere.



FIGURE 2. — Placing electrodes in a 7-ton block of shale.

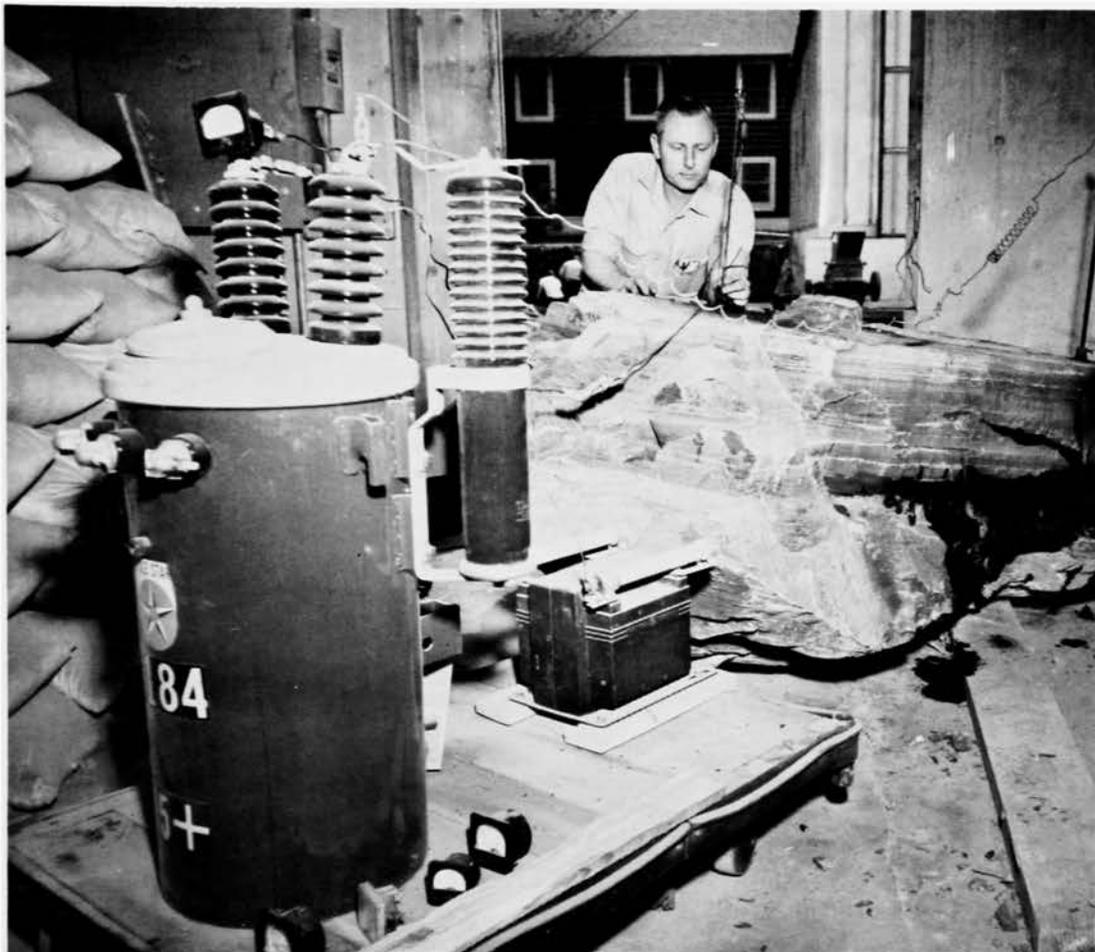


FIGURE 3.—Large block of shale dissected to show fracture plane and retorted oil produced by the electric current.

SMALL-SCALE FIELD TESTS

MINE-TUNNEL EXPERIMENTS

Laboratory experiments did not permit adequate spacing of electrodes or a means of studying the influence of overburden, natural fractures, or other natural surroundings that would be present in the field. In order to study these factors, some small-scale field experiments were made in an abandoned exploratory oil shale tunnel located 1-1/2 miles southwest of Green River, Wyo. The tunnel was relatively small, having a cross section of approximately 7 by 7 feet and a length of approximately 90 feet (fig. 4). The oil shale in this area is a lean shale (ranging from 11 to 19 gallons of oil per ton) located in the Wilkins Peak member of the Green River Formation.

Nine sets of horizontal boreholes were drilled into the sides of the tunnel. The holes were drilled in pairs in the same bedding plane; spacings between holes ranged from 3 to 58 feet. Another pair of holes was spaced at 129 feet; one of these holes was drilled in the back of the tunnel and the

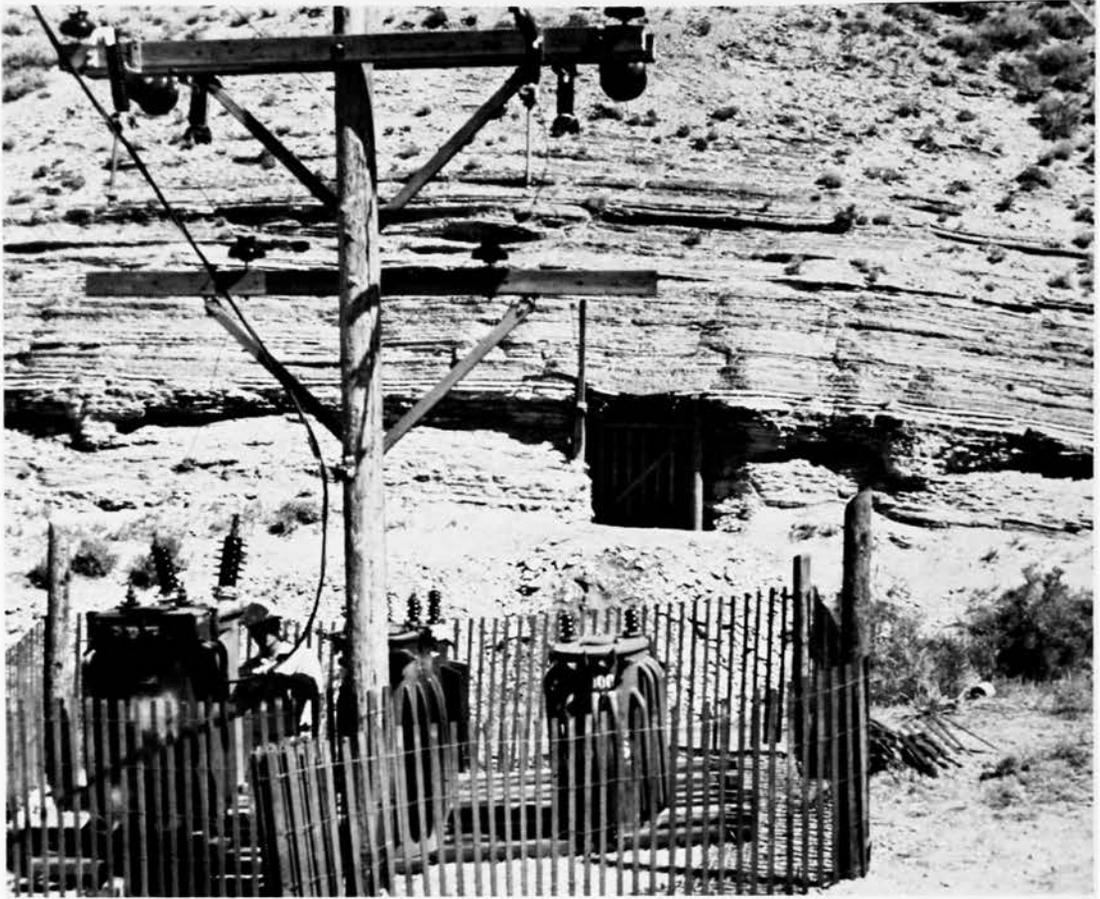


FIGURE 4.— Entrance to Green River mine tunnel with transformers in foreground.

other in the face of the cliff a short distance from the tunnel entrance. The overburden above the test area ranged from 43 to 53 feet.

Prior to the electrical tests, all of the holes were thoroughly cleaned. Visual examinations made with a borescope showed the holes to be in good condition with very few fractures.

The electrical installation (fig. 5) consisted of a 277-volt source with a safety switch and fuse, a low-voltage autotransformer, metering instruments, step-up transformer, output fusing, grounding switches, lines to the electrodes, and the electrodes themselves. The metering equipment consisted of appropriate current transformers, ammeter, voltmeter, wattmeter, and watt-hour meter on the input to the step-up transformer. Step-up transformers were available to provide the following nominal voltages: 1,200, 2,400, 4,160, 7,200, 14,400, 20,000, and 34,500 volts. By using taps and varying the input voltage a rather wide range of voltages was available for the tests. The electrodes were constructed with small contact areas that made intimate contact with the sidewalls of the 1-1/2-inch-diameter boreholes.

Current flow was obtained between all sets of holes, but in most cases electrical behavior differed from that previously observed in the laboratory.

In the laboratory experiments, when a fracture occurred it was usually accompanied by a sudden increase in current flow. In the mine-tunnel tests, the current flow gradually increased, but, with one exception, no sudden changes occurred. The one case in which a sharp break occurred was in the boreholes spaced 58 feet apart. In this case, the impedance started to drop immediately and at the end of four minutes had decreased from 35,000 to 2,000 ohms, at which point the power was shut off.

After the fracturing experiments were completed, all holes were cleaned and examined with a borescope. This examination revealed new horizontal and vertical fractures in all of the boreholes, particularly in the areas of the electrode contact points. The fractures in the two holes spaced 58 feet apart were created with a very small expenditure of energy and were apparently signaled by the rapid decrease in impedance values.

At the conclusion of the electrical experiments, air-injection tests were made to determine whether the induced fractures and carbonized paths would permit communication of air between the various pairs of holes. In general, the air-pressure tests were inconclusive because of excessive leakage through fractures in the tunnel wall. Definite air communication between holes was established in only three sets of holes.

Most of the experiments were made to accomplish fracturing only, but a few combination fracturing and carbonization tests were made to provide electrical paths that could be more easily traced. The area in which the carbonization experiments were made was mined out to determine the location and size of the carbonized paths. Most of these were not carbon paths but were paths of partially burned shale and retorted oil. Only one full-length carbon path was intercepted. This path was cylindrical in shape, about 1-1/2 inches in diameter and was located in a lean shale layer assaying 11.6 gallons of oil per ton.

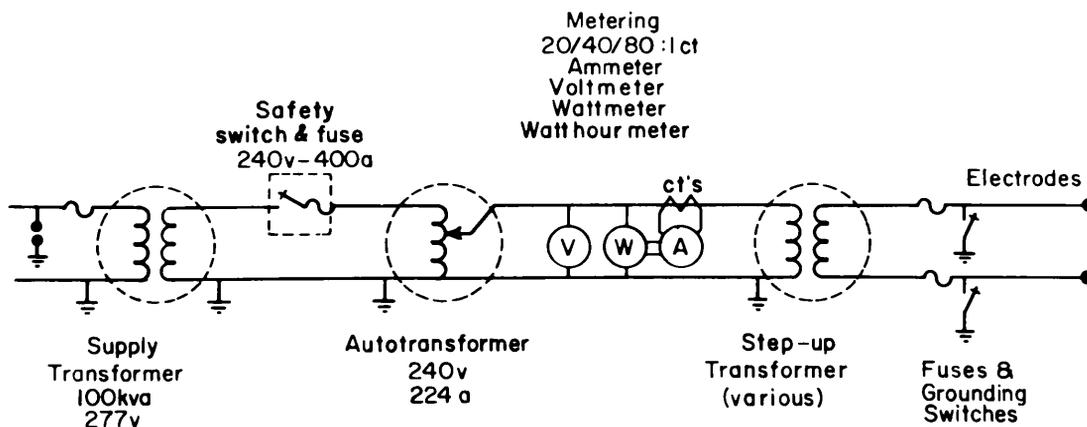


FIGURE 5. — Electrical installation at Green River mine tunnel.

The experiments in the oil shale tunnel were of value in supplying information concerning spacing of electrodes, power application, and changes in electrical resistance of the shale during the fracturing process. For example, during one fracturing test the equivalent impedance between the electrodes decreased from 100,000 ohms to 100 ohms. This wide variation of impedance became the controlling factor for the electrical tests. For example, when starting a fracturing test using 15,000 volts, with an equivalent shale impedance of 100,000 ohms, the current flow would be 0.15 amperes, and the power required would be 2.25 kva. When the equivalent impedance had dropped to a value of 100 ohms, a 15,000 volt source would supply 150 amperes, a power of 2,250 kva, which would greatly exceed the power source available. Therefore, as the shale impedance dropped, the voltage to the electrodes was lowered as required to stay within the limits of the capacity available.

At a constant voltage, the impedance of the shale gradually decreased with time. When the power was interrupted, however, the impedance of the shale increased somewhat, so that when power was reapplied, the impedance was higher than it was immediately before the interruption but lower than it was originally. It was also noted that a minimum power level was required to cause the equivalent shale impedance to decrease with time. If the minimum power requirement was not maintained, the shale impedance would gradually increase with time.

The steady lowering of impedance from the start of tests along a given path indicates a permanent change in this path between the electrodes, such as carbonization of the shale. But the small increase in the impedance from the end of one test to the start of the next (while the power is off) indicates that there is also was a temporary change. This could be due to loss of conductive materials evolved from the shale during power application.

SHALLOW-WELL EXPERIMENT

As a result of the mine-tunnel experiments, the field program was expanded to investigate electrical fracturing in shallow wells drilled in the Tipton member of the Green River Formation. The test site selected for these experiments is located 7-1/2 miles west of Rock Springs, Wyo. (fig. 6). Five wells were "spotted" in a pattern that permitted electrode spacings ranging from 25 to 112 feet (fig. 7). To avoid water problems experienced at a previous site, four of these wells were completed at a total depth of 80 feet. Water was encountered in the fifth well which was plugged and abandoned. Upon completion of the drilling operations, power lines were extended to the location, and the assortment of transformers previously

used at the mine tunnel were installed. Air-tight wellhead fittings, an air compressor, and flow measuring equipment were installed so that air communication between wells could be determined before and after the electrical tests.

A photographic survey of the wells was made with a Laval downhole camera. Pictures taken at 1-foot intervals showed the wellbores to be in very good condition with no visible fractures or cavities.

The electrical equipment above ground was very similar to that previously used in the mine tunnel, but several modifications were made in the downhole equipment. The electrodes were suspended in the hole on a string of standard 7/8-inch steel sucker rods which served as the conductor for current to the electrode. The electrodes were designed to provide small contact areas held in close contact with the wellbore by spring tension.

Fracturing Tests

Air-injection tests made prior to the electrical tests showed the presence of natural permeable zones that permitted large volumes of air to flow between wells. Because of this, only major improvements in permeability would be detectable.

The first series of tests was made on wells No. 1 and 3 which were spaced 90 feet apart. These tests were made to study the electrical characteristics of the shale in this area, and to determine whether fractures could be created

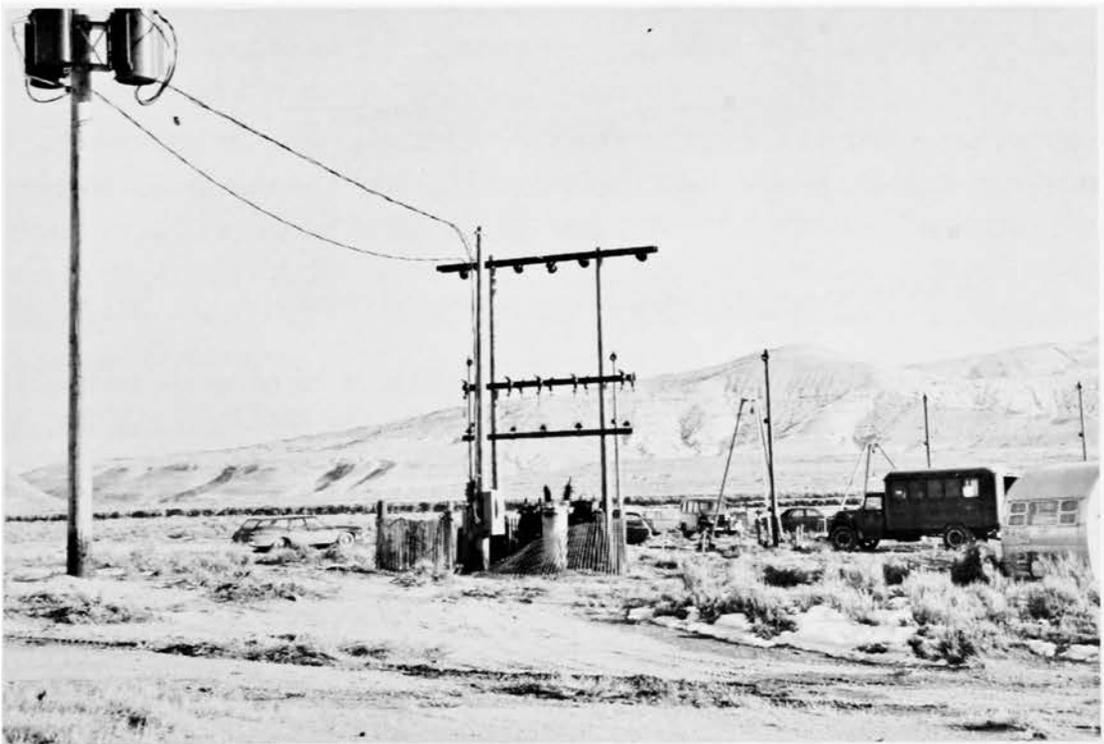


FIGURE 6. — Site of shallow-well electrical tests.

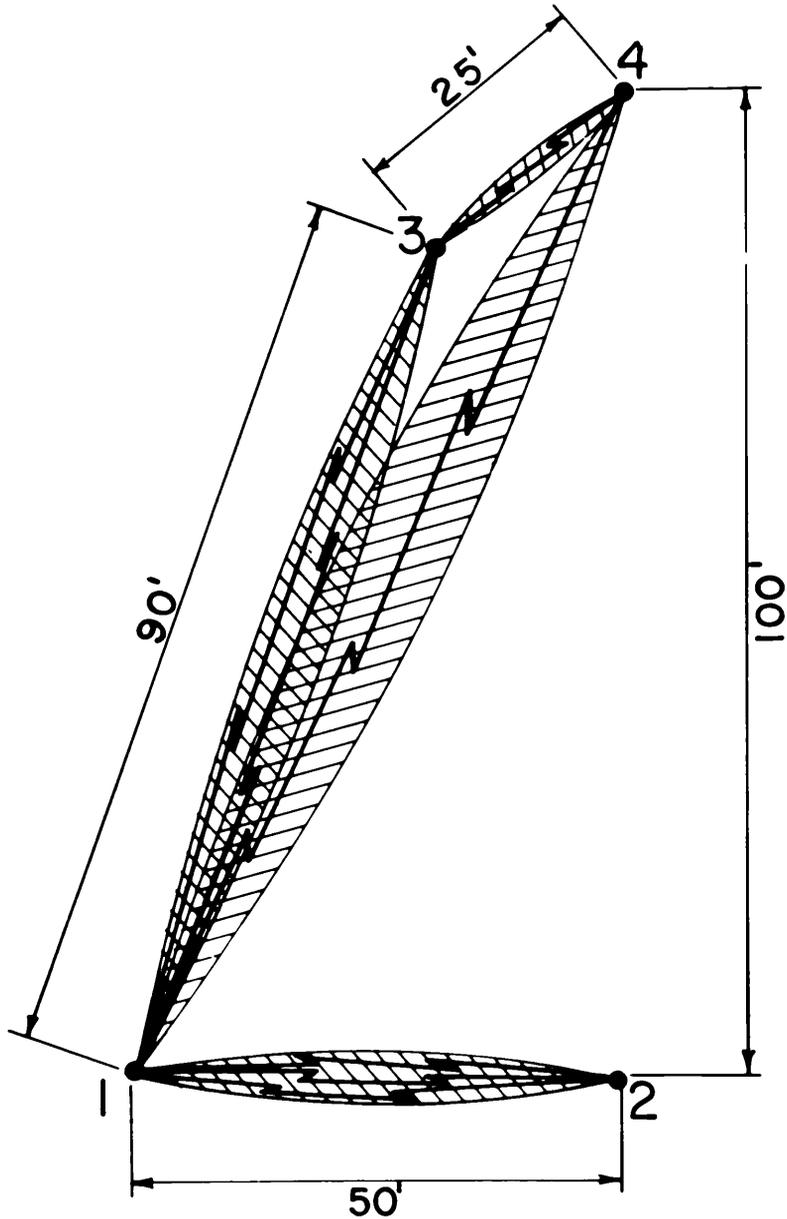


FIGURE 7. — Well pattern at electrical test site.

with a very small power input. Runs were made at three levels vertically spaced three feet apart. The tests were started with the electrodes set at the lowest level of 62 feet in well No. 1. Power application was limited to 30 minutes for each run. These tests revealed that much lower voltages would be required in this shale than in the shale in the tunnel.

A second series of tests was made on the same wells using the same electrode settings as the first series, but in this case it was planned to apply the power for a longer period of time at each electrode setting. At the lowest setting, 2,800 volts were applied for a period of 2-1/2 hours. Total power consumption for this run was 144 kwh.

The electrodes were reset at the next higher level where a much longer run was planned, but this test was terminated at the end of three hours by a violent explosion which blew the electrode out of well No. 1.

Air-injection tests following the electrical tests indicated that no major change had taken place in the amount of air communication between the two wells.

In order to evaluate the results of the next series of tests more accurately, all of the wells except No. 4 were plugged back to a depth of 60 feet to seal off the natural permeable zones. These zones were accurately located by means of air-injection tests with inflatable packers. Subsequent air-injection tests showed that in most cases air flow between the wells was reduced to zero.

After plugging back the wells, the first series of tests was made between wells No. 1 and No. 2, spaced 50 feet apart. Gas explosions were controlled by injecting carbon dioxide into the wells prior to each electrical test. The first test was made with the electrodes set at a depth of 54 feet, and was continued for a period of 5-1/2 hours. During this time the impedance dropped from 667 to 29 ohms, and 368 kwh of energy was consumed. The second test was made with the electrodes set four feet above the first setting. The initial impedance of this test was only 99 ohms which dropped to 33 ohms in less than an hour. This behavior suggests that the current did not follow the new path but dropped down and followed the previous path. The third run was made with the electrodes set at 45 feet. The electric current was applied for a period of 4-1/2 hours which resulted in a drop of impedance from 344 to 19.4 ohms. A total of 320 kwh was used for this test.

Following the electrical tests, downhole pictures were taken to observe changes that had occurred in the wellbores. The pictures revealed extensive damage and caved-out areas at the levels used for electrode settings. An electrode which was lost in well No. 2 during the first test appeared to be completely embedded in a solid mass of carbon which probably blocked any fractures in this area.

Air-injection tests made at 37 psig showed that both wells were still tight after the electrical tests. The wells were cleaned with kerosene followed by a detergent and water. This treatment slightly improved injectivity of air into No. 2 but had no effect on well No. 1. Both wells were then acidized with 15 percent hydrochloric acid followed by a detergent and water. This treatment had no effect on the injectivity of well No. 1 at injection pressures as high as 70 psig. When well No. 2 was subjected to a pressure of 70 psig after acid treatment, its injectivity increased so that a pressure of only 54 psig could be maintained at compressor capacity. The permeable zone in well No. 2 was isolated with packers and found to be at a depth between 43

and 45 feet which corresponds to the electrode setting during the last test made on this well.

The next tests were made on wells No. 1 and No. 4, spaced 112 feet apart which was the longest spacing available at this test site. All of the previous electrical tests were made in open holes, but this series of tests was made with the wellheads in place. After the electrode was in place, the attached sucker rod string was secured in a fixed position by an oil-saver packing box. Installation of the wellhead equipment provided a means of controlling explosions that might occur during the electrical tests (fig. 8).



FIGURE 8. — Wellhead with electrode in place.

Two runs were made with the electrodes set at a depth of 53 feet. Power was applied for a period of 3 hours during the first run and 10 hours during the second run. Total energy consumed during the two runs was 952 kwh.

Figure 9 shows the electrical characteristics of the shale during these tests. Note the extremely rapid drop in impedance at the start, from 115 to 37 ohms in only 6 minutes, accompanied by a rise in power from 66 to 194 kilowatts. As this approached the available power limit, an outage was necessary to lower the voltage. Also note that each time current application

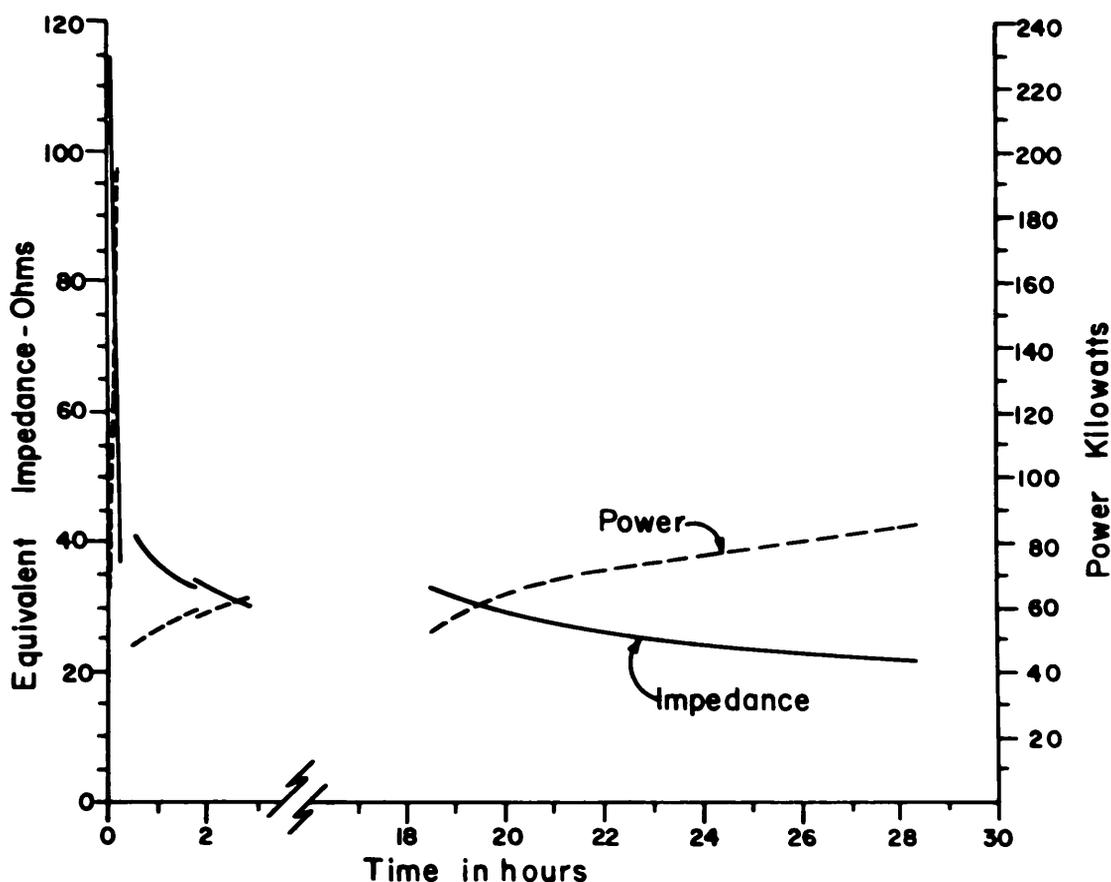


FIGURE 9. — Power and equivalent impedance versus time.

is interrupted the impedance increases slightly. The right-hand portion of the curve is typical of any sustained run at a given voltage. As time increases there is a slow, gradual decrease in the equivalent impedance and a gradual increase in the power due to increasing current.

The gas produced in well No. 4 was measured with a displacement meter attached to the wellhead. A total of 51 cubic feet of gas was produced during both runs, and contained 75.2 percent air, 12.2 percent hydrogen, 9.7 percent carbon dioxide, 2.5 percent methane, 0.3 percent ethane, and 0.1 percent hydrogen sulfide.

Air-injection tests made immediately after the electrical tests showed both wells to be almost completely sealed off. Both wells were cleaned with diesel fuel followed by water and a detergent. This treatment did not improve the air communication from well No. 1 to well No. 4, but when air was injected into well No. 4 it was found that air communication from it to well No. 2 was appreciably improved.

A double packer was used to locate the permeable zones in wells 1 and 4. This packer, which consisted of two inflatable sections connected by a section of perforated pipe, permitted isolation of the individual permeable zones

through which air left the injection well. The first attempt to run the packer into well No. 1 was unsuccessful because the packer would not pass the 53-foot level at which the electrode had been set for the electrical test between wells 1 and 4. Downhole photographs showed the wellbore to be badly damaged at depths between 52 and 55 feet. The well was reamed and redrilled to a total depth of 76 feet and packer tests were made to a depth of 70 feet. Increased permeability was found at all levels corresponding to the electrode settings. The tests in well No. 4 were not as conclusive because wellbore damage in the immediate vicinity of the electrode prevented a good packer seal, but a good permeable zone was found two feet below the electrode setting. The packer tests indicated that electrical fractures were created at the predetermined levels in the separate wells, but continuous air communication paths from one well to another were found to exist only at a depth of 45 feet. The discontinuity of the paths at the other levels might have been caused either by partial collapse of the fractures or by plugs of congealed shale oil or oxidation products.

An attempt was made to reopen the electrically induced fractures with nitroglycerin. Conventional wellbore shots were made at two levels in well No. 1. The levels corresponded to those previously used for electrode settings. The first shot was made with four quarts of nitroglycerin in a 2-foot shell set at a depth of 61 to 63 feet. The second shot consisted of an 8-quart charge in a 4-foot shell at a depth of 50 to 54 feet. The first shot was tamped with water and the second shot with sand. In both cases, the tamps were blown to atmosphere by the detonations, (fig. 10).

Following these detonations, air flow tests were made from well No. 1 to each of the other wells. Injection pressure was 37 psig. As shown in the following table, total air flows from well No. 1 to each of the other wells were appreciably increased.

<i>Air flow path</i>	<i>Air flow from production well, cfh</i>	
	<i>Before nitro shot</i>	<i>After nitro shot</i>
From #1 to #2	3.0	9.0
From #1 to #3	2.4	19.2
From #1 to #4	0	15.0

Packer tests were made to locate the communication channels, but due to damaged wellbores the tests were limited to wells 3 and 4.

The packer tests in well No. 3, which had been deepened to 76 feet, showed that the majority of the air was entering the well below 60 feet and the re-



FIGURE 10.—Water tamp blown to atmosphere by nitroglycerin shot.

mainder of the air was entering between 50 and 60 feet. Following these tests well No. 1 was plugged back from a depth of 76 feet to a total depth of 61.5 feet, and the air flow tests were repeated. Plugging back well No. 1 reduced the total flow from it to No. 3 from 19.2 to 14.4 cfh, but did not change the zones at which air was entering No. 3. This indicates that the flow between the two wells is in the bedding plane just above the top of the plug in No. 1, the same plane in which the fractures were induced by the initial fracturing experiment.

Although the width of the electrical fracture between wells 1 and 4 at a depth of 52 feet is not known, the fracture could have extended over an area that included well 3, thus explaining the air flow at this level.

CONCLUSIONS AND FUTURE WORK

Work up to the present time has shown that oil shale can be fractured at selected levels by the application of electrical energy. Fracturing was accomplished at all electrode spacings used. These ranged from 4 inches to 129 feet. The controlled fracturing was accomplished not only in the laboratory but also under actual field conditions. The initial electrical fracture can be further developed by conventional fracturing methods, such as hydrofracturing.

The next series of experiments will be conducted at a new test site where five wells have been drilled in a small, five-spot pattern measuring 25 feet on each side. Several changes will be made in the electrical procedure. The changes are expected to provide more precise control over the voltage and power levels in the shale. By having adequate control, the voltage can be set to just above the minimum level which will continue the reaction but prevent damage from overpowering, such as melting the shale and electrodes. This finer control will also assist in impedance evaluation.

Measurements of earth surface voltage gradients will be made to determine possible personnel hazards due to the current flow in the earth between the electrodes.

ACKNOWLEDGMENTS

Work covered in this paper represents contributions by personnel of the Bureau of Mines at the Laramie Petroleum Research Center, Laramie, Wyo., and the Bartlesville Petroleum Research Center, Bartlesville, Okla., and by personnel of Pacific Power and Light Co., who were assigned to the project to supply technical assistance for the electrical portion of the tests.

Appreciation is expressed to the Union Pacific Railroad Co. and the Rock Springs Grazing Association for permission to conduct the tests on their property.

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EXPLOSIVE FRACTURING TESTED IN OIL SHALE

J. S. MILLER and W. D. HOWELL

ABSTRACT

An explosive-fracturing experiment was performed in Green River oil shale near Rock Springs, Wyo., as a prelude to research on in situ retorting oil from the shale. The objective of the test was to determine if a liquid explosive displaced in a sheet-like layer and detonated in the oil shale would explode with sufficient force to significantly crack the rock. Although the evaluation of results from this research is continuing, preshot surveys and comparable postshot tests indicate that a charge of 190 quarts of desensitized liquid nitroglycerin, (NGL) was displaced a lateral distance of 22 feet at a depth of 147 to 149 feet and successfully detonated in the oil shale. Fracture-improvement ratios determined from before- and after-flow tests in six holes averaged 3.5.

INTRODUCTION

The broad purpose of the explosive-fracturing research is to improve the ultimate recovery from low-permeability oil and gas reservoirs, to improve the performance of underground natural gas-storage reservoirs and to create permeability in oil shale. This paper describes the latest development of an explosive method to obtain rock breakage, increase permeability, and support in situ retorting in oil shale.⁸ The test method is to introduce and displace a liquid explosive into a permeable zone, detonate and propagate an explosion through the thin zone, and thus create extensive fractures and breakage for in situ retorting of the shale.

Several papers and related patents^{2 3 4 6 7} pertaining to explosive fracturing are available in the literature.

The results of a field application of explosive fracturing were reported by Dowell Division of the Dow Chemical Company at a meeting of the American Petroleum Institute in April 1965. The "Stratablast" process uses a multiple-component system of hypergolic fluids that explode when combined in the formation. Dowell offers two blasting services for the petroleum and mining industry.⁹ One uses rocket-type fuels altered to behave as liquid

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explosives and the other employs a heavy slurry of metalized ammonium nitrate. The slurry has been tested in several oilfield applications.

A paper⁵ generally describing the explosive-fracturing research program and field testing was presented at the Third Conference on Drilling and Rock Mechanics in January 1967.

Few results and discussions have been reported on work relating to the theory of rock breakage by explosive forces in a confined environment. However, it is known that the detonation of an explosive in a densely packed hole can develop pressures in excess of 100,000 atmospheres. The accompanying shock wave may travel in rock at velocities from 3,000 to 5,000 meters per second. The heterogeneity of the rock may alter the velocity of the shock wave and create a series of shear stresses which in turn may crack the rock. Some cracks can be formed by the reflected shock waves changing the principal stress in the rock from compression to tension. A wedging action of the expanding gases tends to extend fractures simulating the mechanism in hydraulic fracturing.

The test method involves open hole completion, the placement of drillable materials near the detonation point and no steel tubular goods near the explosive zone. Liquid explosives are placed on the bottom of the hole and displaced from the wellbore in a sheet-like layer into a naturally fractured or permeable zone by steady hydraulic or pneumatic pressure. Confinement of the explosion to the zone is obtained by tamping the holes with either a water column, sand fill, or a cement plug. Detonation is accomplished by firing an electric cap and primer charge suspended in the wellbore adjacent to the NGI-impregnated zone.

EXPERIMENTAL PROCEDURES

The explosive-fracturing experiment was performed about 7½ miles west of Rock Springs, Sweetwater County, Wyo. The test site (fig. 1) was prepared by leveling an area 180 by 80 feet to remove the weathered shale. The dip of the formation is generally west at 4 feet per 100 feet.

A 5-spot pattern of holes was air drilled on 50 feet spacing to a depth of approximately 200 feet near the bottom of the Tipton member of the Green River oil shale formation. Holes 1 and 5 (fig. 2) were cored to a depth of about 280 feet to determine the thickness and oil content of the shale. Approximately 30 feet of 7-inch casing was set and cemented to the surface in the five original holes to exclude surface water.

Although oil shale has low permeability, several thin sandy zones, natural fractures, and water-bearing zones were encountered by drilling and coring through the oil shale formation. Water-bearing zones were found at about



FIGURE 1.—View of exposed oil shale at Test Site 3.

100 feet and 145 feet. Continuity of the permeable zones within the 5-spot pattern was determined by applying air pressure to the central wellhead and observing pressure increases in offset holes.

Detailed studies of the open-hole sections were made with Downhole Camera surveys. Numerous rings or grooves in the formation were observed in the stereoscopic pictures taken at various depths. Prominent washouts appeared from 145 to 149 feet. Caliper logs and Gamma Ray-Neutron logs were run on each hole to detect irregularities in wellbore diameters and to correlate formation lithology.

Although little work has been reported covering log analyses of oil shale, a study¹ conducted on Green River formation oil shale discusses the application of several types of logs to oil shale evaluation. The results of this study suggest a relationship between shale oil yield and neutron log response. These investigations note that a comparison of the neutron log trace with the assay oil yield indicates a definite qualitative response. A low assay oil yield gives high neutron response and a high assay oil yield gives low neutron response.

An attempt was made to apply this concept to the explosive-fracturing study through a correlation between neutron response and permeability.

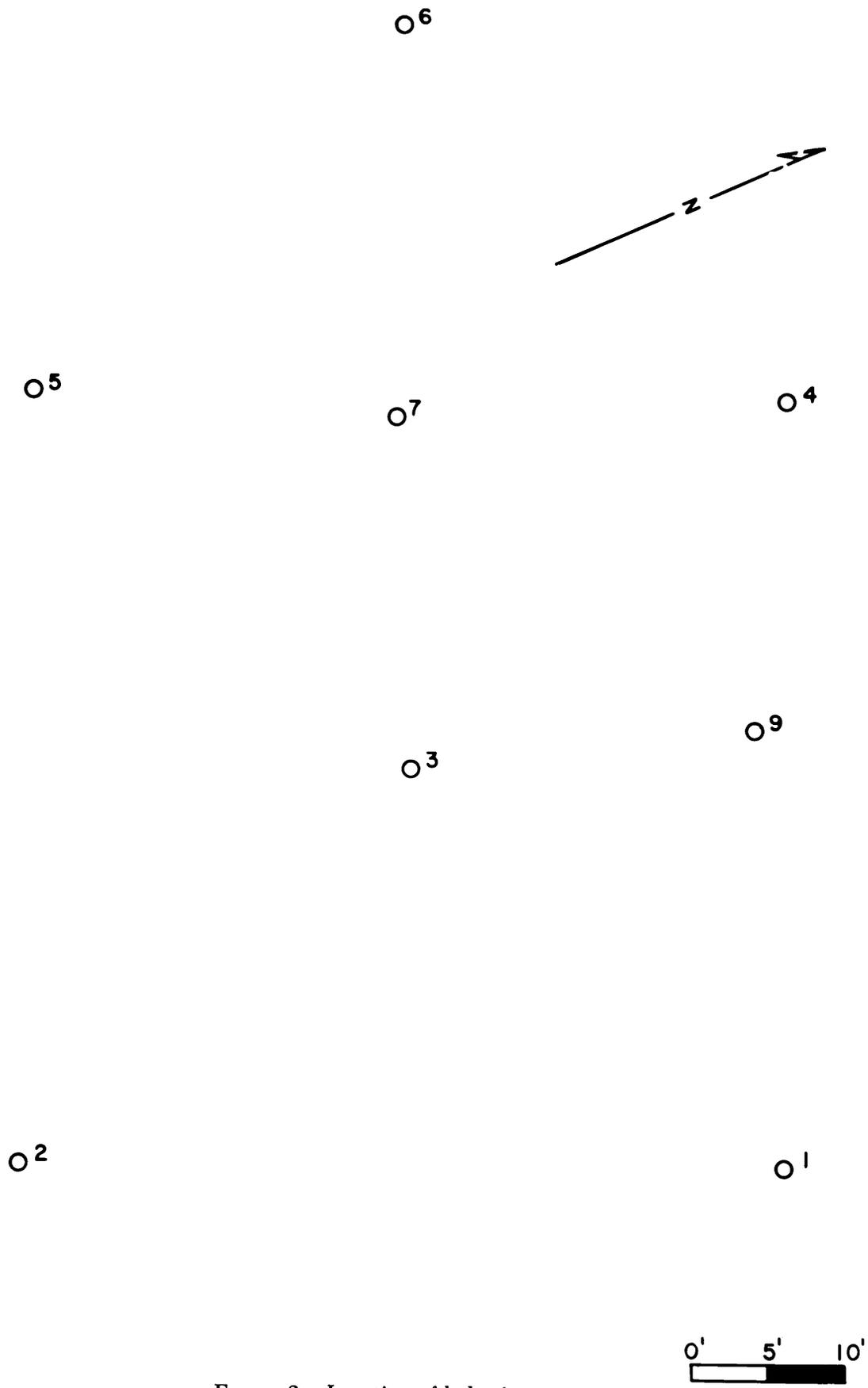


FIGURE 2.—Location of holes in test pattern.

The authors reasoned that low oil yield assay could reflect volcanic tuff, sand, clay, or other mineralized zones.

Neutron logs run on all original holes in the pattern showed a high neutron response at depths from 145 to 149 feet. Air-flow tests were run at 1-foot intervals by isolating zones with inflatable-stacked packers set on each hole from the bottom of surface casing to total depth. The results of the packer tests revealed good correlation with neutron-log response in that the most permeable zone, found in the 145-149 foot interval, coincided with a high neutron response on the log trace. Figure 3 presents this correlation. It was possible to correlate the zone for each hole in the pattern by this method. Authorities in the field of log interpretation are assisting with the evaluation of this concept in oil shale.

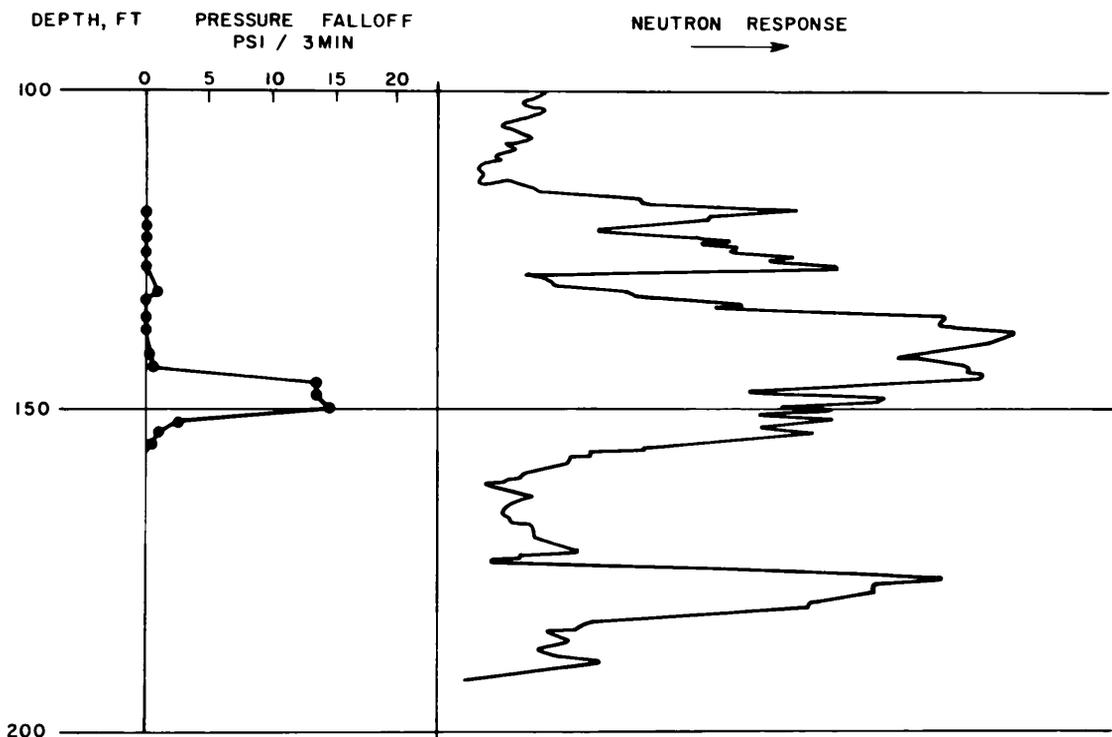


FIGURE 3.—Relationship between pressure falloff and neutron response, hole 5.

The data obtained from the air-flow tests indicated a permeability trend from southeast to northwest with evidence of increasing permeability in the northeast quadrant of the 5-spot pattern of holes. Three additional holes 6, 7, and 9 were drilled to 140 feet and cored to a depth of about 165 feet in this permeability trend as shown in figure 4. Caliper logs, Gamma Ray-Neutron logs, and air-flow tests were run on the additional holes to confirm the depth interval of the permeable zone in the original test pattern.

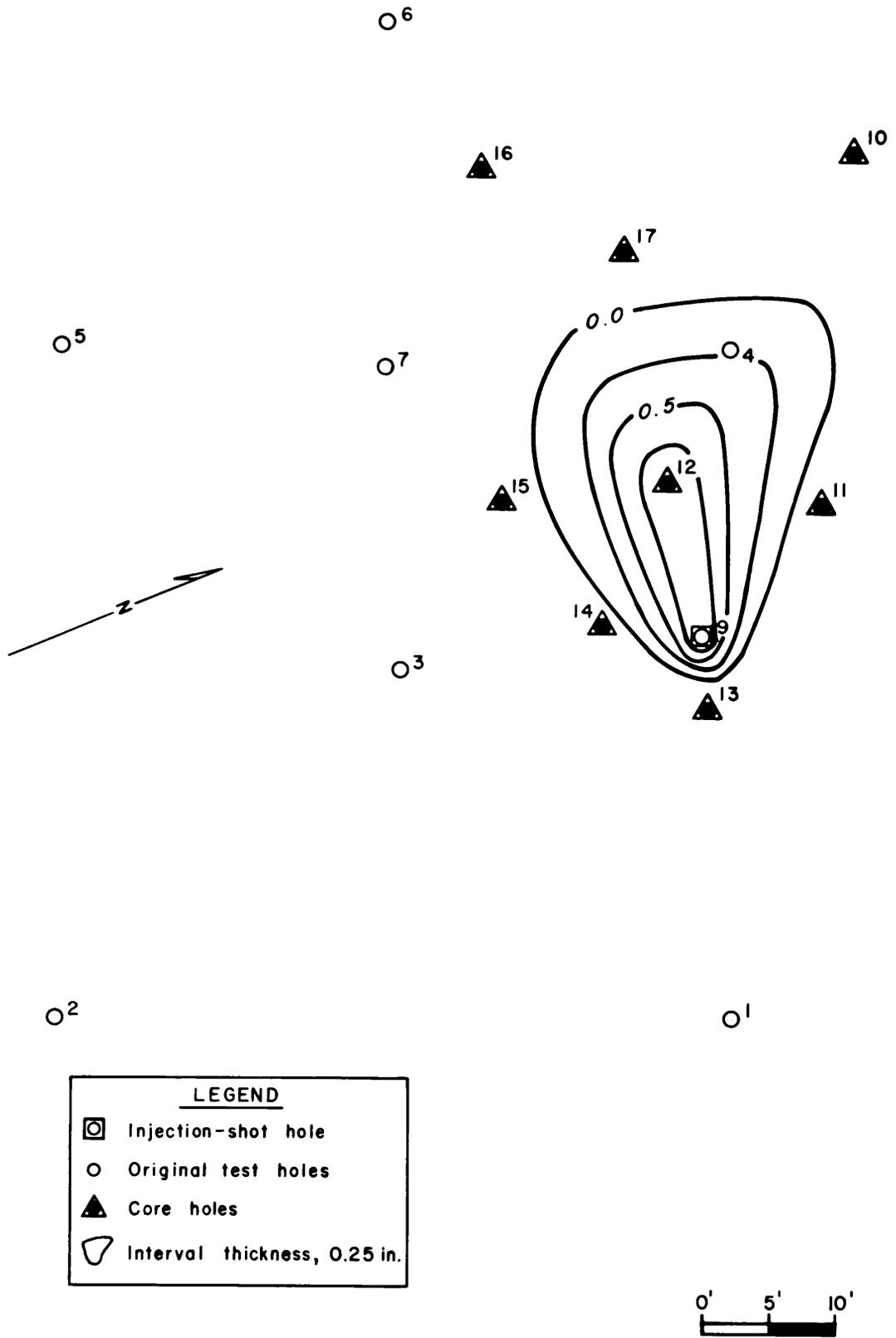


FIGURE 4.—Location of holes and probable configuration of displaced NGL.

To protect the permeable zone all holes were filled with fracture-propping sand to depths immediately above the zone of interest. A gypsum-cement plug was placed on top of the fracture-propping sand allowing the casing to be set directly above the permeable zone. The casing string consisted of one joint of 4-inch Fibercast pipe on bottom and 4-inch steel pipe from there to the surface. Self-shorting pins attached to the bottom of the casing and cemented in the test holes were intended to actuate the detonation velocity-measuring system. When exposed to sufficient impact these self-shorting or shock-sensitive pins act as switches in starting and stopping electronic counters as the explosion propagates from one hole to another. Experimental data on the effects from high- and low-order detonations under confinement should aid in interpreting future explosive-fracturing experiments. Cement was circulated through the casing to the surface. The cement plugs and sand were drilled out to approximately 151 feet. Final gypsum-cement plugs were placed to fill the holes to the approximate bottom of the exposed water-bearing zone.

The rate of formation water production precluded air-flow testing under dry hole conditions. Preshot flow tests were run on all holes in the pattern. Compressed air at 90 psig was injected into hole 9 during the test period. The pressure stabilized in the surrounding holes and air-flow rates were measured. Tests in hole 2 indicated no measurable communication with other holes in the pattern.

A charge of 190 quarts of NGI was poured through a hose into the injection shot hole 9. Except for hole 1, this hole was generally up dip from surrounding holes and was selected following a careful examination of data obtained during preshot testing. The NGI was displaced into the zone by a hydrostatic head of water and the NGI-water interface was monitored by a hydrometer. Offset holes were sampled continually during injection to detect NGI migration within the pattern. Samples indicated the explosive migrated a distance of 22 feet to hole 4 during the injection period. Air pressure at 15 psig was applied to displace the last 20 quarts of NGI into the permeable zone. All holes in the pattern were sand tamped from the top of the gypsum-cement plugs to the surface.

After the NGI was displaced into the zone, the detonating device in a shell containing seven 1/3-pound primers connected to an electric blasting cap was placed opposite the NGI-filled zone in hole 9. The 2-foot long by 2-inch diameter shell had an anchor on bottom and an umbrella on top. Crushed rock and pea gravel were dropped into the umbrella and the injection-shot hole was sand tamped to the surface. Figure 5 shows the assembled detonating device and umbrella. The shot was detonated by an electrical firing device from the laboratory truck.

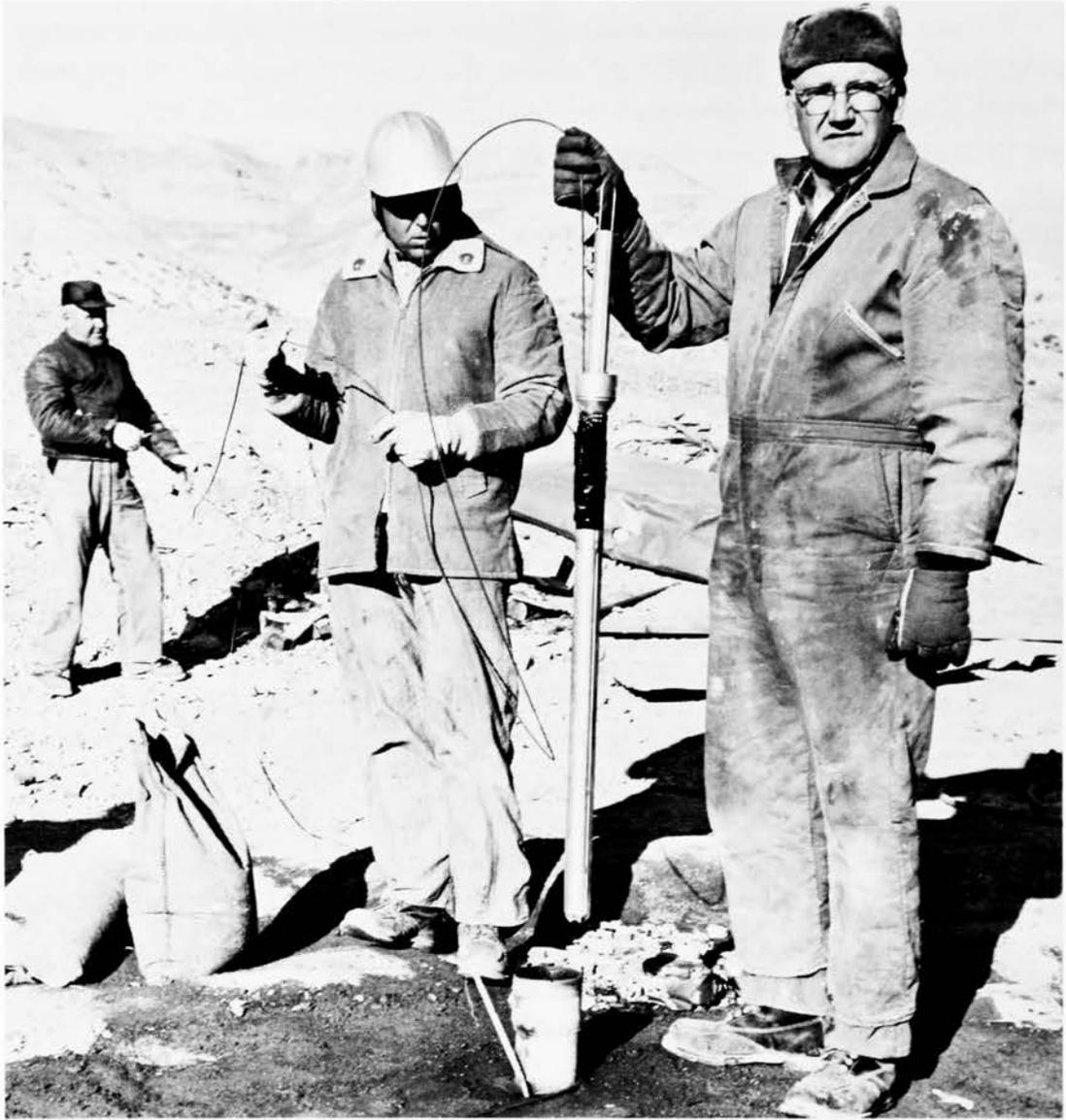


FIGURE 5.—Assembled detonating device and umbrella.

Detonation velocities of this contained shot were not obtained; it was concluded that the velocity-measuring system failed because of the protection of the cement sheath around the self-shorting pins and the distance between the explosive zone and the pin placement. Elevations run on the casing heads prior to, during, and after the shot indicated no lifting or crowning of the overburden as was experienced during a previous experiment.⁵

Following the shot all holes were cleaned to a depth of 160 feet prior to testing for fracture improvement. Attempts to perform air-flow tests were halted when the individual wellhead pressures stabilized below preshot values. Water produced from all holes following the shot contained a high concentration of solid material. The material was analyzed as bentonite containing approximately equal parts of swellable montmorillonite and a waxy clay.

Water injected into the holes at rates regulated to not exceed 30 psig was mixed with formation water to flush the loose bentonite from the explosively fractured zone. This washing procedure was successful in restoring the fractured zone to a condition suitable for testing.

EVALUATION OF RESULTS

It was determined impractical to control the movement and static level of water in the test area before and after the shot. Bailing failed to reduce the influx of water to permit satisfactory air-flow testing. Consequently, different static water levels in the holes during air-flow tests could have contributed to the high fracture-improvement ratio for hole 3, table 1.

After pressure stabilization was achieved, air-flow tests made from the injection-shot hole to test holes, Q_f , as compared to the preshot flow rates, Q_i , showed a fracture-improvement ratio, Q_f/Q_i , ranging from minus 0.9 to plus 11.1 and averaged 3.5. Flow rates were corrected to standard conditions at 14.73 psi and 60°F.

TABLE 1.—*Fracture-improvement ratio from air-flow tests*

<i>Hole, No.</i>	<i>Air Flow</i>				<i>Improvement Ratio Q_f/Q_i</i>
	<i>Preshot</i>		<i>Postshot</i>		
	<i>Mscfd at psia</i>		<i>Mscfd at psia</i>		
1	3.514	52.5	3.307	50.5	-0.9
3	1.169	57.0	12.914	86.5	11.1
4	59.249	52.5	59.791	53.5	1.0
5	1.040	38.5	2.707	41.5	2.6
6	3.216	67.5	15.946	59.0	5.0
7	1.348	36.5	2.805	43.0	2.1
				Av.	3.5

Data obtained from air-flow tests indicated that the blast effects extended at least to the peripheral holes at an approximate distance of 52 feet in the test area. These beneficial effects resulted from the shock waves and sudden liberation of about one million cu. ft. of gaseous products from detonating 190 quarts of liquid explosive. Cooperative efforts to study the seismic effects from confined underground explosions are being initiated.

An assumed configuration of the area in which 190 quarts of NGI was displaced into the porous zone is shown in figure 4. This configuration was

based on the premise that the NGL would occupy a zone varying in thickness from 1 inch at the detonation point to 0 inch at the outer boundary of the zone defined by coring.

Five preshot cores cut from holes 1, 5, 6, 7, and 9 showed no evidence of a bentonite zone, but core recovery was only 80 percent and may have prevented its detection. A punch-type core barrel capable of sampling and recovering more of the soft bentonite zone was designed and used successfully.

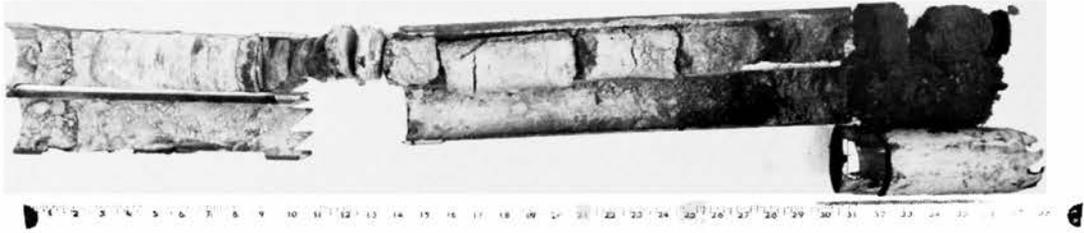


FIGURE 6.—Punch-type core barrel with blackened core indicating retorted shale.

A bentonite zone at a depth of 147 to 149 feet ranged in thickness from 8 to 12 inches. It was identified by the core recovered from hole 10 (fig. 6) and from Downhole Camera surveys in the 5-spot pattern. The core recovered from hole 12 located 12.5 feet from the injection-shot hole contained a blackened-unconsolidated interval immediately below the bentonite zone, indicating that the detonation caused crushing and shattering of the shale. Temperatures attained during detonation retorted a portion of the shale as shown in figure 6. Hydrogen sulfide and methane were detected in the recovered core and drill pipe. The unmeasurable volume of gaseous product, when ignited, burned with a yellow flame. Laboratory tests gave further evidence that temperatures of 750°F to 930°F occurred in the blackened interval during the NGL detonation.

Five additional holes 13 through 17 were drilled and cored at locations shown in figure 4 in an attempt to define the boundary of the blackened interval. Visual examination of the five cores revealed no retorted, crushed or shattered intervals such as that found in hole 12.

CONCLUSIONS

The displacement, confinement, and detonation of 190 quarts of NGL in contact with formation water in a permeable zone of oil shale formation were successfully accomplished at a depth of 147 to 149 feet. Fracture improvement attributable to the combined effects of the shot and subsequent water washing of solids from the shot zone was shown by increases of air-flow

rates across the test pattern. The fracture-improvement ratios averaged 3.5 for the six holes tested.

A relationship between neutron-log response and permeability was used to identify and select the permeable zone into which NGI was displaced.

Conventional coring techniques proved inadequate in recovering thin-porous, soft-unconsolidated bentonite and retorted oil shale zones.

Extensive postshot coring and clean-out operations revealed no evidence of liquid explosive.

The increased permeability obtained as a result of this experiment is a step forward toward the goal of fracturing oil shale to create permeability needed for the application of in situ combustion in underground retorting. This study revealed a need for further investigations into the areas of log interpretation, coring techniques, and fracture evaluation in oil shale.

ACKNOWLEDGMENTS

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THE CHARACTERISTICS OF A LOW TEMPERATURE IN SITU SHALE OIL

GEORGE RICHARD HILL and PAUL DOUGAN

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ABSTRACT

A 40° A.P.I. crude shale oil has been produced from the Green River Formation in the Piceance Creek Basin of Colorado by injection of hot natural gas at a controlled temperature. The quality of the shale oil differs very markedly from the customary shale oil from the same formation produced in a high temperature retort. The characteristics of the oil fractions have now been determined. These include distillation analyses, viscosity, and pour point determination.

Kinetic data on the production of the shale oil under the conditions used in the field, but carried out on a small scale in the laboratory, will be presented. A possible mechanism for the production of this oil, as well as a mechanism for the production of shale oil by more usual high temperature methods, is included.

TEXT

Various methods for the production of shale oil by in situ techniques are being investigated in the United States. The method with which this paper is concerned involves the use of hot natural gas as the energy conveying medium to convert the kerogen in the oil shale to a petroleum-like liquid. The basic concept, which was developed by the late J. L. Dougan of Equity Oil Company and tested in the Fuels Engineering Department laboratories at the University of Utah and subsequently field tested in the Piceance Creek Basin of Colorado, is basically a low temperature conversion and distillation process.¹ Natural gas is heated to a temperature below its thermal decomposition temperature and injected through an insulated pipe into the Green River Oil Shale formation where it loses its heat rapidly to the oil shale, gradually raising the temperature of the shale toward that of the injected gas. The kerogen is converted to bitumen and finally to a low pour point, high gravity crude oil.

Since the temperature of the natural gas is below that for thermal decomposition of the mineral carbonates in the oil shale, little CO₂ is produced.

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The natural gas is compatible with the oil, being soluble in it; this aids in the penetration of the formation by the natural gas and in the heat transfer. Since the heating gas is completely free from oxygen, no oxidation induced polymerization of the oil occurs.

Prior to the field experiment, oil shale cores from the Piceance Creek Basin were heated in a natural gas stream under two conditions. Some experiments were run at a gas pressure of 300 lb/sq inch. Experiments were also run with the gas at atmospheric pressure. In both cases it was demonstrated that the natural gas did, in fact, heat the oil shale to kerogen decomposition temperature and did convey the oil produced out of the retort and into condenser systems. Because of the large volume of gas used as a heating agent, the light ends of the produced shale oil were present at such low partial pressures that they were not condensed in the system available in the laboratory. The product was a waxy crude oil.

Subsequent experiments were carried out in non-flow systems or in systems using minimal amounts of natural gas or helium as a conveying agent. In these instances, yields of shale oil approaching 80 percent of the Fischer Assay yield of shale oil from the same cores, were obtained. Typical product evolution curves are shown in figure 1. In each case a relatively rapid, first

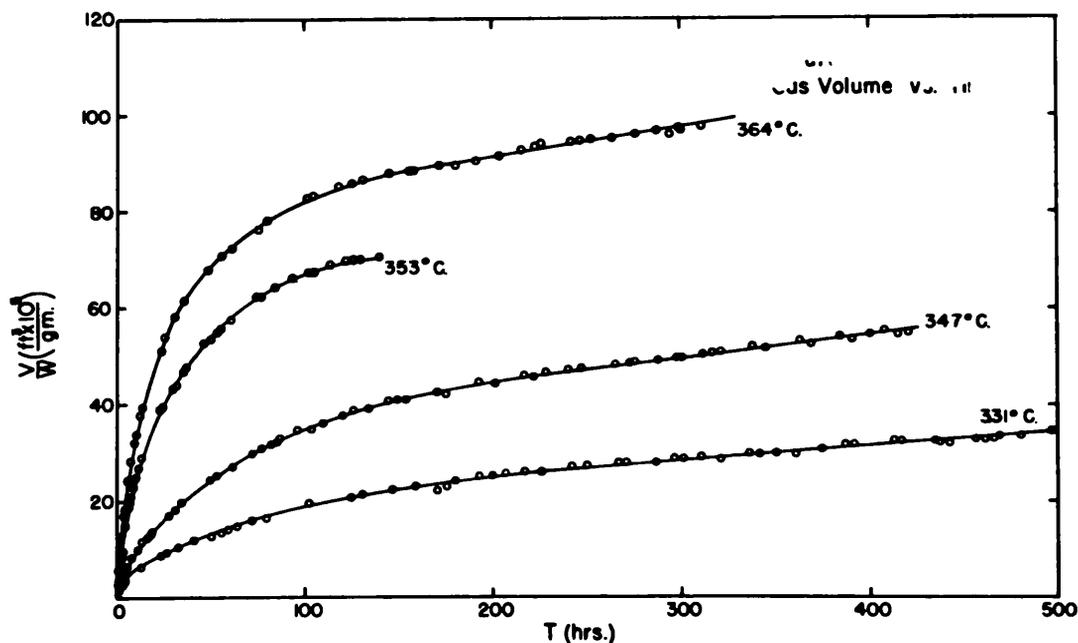


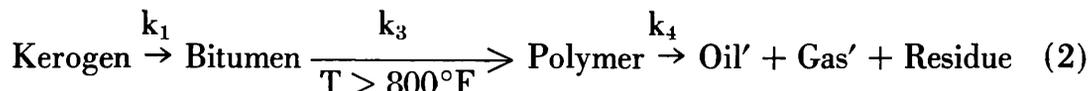
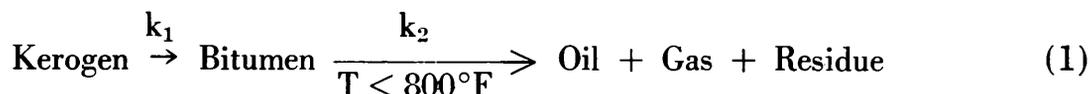
FIGURE 1.—Shale Oil Decomposition Isotherms.

order kerogen decomposition occurred followed by a zero order decomposition. Products continued to be evolved at a constant rate until finally almost all of the kerogen decomposable at that temperature had been evolved. The total distillate from these experiments had a pour point in the range of -20°C

and had an A.P.I. gravity of about 40°. The nitrogen content of the low temperature shale oil was less than 0.8 percent. Table 1 gives typical data on product yield and quality.

Since this shale oil differed so markedly from the shale oil produced by high temperature retorting methods, a careful analysis was made of kinetic studies on the production of bitumen and shale oil and gas recorded in the literature as well as of our experiments.

Based on these studies it has been concluded that two different mechanisms are possible for the production of shale oil from kerogen. These are indicated in equations (1) and (2).



Equation (1) involves rate constant k_1 for the conversion of kerogen to bitumen and rate constant k_2 for the production of oil, gas and residue from the bitumen, and is the path followed below 800°F.

Equation (2) describes the "high temperature reaction." This involves the production of a polymer, rate constant k_3 , from the bitumen or from the primary oil from reaction step k_1 . This polymer then decomposes thermally by step k_4 into a different type of oil plus gas and residue.

In the low temperature process kerogen is converted to an organic soluble bitumen in a first order reaction with an activation energy of between 40 and 41.7 kilocalories. This step was delineated by Zimmerley² in a temperature range of 525°-690°F, and by Hubbard and Robinson³ at the Bureau of Mines in temperature range 750°-890°F.

If the temperature remains low, i.e., below 800°F, the bitumen decomposes to give a paraffin-like oil with a rate constant k_2 the temperature dependence of which gives an activation energy in the range 42.5 to 48.5 kcal. The data used for evaluating rate constant k_2 and the activation energies were those of Hubbard and Robinson,³ of DiRicco and Barrick,⁴ and of Cane.⁵

If the sample of oil shale is heated to temperatures from 840°-1150°F which is a requirement if the oil is to be produced rapidly (as it must be in a retorting operation), the kerogen and initial oil are produced more rapidly than they can escape from the pores and matrix elements in which they are located. During the time of their confinement, they undergo many intermolecular collisions and polymerize to give thermo-dynamically more stable

products. As the heating is continued the polymer decomposes to give higher molecular weight products on the average than the primary oil. Typical high temperature retort oils have pour points of 80°F and A.P.I. gravities of 20°F.

The reaction with rate constant k_3 has an activation energy slightly higher than that of the reaction rate constant k_2 . We estimate this to be in the range of 48-50 kcal. The activation energy for this step is not determinable directly, however, due to the fact that when this path is followed mechanical diffusion of the oil from the pores in the oil shale becomes rate determining. The data of Hubbard and Robinson³ at high temperatures and of Allred and Nielsen⁶ have been used to evaluate the activation energy for the diffusion controlled slow step and it ranges, depending upon the experimental technique used, between 13 and 25 kcal. These data and other data from which activation energies in other temperature ranges were calculated are in table 2.

In the high temperature processes all of the kerogen undergoes decomposition. The nitrogen atoms become an integral part of the polymer and the thermal decomposition of this polymer gives products containing this nitrogen well distributed among the final product molecules.

Based on the experimental results we have concluded that the nitrogen in the kerogen is present in molecules of very high molecular weight which tend to remain in the shale at the decomposition temperatures below 800°F.

To test the polymerization mechanism concept, samples of primary distillate from runs at 750°F were heated to 930°F in closed vessels for periods of 0.5 to three hours. In each instance extensive polymerization occurred.

Subsequent to the laboratory experiments in which the high gravity, low pour point, low nitrogen crude oil was produced, the Equity Oil Company conducted a field experiment in the Piceance Creek Basin of Colorado. In this experiment several holes were drilled into the Green River oil shale. Hot natural gas was injected through a central hole and the gas was returned through the peripheral holes in the matrix. The natural gas was reheated and recycled. The observed variations in recycle efficiency are being studied. Following a period of injection which was sufficient to heat a section of the formation to the kerogen decomposition temperature, shale oil from the formation was collected in a separator on the site. Samples were brought to the Fuels Engineering Department laboratory at the University of Utah for testing and other samples were submitted to the Atlantic Richfield Company for evaluation as a petroleum refinery feed stock. (Data-Table 2-16)

The oil from the field experiment was found to be essentially identical with that produced in non-flow tests at comparable temperatures in the laboratory experiments.

In figure 2 we have a distillation curve for the field shale oil sample and for a typical gas combustion retort shale oil sample. Figure 3 is a G. L. C. temperature programmed chromatogram of the oil. Table 3 gives the pertinent information on the fractions collected from the atmospheric pressure distillation of the oil. Additional properties of the distillate are shown in tables 4 and 5.

Tables 6 and 7 give analyses of the light ends from propylene through the C_6 family. Table 8 gives the paraffin hydrocarbon analysis of the fractions. In table 9 are tested olefin hydrocarbons. Table 10 gives data on various alkylbenzenes, indans, and naphthalenes.

In table 11 are listed the product distribution for the furnace oil and gas oil fraction of the light oil.

In order to determine the suitability of the shale oil as an oil refinery feed stock, cuts one and two have been blended, debutanized, and hydrotreated

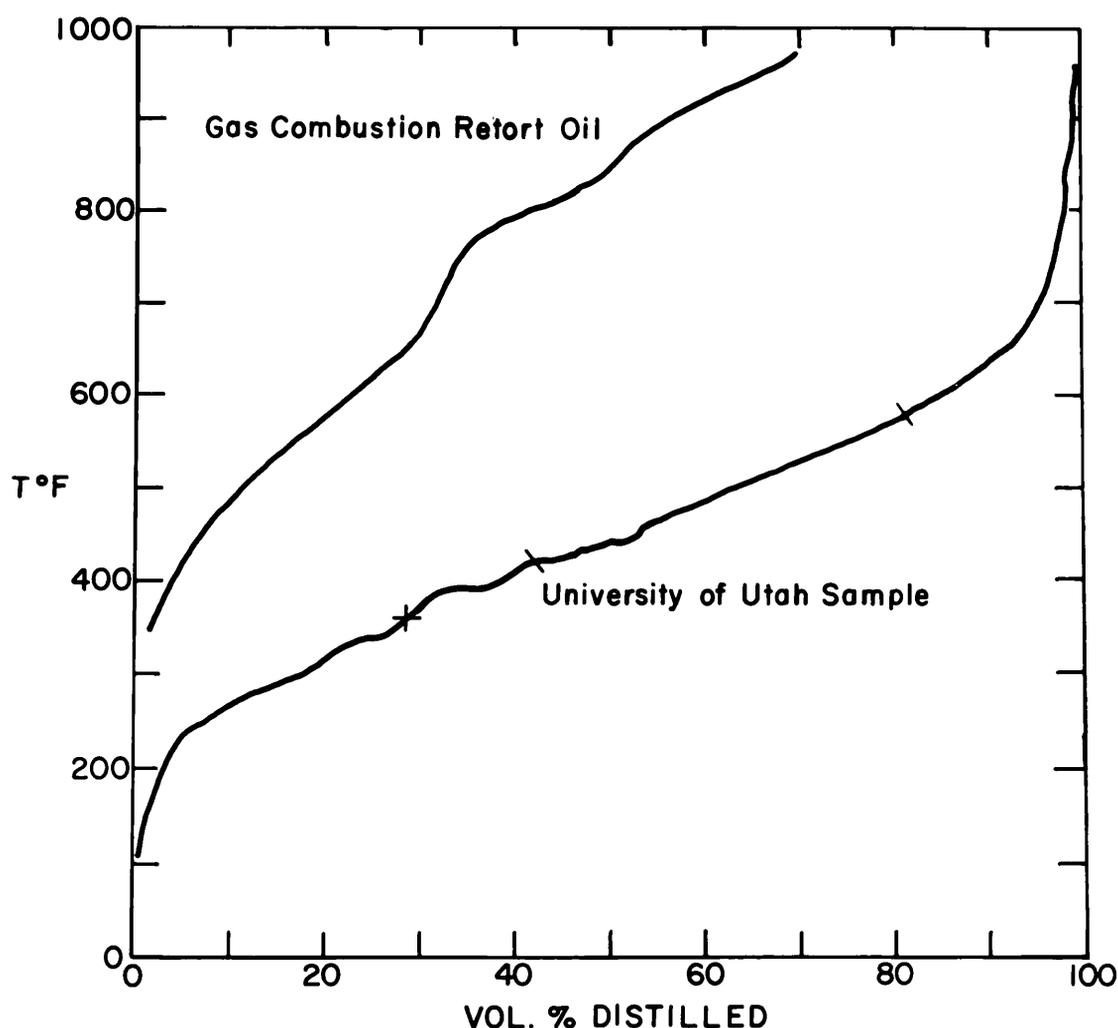


FIGURE 2.—Shale Oil Distillation Curves.

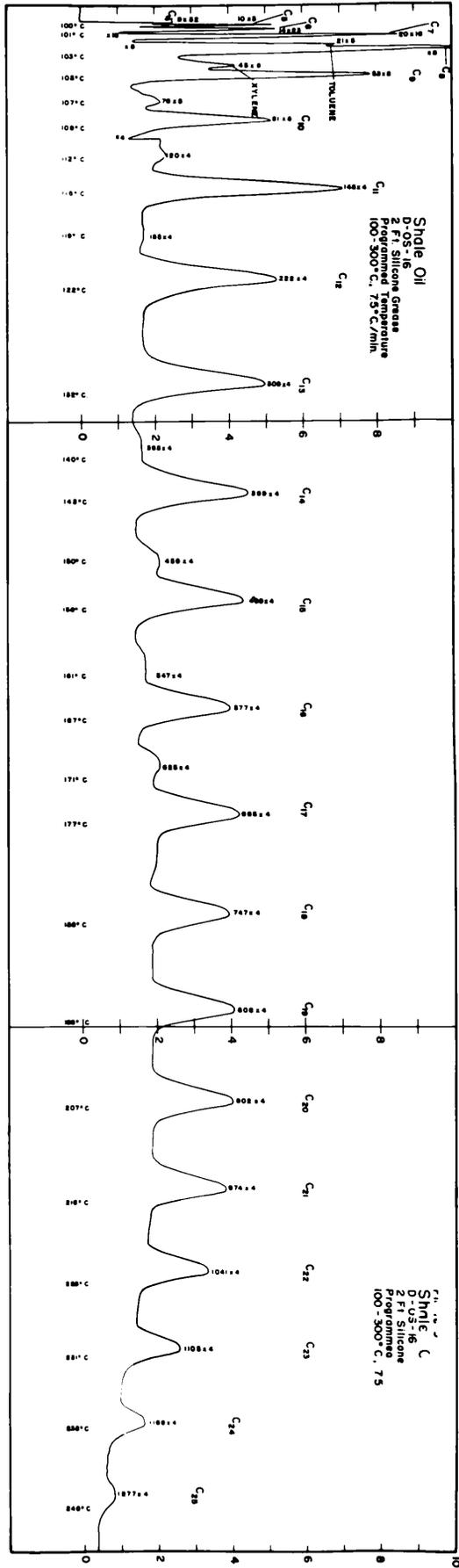


FIGURE 3.—Programmed Temperature Chromatogram of Shale Oil.

for olefin saturation and sulphur and nitrogen removal—all by calculation. In table 12 are given the data for the resulting pretreated reformer stock. This pretreated reformer stock has been fed into a reforming correlation using 350 lb/sq inch pressure; 7-1 hydrogen to hydrocarbon ratio; weight space velocity of 2; with Rd 150 catalyst. The results are given in table 13.

Table 14 gives the yield data from intermediate processing as percent of charge in a fluidized catalytic cracking unit. Table 15 is an evaluation of finished products from the standard catalytic cracking evaluation test of Atlantic Richfield. Table 16 completes the data from the laboratory catalytic cracking of Equity shale oil. Two conditions were used for each oil.

We conclude from these data that this oil should be hydrotreated prior to being cracked.

The ultimate analyses of three shale oil fractions are given in table 17.

SHALE RESIDUE

Microscopic examination of the shale residue following distillation unconfined and distillation of sample confined at 300 lbs/sq inch pressure show interesting results.

As the kerogen decomposes and volatilizes, voids appear to be left in the otherwise unaltered rock. These voids provide an interconnecting network and an internal porosity in the previously impermeable shale. The data in table 18 are new results from oil shale retorted under confining pressure. The final line in the table gives the data for the oil shale prior to treatment. These results confirm the important findings of Thomas⁷ of Sinclair Oil.

The porosity introduced corresponds very closely to the volume occupied by the kerogen prior to its conversion to oil. Undoubtedly the porosity and permeability introduced into the shale will be important in continued production of oil from the formation.

TABLE 1.—*Effect of temperature on oil, yield and quality*

<i>Temp. °F</i>	<i>Time (hours)</i>	<i>Oil yield % of F.A.</i>	<i>Oil gravity °API</i>	<i>Pour point °F</i>
628	550	33.6	40.7	−40°
657	425	40.4	40.5	−49
667	159	39.1	39.4	− 9.4
687	312	52.6	41.6	− 0.4
743	71.0	71.6	37.4	− 4.0
750	88.5	72.8	39.4	− 9.4
788	38.0	72.8	38.6	− 4.0
801	37.5	78.1	27.7	+23
801*	14.7	72.9	42.3	− 7.6

*1000 p.s.i.

TABLE 2.—*Energies of decomposition of oil shale kerogen*

<i>Author</i>	<i>R</i>	<i>R. D. Step</i>	<i>T Range °C</i>	<i>E_a</i>
Zimmerley	B	(k ₁)	275-365°	41.7
Hubbard & Robinson (U)	B	(k ₁)	400-475	40.0
Hubbard & Robinson (U)	O+G	(k ₂)	350-450 (52.6g/t)	46.2
Hubbard & Robinson	O+G	(k ₂)	400-450 (26.7g/t)	42.4
DiRicco & Barrick	O+G+B	(k ₁ , k ₂)	250-465	45.5
Cane	O+G+B	(k ₂)	350-400	48.5
Hubbard & Robinson (A)*	O+G	(k ₂)	429-477	40.5
Hubbard & Robinson (U)	O+G	(k ₂ , k ₃ , k ₄)	450-525 (52.6g/t)	27.0
Hubbard & Robinson (U)	O+G	(k ₃ , k ₄)	475-525 (26.7g/t)	19.0
Allred and Nielson*	O+G	(k ₃ , k ₄)	477-531	25.8
Allred and Nielson*	O+G	(k ₄)	531-616	13.6
This research	G		331-427	27.0
Hubbard & Robinson (U)	G		400-525	22.0

*In $\left(\frac{1-R}{R}\right) = -kt$; others are all $\ln(1-R) = -kt$ where $R = \frac{x}{\text{kerogen}}$

(U) Calculated at Univ. of Utah from data in reference.

TABLE 3.—*Equity shale oil distillate cut properties*

<i>Cut</i>	<i>Over-180°F</i>	<i>180-360°F</i>	<i>360-420°F</i>	<i>420-580°F</i>	<i>580°+F</i>
Crude Range Volume %	¹ 0.5-2.5	2.5-28.9	28.9-42.0	42.0-81.0	81.0-100
Crude Yield Volume %	2.0	26.4	13.1	39.0	19.0
Gravity-°API	73.7	52.9	43.8	36.6	30.3
Percent Sulfur	0.13	0.40	0.36	0.70	
Percent Nitrogen	0.01	0.16	0.37	0.36	
Research Octane 0 cc	²	42.5	38.9	—	
3 cc		56.9	51.4	—	

¹0.5 percent H₂O and gas²Octane on blends of cuts 1, 2 and 3 = 40.0TABLE 4.—*Equity shale oil distillate cut properties*

	<i>0-360°F</i>	<i>360°-580°F</i>	<i>580°-995°F</i>	<i>955°+</i>
Yield on Crude, Vol. Percent	28.5	52.4	18.4	0.7
°API	54.2	38.2	30.9	0.4
Sulfur, Wt. Percent	—	0.61	0.75	(High)
Nitrogen, Wt. Percent (Total)	—	0.36	0.75	—
CFRR, Oa Tel	40.5	—	—	—
Rams. Carb. Res.	—	0.13	0.17	—
Viscosity			{ 299 SSU @ 275°F 1900 SSU @ 210°F 65000 SSU @ 122°F	
RI at 67°C	—	—	1.47050	—
RI at 80°C	—	1.4635	—	—
Pour, °F	—	-15	60	—
Bromine #	—	17	10.7	—

TABLE 5.—*Equity shale oil distillate cut properties*

<i>Distillation</i>	0-360°F	360°-580°F <i>atm</i>	580°-955°F 10 mm
IBP		400	290
5		413	334
10		420	340
20		430	352
30		438	362
40		448	372
50	265	459	382
60		471	394
70		486	408
80		503	428
90	325	525	460
95		541	492
EP		564	530
Rec.		98	91

TABLE 6.—*Equity shale oil analysis*

<i>Cut</i>	<i>Over-180°F</i>
Propylene	0.1
Propane	0.4
AV Butylenes	0.1
i Butane	1.0
n Butane	4.2
Pentanes	2.0
i Pentane	5.7
n Pentane	11.7
Cyclopentane	
	Light Ends by POD

TABLE 7.—*Equity shale oil analysis*

	0-360°F
iC ₄ , Vol. Percent	0.1
nC ₄ , Vol. Percent	0.3
C ₅ 's Vol. Percent	1.3
C ₆ + P, Vol. Percent	63.4
C ₆ + N, Vol. Percent	25.1
C ₆ + A, Vol. Percent	9.8
C ₆ + Mol Wt.	124

TABLE 8.—*Equity shale oil analysis*

<i>Paraffins</i>	<i>Over-180°F</i>	<i>180-360°F</i>	<i>360-420°F</i>
C6	35.9	1.5	0.7
C7	15.1	7.6	0.5
C8		15.2	0.6
C9		19.2	0.8
C10		14.4	10.6
C11		2.9	33.2
C12			14.1

TABLE 9.—*Equity shale oil analysis*

<i>Cut</i>	<i>Over-180°F</i>	<i>180-360°F</i>	<i>360-420°F</i>
MCP	15.1	18.5	16.4
Monoolefin	3.6	3.3	2.3
DCP	0.1	1.5	0.2
CODA	1.3	2.6	
TCP			0.7
Cydiolefins	0.1	2.6	4.9

TABLE 10.—*Equity shale oil analysis*

<i>Cut</i>	<i>Over-180°F</i>	<i>180-360°F</i>	<i>360-420°F</i>
Alkylbenzene			
C6	3.1	0.3	0.1
C7	0.5	1.8	0.5
C8		3.1	0.9
C9		3.6	2.1
C10		1.0	3.9
C11		0.1	2.5
C12			0.5
Indans		0.3	3.6
Napthalene		0.4	0.9

TABLE 11.—*Equity shale oil analysis*

	<i>Furnace Oil</i> <i>360-580°F</i>	<i>Gas Oil</i> <i>580-955°F</i>
Volume % Crude	42.1	19.0
Analysis		
Normal Paraffin	31.5	0.8
Isoparaffin	13.8	38.3
Mono and non-condensed Cycloparaffin	18.8	15.3
Polycycloparaffins		2.3
Olefins	4.6	5.1
Mono Aromatics	25.0	21.6
Naphthalenes	5.6	8.5
Phenanthrenes	0.7	6.0
Benzanthrenes + 5 ringers		1.0
Chrysenes and Pyrene		1.1
Total Arom.	31.3	38.2
Mono Ar. in total percent	80.0	56.5
NP + IP	49.9	44.2

TABLE 12.—*Equity shale oil pretreated reformer stock*
(Blends of Cuts 1 and 2)

<i>Volume Percent</i>	
C ₅ 's	1.3
C ₆ + Paraffin	63.8
Napthalenes	25.1
Aromatics	9.8
54.2° API	
50 Percent at 285°F	
90 Percent at 325°F	
40.5 Clear Octane	

TABLE 13.—*Reformer product qualities (calculated)*

<i>C₅+F-1 0 cc</i>	85		90		95	
	<i>Wt</i>	<i>Vol</i>	<i>Wt</i>	<i>Vol</i>	<i>Wt</i>	<i>Vol</i>
H ₂	1.5		1.6		1.7	
C ₁	1.1		1.5		1.8	
C ₂	1.8		2.4		3.2	
C ₃	2.5	3.7	3.0	4.5	3.6	5.4
C ₄	2.4	3.2	2.9	3.8	3.4	4.5
C ₄	9.3		11.4		13.7	
C ₅ + API	47.1=.7923		45.3=.8003		43.1=.8104	
C ₅ +	90.7	87.2	88.6	84.4	86.3	81.1
C ₅ 's in C ₅ +	5.6		6.9		8.5	
C ₅ +RVP	2.5		2.8		3.3	
F-1 3 cc	95.5		98.4		101.2(W)	
F-2 0 cc	77.4		80.7		84.0	
F-2 3 cc	86.8		89.2		91.5	
St. Temp.	910		923		938	
BBL/# Lives- First Cycle	36		20		11	
BBL/# Lives- Ult.	150		85		45	

TABLE 14.—*Intermediate processing yields as percent of charge Equity shale oil*

<i>Process</i>	<i>Reforming</i>	<i>853 FCCU Cracking (Pace)</i>	
<i>Charge stock</i>	<i>Reformer stk.</i>	<i>“Normal” gas oil (taking virgin F.O.M. “as such”)</i>	<i>“Long” gas oil (includes virgin F.O.M.)</i>
" Cut pts.	0-360°F	580-955°F	360-955°F
" % Crude	28.54	18.55	70.95
<i>Products</i>			
Hydrogen (SCF/B)	614.6	—	—
Therms/Bbl.	2.21	4.06	1.50
Propane	5.34	3.75	3.45
Propylene	—	5.00	3.00
n-Butane	2.89	1.50	1.95
i-Butane	1.78	3.15	4.65
Butylene	—	.95	1.60
Gas. Comp (C5+)	84.85	46.30	43.60
F.O.M.	—	33.70	41.10
<i>Gas. Comp. Properties</i>			
RON—0	85.00	91.91	80.92
RON—3	95.23	97.65	87.20
MON—0	77.93	82.38	75.07
MON—3	88.09	87.48	80.01
RVP	3.26	4.37	4.62

TABLE 15.—*Standard catalytic cracking evaluation-finished products Equity shale oil*

	<i>Virg. FOM as FOM</i>	<i>Virg. FOM to GO</i>
Reg. Gasoline, B/B of Crude	.384	.660
FOM, "	.588	.291
Plant Fuel, "	.030	.029
#6 Fuel, "	-.023	-.023
Propane, "	.022	.038
n-Butane, "	-.031	-.038
Hydrogen, MCF/B	(.25)	(.23)
Gas, Therms/B	(3.6)	(5.0)
Gas and Loss	.030	.043
Total	1.000	1.000

TABLE 16.—*Laboratory catalytic cracking of Equity shale oil*

	360-580°F	<i>Furnace oil</i>	580-955°F	<i>Gas oil</i>
430°F Conversion—				
Vol. Percent	21.6	29.7	26.6	38.3
Wt. Percent coke	3.4	4.4	5.7	7.7
Wt. Percent C ₃ and lighter	2.1	3.8	3.5	5.1
Vol. Percent C ₄ 's	2.9	5.5	4.6	7.0
Vol. Percent C ₅ to 430°F	40.4	39.5	16.3	22.5

TABLE 17.—*Equity shale oil fractions ultimate analysis*

<i>Fraction</i>	<i>S</i>	<i>O</i>	<i>C</i>	<i>H</i>	<i>N</i>	<i>Carbon Residue</i>
Gasoline (<354°F)	0.52	0.64	85.4	14.1	0.5	0.1
Kerosene (354-473°F)	0.72	0.75	83.6	13.3	0.8	1.3
Residue >473°F	0.67	0.55	86.2	12.8	1.1	2.0

TABLE 18.—*Retorted oil shale under confining pressure*

<i>Time</i>	<i>Retort</i>	<i>Volume</i>	<i>Weight</i>	<i>Induced Permeability</i>		
<i>Above</i>	<i>Temp.</i>	<i>Change</i>	<i>Loss</i>	<i>Induced</i>	<i>Plug Md.</i>	<i>Whole</i>
<i>650°F</i>	<i>°F</i>	<i>%</i>	<i>%</i>	<i>Porosity</i>	<i>Core Md.</i>	
<i>Hours</i>						
48	805	+3.2	15.32	28.4	0.3	46
48	799	+1.9	16.28	26.8	0.1	128
40	800	+2.7	15.38	27.6	0.1	197*
0	75	0	0	0.8	0.0	0

*Cleavage parted core completely

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SHALE OIL DEVELOPMENTS: KINETICS OF OIL SHALE PYROLYSIS

V. DEAN ALLRED

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Colorado oil shale consists of organic matter embodied in an inorganic matrix. This organic material is a complex mixture with an ultimate analysis of about 76 percent carbon, 10.5 percent hydrogen, 9.5 percent oxygen, 2.6 percent nitrogen, and 1.4 percent sulfur.^{1 2} Although largely insoluble in common organic solvents, it does have soluble and insoluble fractions. However, the soluble material normally amounts to only about 8 to 10 percent by weight of the total organic matter present.³ The soluble fraction is often called natural bitumen while the insoluble fraction is commonly referred to as kerogen.

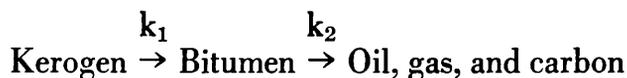
Upon heating, the organic materials—both the natural bitumen and the kerogen—decompose into water, carbon dioxide, liquid hydrocarbon, and a carbonaceous residue. A typical oil shale (26.7 gal/ton assay) will yield, upon heating at about 900°F, the products shown in table 1.

TABLE 1.—*Pyrolysis products from Colorado oil shale (3)*

<i>Material</i>	<i>Weight percent</i>	
	<i>Total shale</i>	<i>Organic portion</i>
Solids (ash)		
Devolatilized shale	83.5	—
Carbonaceous matter	2.2	13
Subtotal	85.7%	13%
Vapors (volatile matter)		
Water	1.4	9
Gases	2.5	15
Oil	10.4	63
Subtotal	14.3%	87%
Grand total	100%	100%

Marathon Oil Co., Littleton, Colorado.

The mechanism and rate by which the pyrolysis of oil shale takes place has naturally been of considerable interest and has been investigated on occasion during the past fifty years.^{3 4 5 6} However, with the very complex nature of the organic matter, the unraveling of these kinetics has not been a straightforward matter. Generally, past investigations have led to the conclusion that upon heating kerogen decomposes by a consecutive reaction into bitumen which in turn decomposes to form the final products of oil, gas, and a carbonaceous residue on the spent shale. This can be represented as follows:



Further, the reaction rate has generally been treated as though it were first order with respect to the concentration (weight fraction) of kerogen in the formation of bitumen and also first order with respect to pyrolysis of bitumen in the subsequent formation of oil and gas. However, critical examination of some of the data, particularly that of Hubbard and Robinson, seems to indicate that this is not the case and that actually a more complex mechanism is involved.³

COMPONENTS OF PYROLYSIS

With regard to the work of Hubbard and Robinson, it is a particularly significant investigation and these men are to be complimented on their experimental work. Of particular interest is their data for the formation of the various components of pyrolysis, *e.g.*, the bitumen, oil, and gas with time and temperature. However, it is somewhat unfortunate that they did not carry their evaluation a little further and calculate the amount of kerogen remaining and the carbonaceous residue formed, since these data can be obtained from a simple material balance.

A critical examination of their data yielded the following observations:

(1) The weight fraction of the total kerogen appearing as bitumen plus oil and gas became constant at the time the bitumen concentration reached a maximum. This was interpreted to mean that little or no carbonaceous matter was formed after this time. It was also interpreted further to indicate that at this point all of the kerogen has been converted to bitumen, gas, and carbonaceous residue.

(2) The weight fraction of oil and gas combined at the point of maximum bitumen concentration was nearly equal to the weight fraction of bitumen disappearing. Therefore, about one-half of total product was produced during

this latter time period. This indicated that the kinetics of bitumen pyrolysis should be directly related to the appearance of volatile matter during the last half of the reaction.

MATERIAL BALANCE

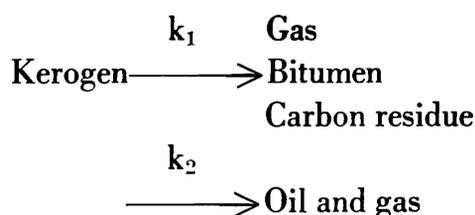
Based on these observations the amount of kerogen and carbon residue can be directly calculated from a simple material balance as follows:

$$W_T = W_K + W_R + W_B + W_O + W_G \quad (1)$$

where W_T is the weight of total organic matter, W_K is the weight of kerogen at time t , W_R is the weight of carbonaceous residue at time t , W_B is the weight of bitumen at time t , W_O is the weight of oil at time t , and W_G is the weight of gas at time t .

$$\left[\frac{W_K}{W_T} + \frac{W_R}{W_T} \right] = 1 - \left[\frac{W_B}{W_T} + \frac{W_O}{W_T} + \frac{W_G}{W_T} \right] \quad (2)$$

The right-hand portion of equation 2 was available from the experimental data, therefore the amount of solid insoluble matter (kerogen and carbon residue) as a function of time could be readily calculated. With the simple assumption that the decomposition of kerogen and appearance of the carbon residue each follows the same type of function, a set of curves representing them individually was drawn. Figure 1 shows such curves. This readily lead to the following mechanism for the pyrolysis of Colorado oil shale:



EXPERIMENTAL TECHNIQUES

To check these observations experiments were conducted using a thermogravimetric analysis (TGA) technique. Application of this technique to oil shale has been previously reported.⁷ For this particular study it was desirable to bring the sample to temperature as rapidly as possible. This was accomplished using finely ground samples of (-100 to +115 mesh) Colorado oil shale in an aluminum foil sandwich which were placed in a preheated furnace.

Different sizes of samples, for example, 0.25, 0.50, 1.00, and 2.00 g, were used to determine the effect of sample size. The rate of devolatilization would be independent of sample size if the material could instantaneously be

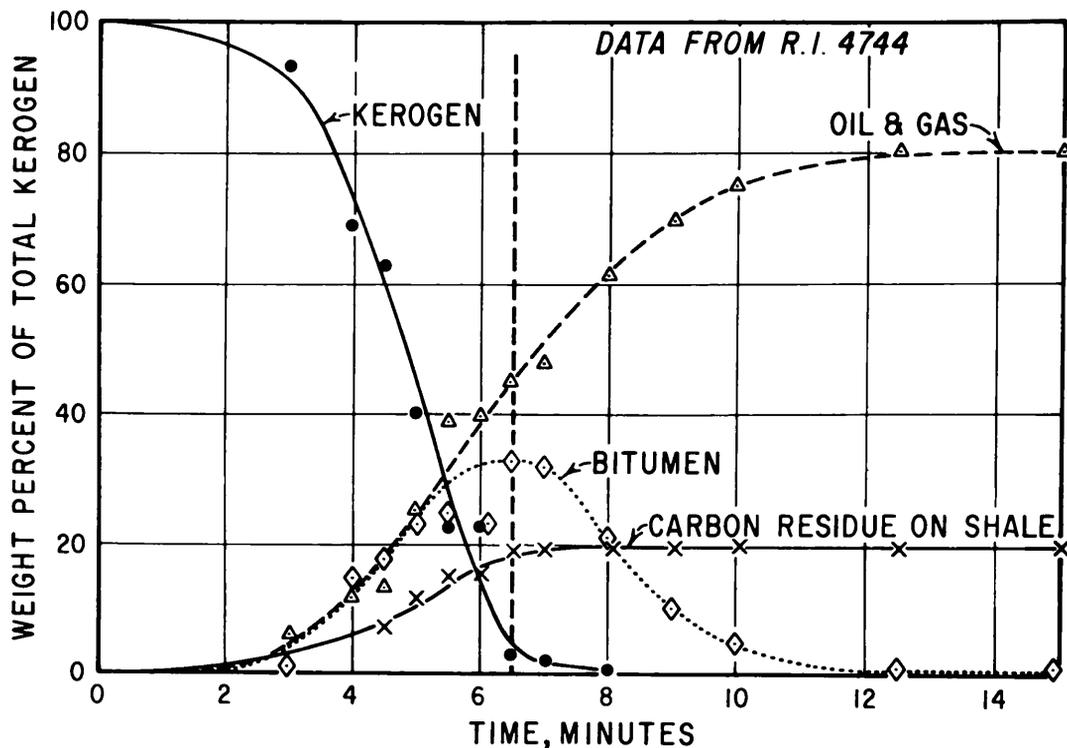


FIGURE 1.—Data showing the rate of disappearance of kerogen and formation of carbon residue on the spent shale.

raised to a given temperature. Since this was not possible, it was believed that by plotting the observed rate constants as a function of sample weight and extrapolating the curve to zero the effect of heat transfer time on the rate constant could be minimized. Some effect was noted due to sample size, however, in general, it was in the same order of magnitude as experimental reproducibility of the rate constants between samples of the same weight.

STEADY-STATE CONSIDERATIONS

The TGA technique was used to develop steady-state pyrolysis data as well as getting kinetic data since it was felt this information was basic to understanding the mechanism of oil shale pyrolysis. The term steady-state pyrolysis data may be somewhat misleading since pyrolysis reactions normally go irreversibly to completion. However, Colorado oil shale does not seem to completely devolatilize until temperatures of about 880°F are reached. That is, for temperatures below this value the extent of volatile matter removed seems to approach a weight loss plateau characteristic of that temperature.

Figure 2 schematically shows this behavior. Upon raising the temperature the shale again lost weight until another pseudo steady-state plateau was reached. From a series of such determinations, data by which a curve showing weight loss as a function of temperature can be determined. Another

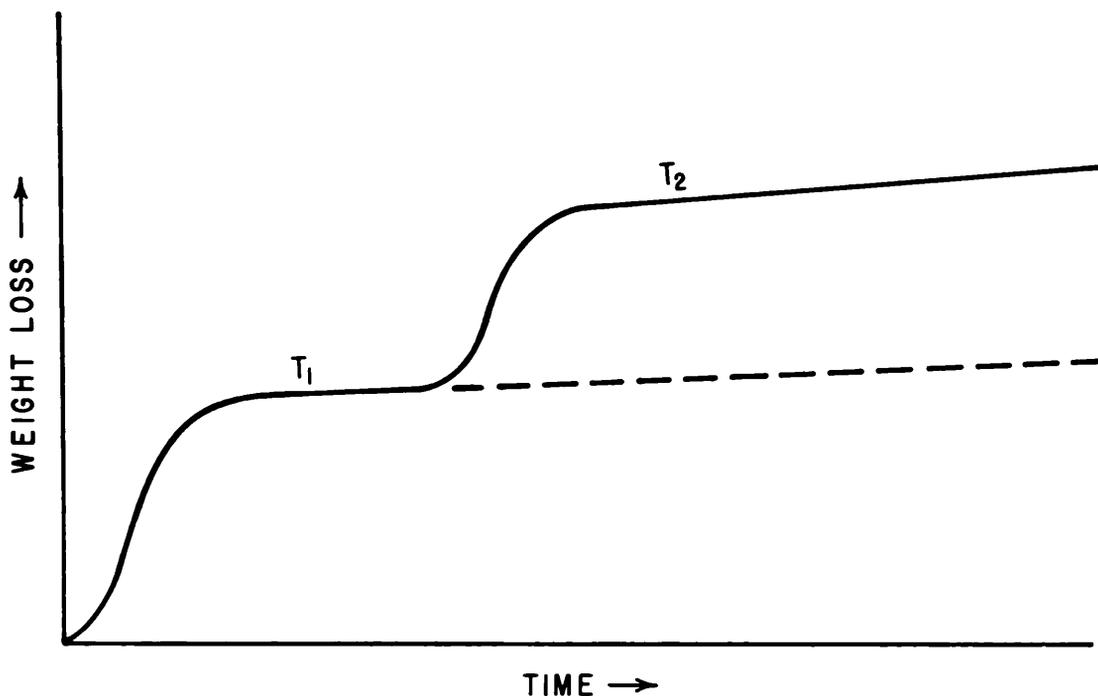


FIGURE 2.—Schematic of TGA trace for isothermal conditions.

method to obtain these data was to heat a sample at a very slow rate. This gave a continuous evaluation of weight loss as a function of temperature. Figure 3 shows such data for a sample of 29 gal/ton Colorado oil shale. These data were obtained by heating a 4 g (-100 to +115 mesh) sample for a period of over seven hours. The average heating rate was 2.74°F/min.

TRUE CONDITIONS FOR DESIGN

Naturally, these data do not represent true chemical equilibrium since, as pointed out previously, pyrolysis reactions are not normally reversible. Undoubtedly over very prolonged periods of time, complete devolatilization would occur even for temperatures of around 750 to 800°F; however, the rate is extremely slow involving many hours of time.³ From a practical stand-points at which the slope changed could be interpreted in terms of the products assumed as representing a true condition for design considerations.

An interesting treatment of such data is to plot the weight fraction volatilized as a function of reciprocal temperature using the van't Hoff-type relationship as follows:

$$\ln \left[\frac{W_O + W_G}{W_T} \right] = \frac{\Delta H_P}{RT} + C$$

Figure 4 shows such a plot which as expected gave straight lines covering a considerable temperature range. From the slope of these lines the ΔH_P

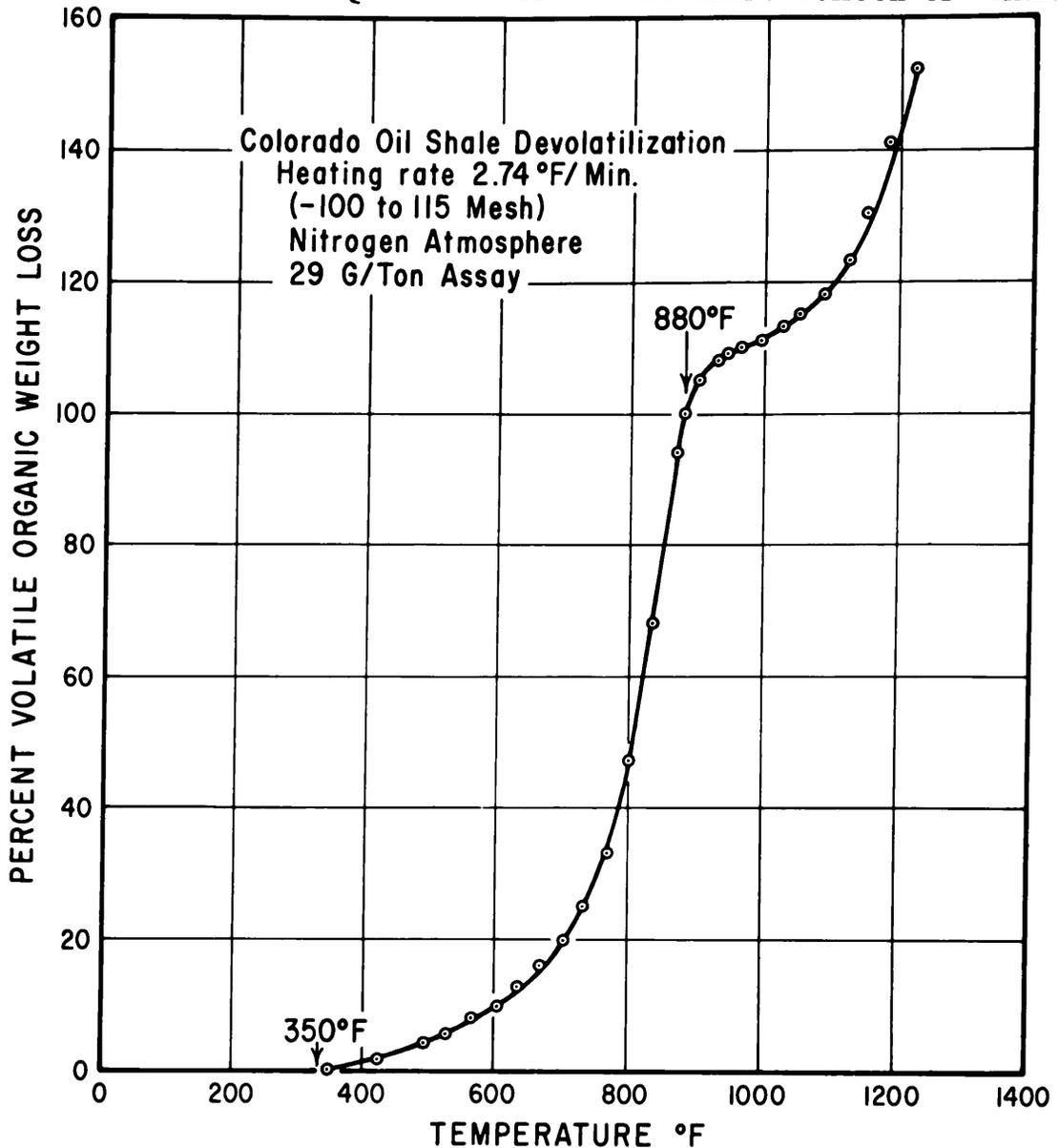


FIGURE 3.—Typical TGA curve for devolatilization of Colorado oil shale at low heating rates.

(combined heat of pyrolysis, vaporization, etc.) was calculated. In addition, points at which the slope changed could be interpreted in terms of the products being evolved.

From curves such as those given in figure 4 the temperature at which pyrolysis of the organic matter was completed (880°F) could be pinpointed with considerable accuracy. About 70 percent of the volatile matter was liberated in the temperature range 765 to 880°F. This was predominantly the shale oil or heavy hydrocarbon fraction. It was assumed that the ΔH_P value of about 20.4 kcal/g mole in the region primarily represented the heat required to break down the bitumen into volatile fragments as well as the heat of vaporization, although other heat effects were undoubtedly present.

It was also desirable to differentiate between the heat of pyrolysis and the heat of vaporization. One approach was to determine the heat used in vaporization of the oily matter from reconstituted shale oil and spent shale. The oil was then vaporized slowly in the TGA equipment. These data are also given in figure 4. From this curve a direct comparison with the data for the combined oil shale pyrolysis and vaporization was obtained. This latter curve gave a value of 9.4 kcal/g mole for the average heat of vaporization. By difference this gave a value of 11.0 kcal/g mole for the average heat of pyrolysis for bitumen.

TIME-TEMPERATURE CONSIDERATIONS

As previously noted, the data of Hubbard and Robinson³ rather conclusively demonstrated that the devolatilization of Colorado oil shale proceeds with the kerogen forming bitumen, gas, and the carbonaceous residue. The bitumen then decomposes to hydrocarbons (gas and oil). With this in mind, if one considers only that portion of the kerogen going to form bitumen, the pyrolysis reaction can be simplified by considering it as follows:

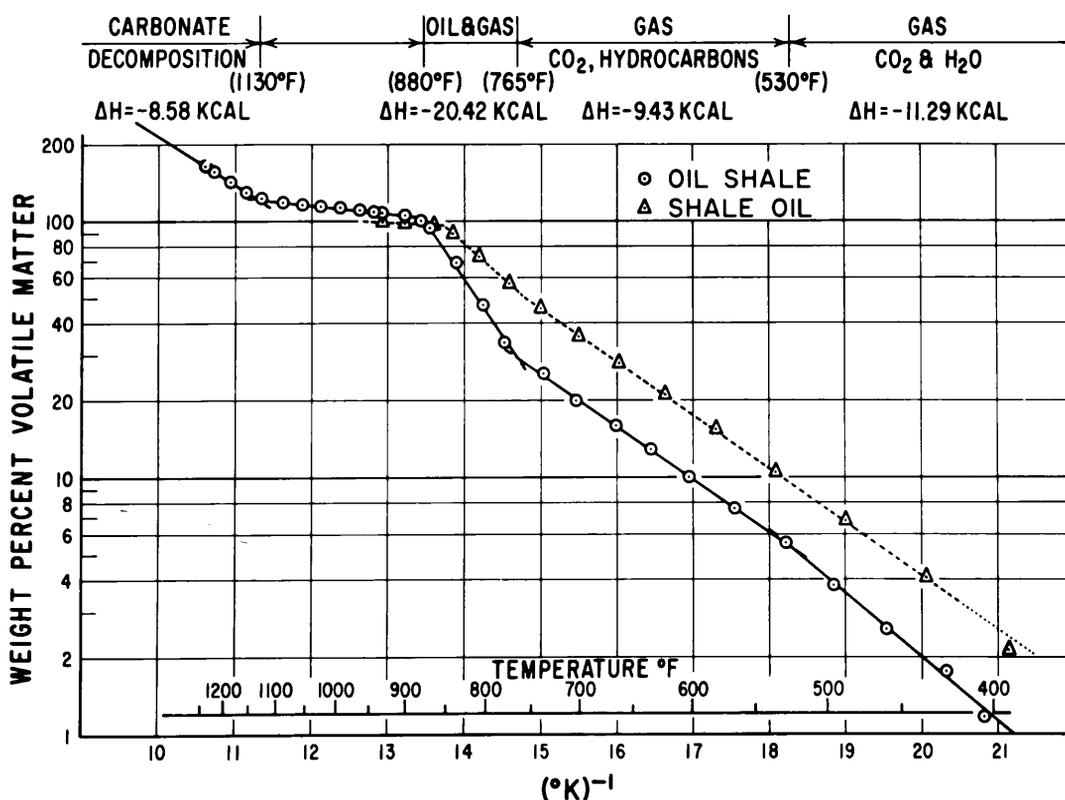
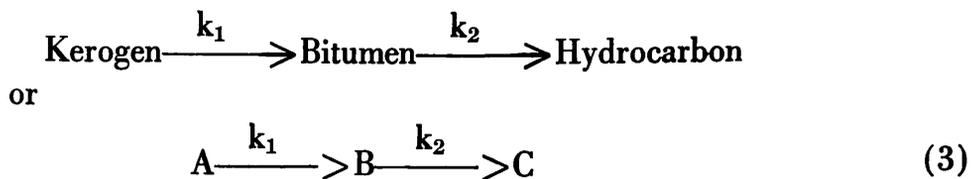


FIGURE 4.—Pseudo steady-state devolatilization of Colorado oil shale showing the effect of temperature on weight loss.



For the case where the reaction proceeds by first order kinetics, the rate of change of components would give curves typical of those shown in figure 5. Comparison of these curves with those given in figure 1 show that the shape of the curves A/A_0 and B/A_0 are markedly different from those determined experimentally. This lead to the conclusion that the pyrolysis reaction was proceeding by a somewhat different mechanism than simple first-order kinetics. The shape of the various curves in figure 1, suggested that a logistic or autocatalytic function was involved.

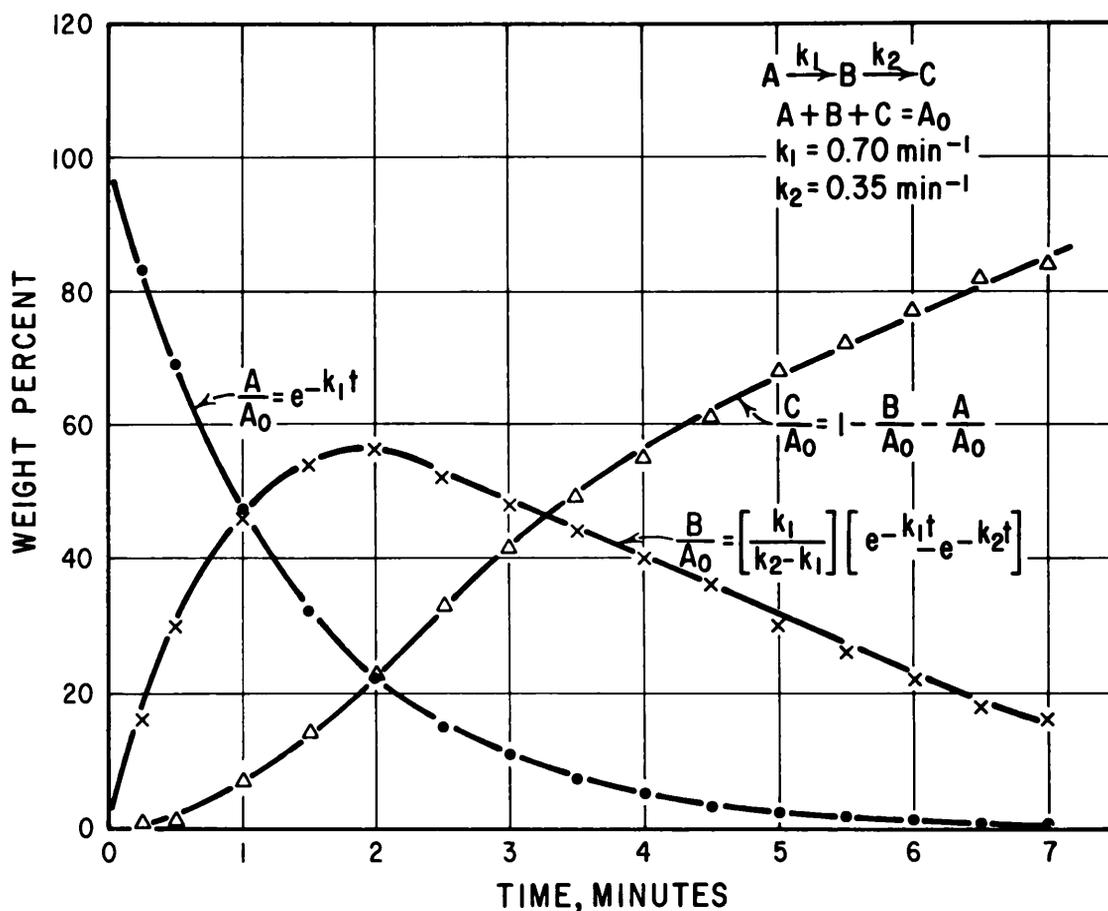


FIGURE 5.—Typical curves for the first-order kinetics of consecutive reactions. Rate constant k_1 characteristic of that predicted for data of Figure 1.

Additional insight was also gained by the observation that the kerogen was essentially all decomposed by the time the bitumen curve reached its maximum. This corresponded to a time when about one-half of the total

oil and gas remained to be produced. Therefore, from the point where $W_C/W_{A0} > 0.5$ the rate of disappearance of bitumen was equal to the rate of formation of final products or:

$$-\frac{d(W_B)}{dt} = \frac{d(W_C)}{dt} \quad (4)$$

In which case, the rate constant k_2 could be evaluated independent of the influence of k_1 . Experimentally, still another advantage was gained by using data obtained during this period. That was the temperature had time to stabilize, thus, one was more certain of having isothermal conditions for the determination.

FIRST-ORDER OR LOGISTIC RATE

If first-order kinetics were being followed, then the rate equation during this period would have been as follows:

$$\ln \left[1 - \frac{W_C}{W_{A0}} \right] = -k_2 t \quad (5)$$

or,

$$\ln (1 - X) = -k_2 t$$

where, $W_C/W_{A0} = X$. This should give a straight line with a slope equal to k_2 for the experimental data when $X > 0.5$. Typical TGA data plotted in this manner are given in figure 6. From the shape of this curve it was evident that these data did not fit equation 5 and the decomposition of bitumen was not a first-order reaction. On the other hand, these data did give a remarkable fit to a straight line when plotted in the logistic function:

$$\ln \left[\frac{1 - X}{X} \right] = -k_2 t + \ln I \quad (6)$$

as is also shown in figure 6.

Further verification of the applicability of equation 6 to the pyrolysis of Colorado oil shale is given in figure 7, where the data of Hubbard and Robinson are plotted for a similar grade of shale pyrolyzed at the same temperature. Significantly, the same slope is observed as had been determined for the data used in figure 6.

TEMPERATURE COEFFICIENT

TGA data for the pyrolysis of shale also lends itself readily to the determination of the temperature coefficient of the reaction rate constants.

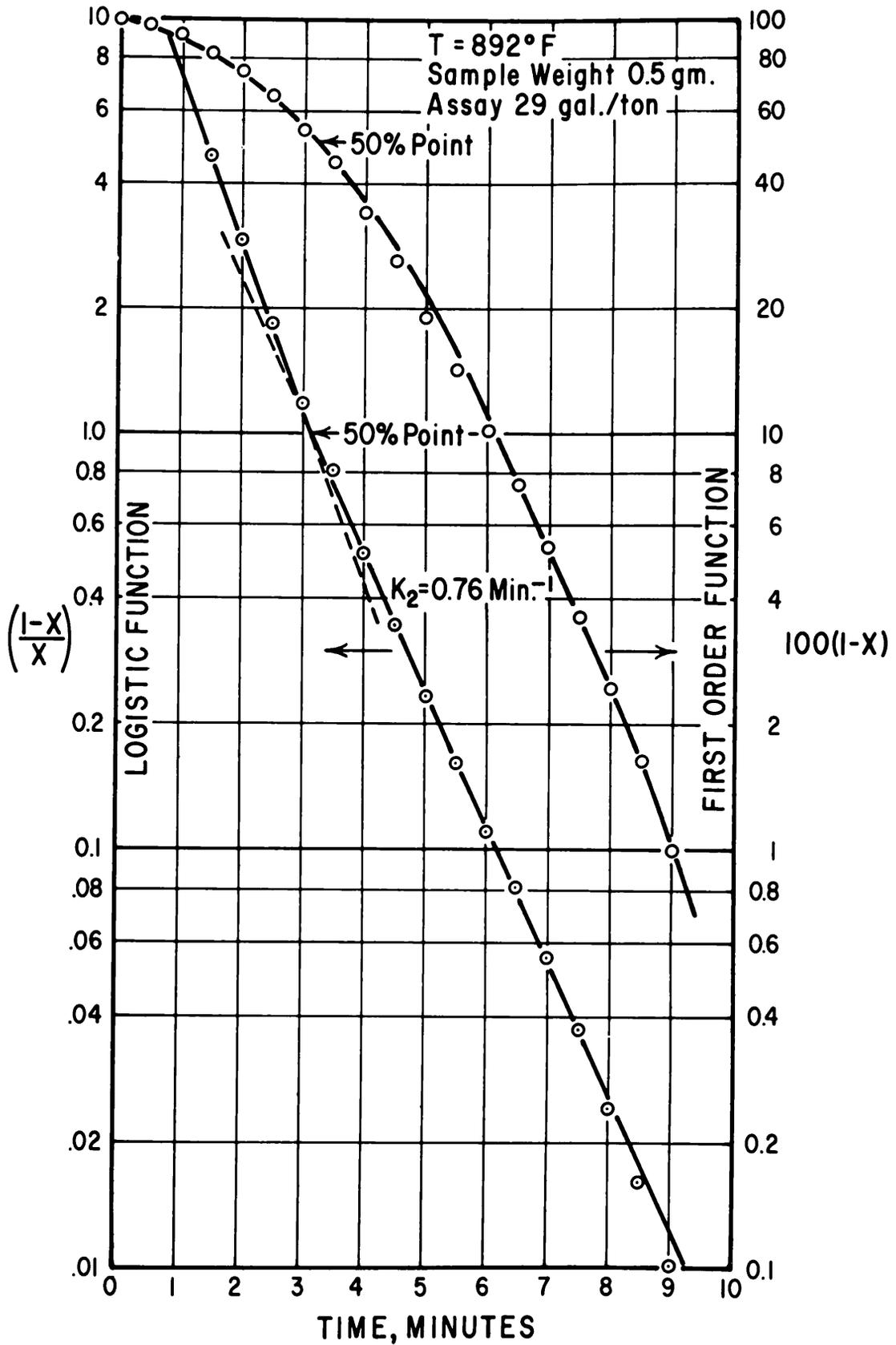


FIGURE 6.—Comparison between first-order and logistic expressions in fitting oil shale devolatilization data.

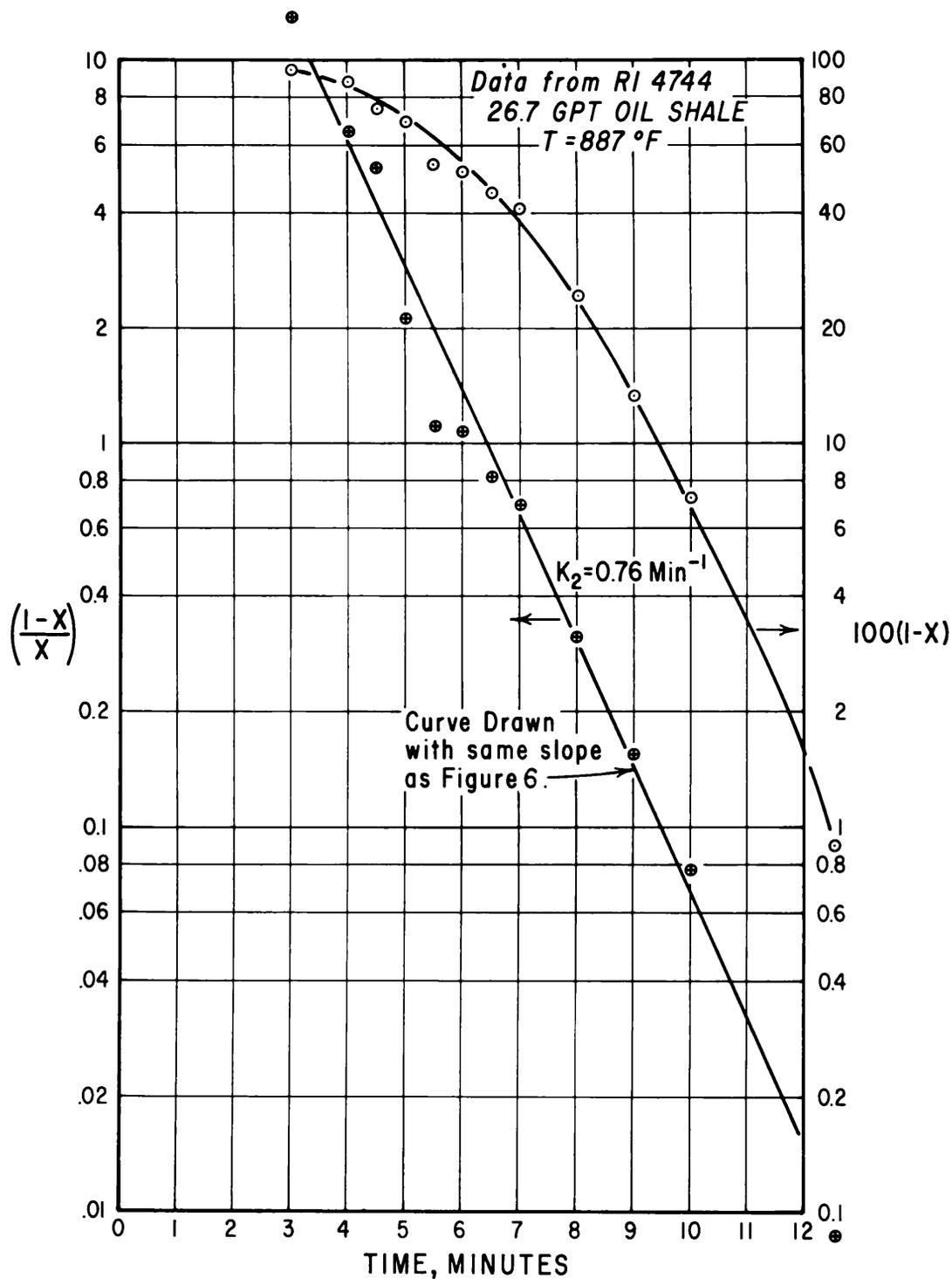


FIGURE 7.—An example of the applicability of the logistic function (Equation 6) to experimental data of Hubbard and Robinson (3).

Such data were determined for several temperatures (890 to 1,140°F) and are given in figures 8 through 11.

These curves also show several other interesting characteristics. First, there is a distinct break at the 50 percent volatilization point, i.e., where $(1 - X)/X$ equals unity, indicating the validity of the previous assumption that the kerogen was all converted at this point.

Second, there is a second change in slope at higher temperatures as shown in figures 10 and 11. In this case these data could be fit either with the logistic or the first-order kinetic expression, however, this is expected since they are approximately the same value at this end of the curve, i.e., $[(1 - X)/X]$ approaches $(1 - X)$ in values as X approaches zero. A significant observation may be that in the first-order case the slope extrapolates to the origin at zero time. This may indicate that reaction involved is one that is normally fast at low temperature, relative to the other reaction, but has a smaller temperature coefficient so that it becomes rate determining at higher temperatures. It is suspected that this could be an actual vaporization step which would probably be diffusion controlled and should have a fairly low temperature coefficient.

COMPLEX REACTIONS

The third observation is that the data for the initial devolatilization, *ca.* 5 to 50 percent, also fit a logistic expression. The exact implication of this is not known since both the decomposition of kerogen and bitumen are actually taking place. However, it may indicate that the rate of decomposition of kerogen is dependent upon the amount of bitumen present. If so, this would be very significant since it would imply that the bitumen has a catalytic or solvent action on kerogen decomposition.

In any event these data demonstrate that the pyrolysis reactions are extremely complex and probably cannot be represented by a simple kinetic expression. On the other hand, they can be broken down into fairly simple expressions for two or three regions, depending upon the temperature. Figure 12 shows these zones together with equations that can be used to calculate a devolatilization curve.

The effect of temperature on the rate constants for each of the rate expressions is summarized in table 2. These data are plotted in a typical Arrhenius type plot in figure 13. As previously inferred, these data seem to bear out that the decomposition of bitumen ceases to be rate determining at about 900°F, and either the decomposition of kerogen and/or the rate of actual volatilization of the oily fluids from the inorganic matrix gradually becomes rate determining.

TABLE 2.—*Effect of temperature on specific rate constants*

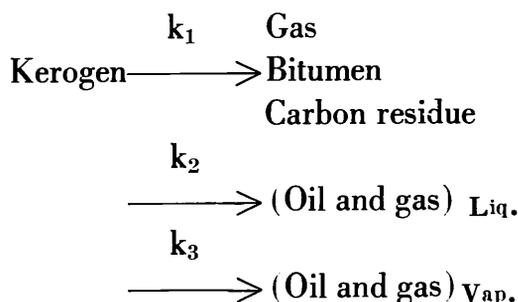
Temperature °F	Rate constants		
	k_1 , min. ⁻¹	k_2 , min. ⁻¹	k_3 , min. ⁻¹
1,140	2.86	5.33	1.11
1,050	1.81	3.35	0.89
990	1.28	2.46	—
940	0.94	1.40	—
890	0.65	0.77	—
850*	—	0.35	—
800*	—	0.11	—
750*	—	0.037	—

*Obtained data from data given in reference (3).

PYROLYSIS MECHANISM

Thermogravimetric analysis has been applied to a study of the pyrolysis of Colorado oil shale. Using very slow heating rates, pseudo steady-state devolatilization data have been obtained. These data show a critical temperature for complete pyrolysis of oil shale to be about 880°F. Analysis of the data in detail also shows a heat of pyrolysis of about 11 kcal/g mole is required to convert the bitumen in oil shale to volatile hydrocarbons. In addition, a heat of about 9.4 kcal/g mole is required to volatilize the hydrocarbons. This leads to a value of 20.4 kcal/g mole required to separate shale oil by pyrolysis from the inorganic materials.

A critical examination of published data has led to a conclusion that in part the mechanism by which Colorado oil shale decomposes is as follows:



At temperatures below 900°F the decomposition of the insoluble organic matter (kerogen) into the soluble bitumen is a fairly rapid step compared

to the decomposition of bitumen to the hydrocarbon-like materials. However, at temperatures above 900°F the decomposition of bitumen appears to be rapid and either the decomposition of kerogen or the physical volatilization, i.e., boiling out of fluid from the shale as a vapor becomes the slow or rate determining step.

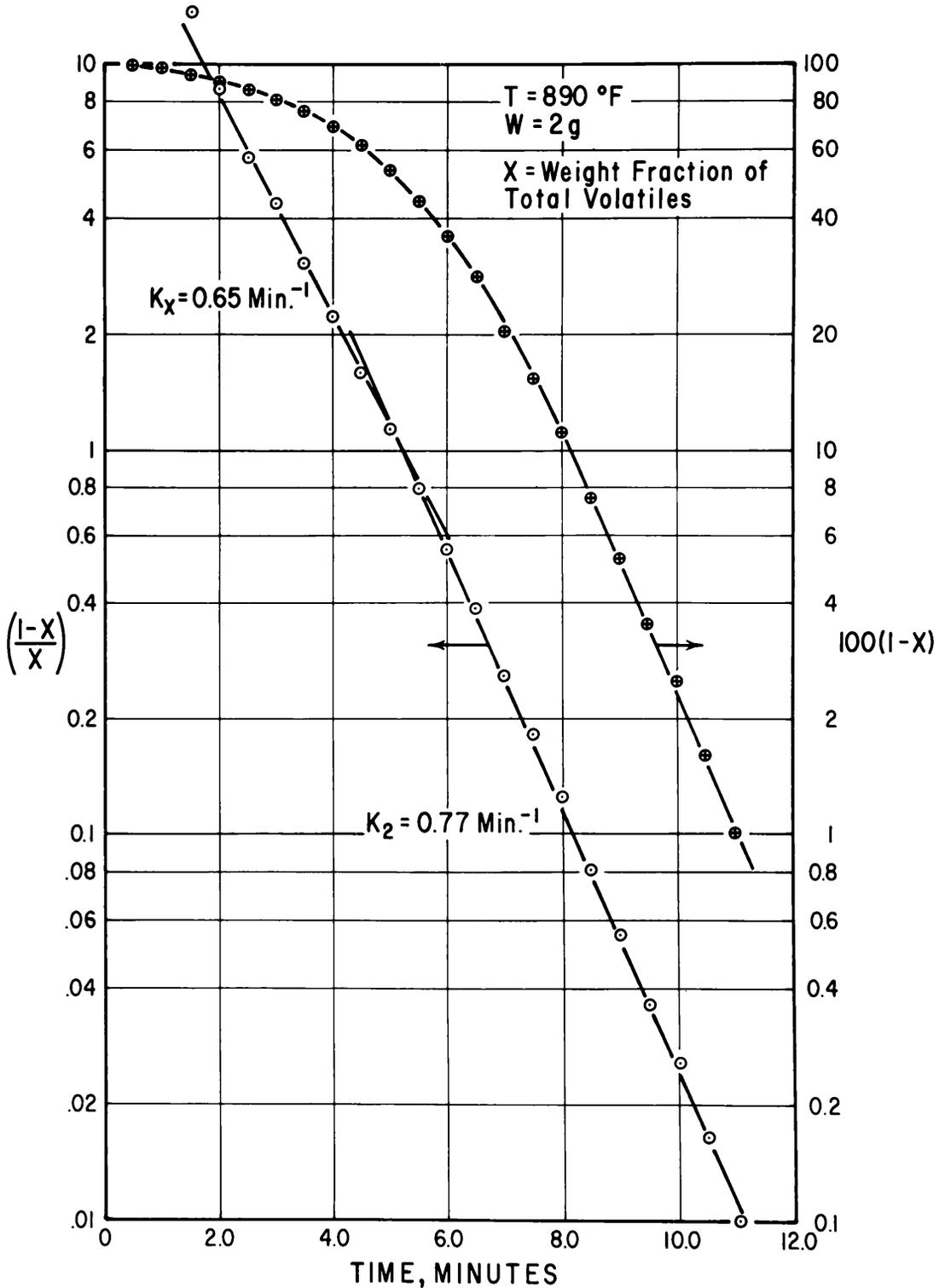


FIGURE 8.—Evaluation of reaction rate constants for oil shale devolatilization at 890°F.

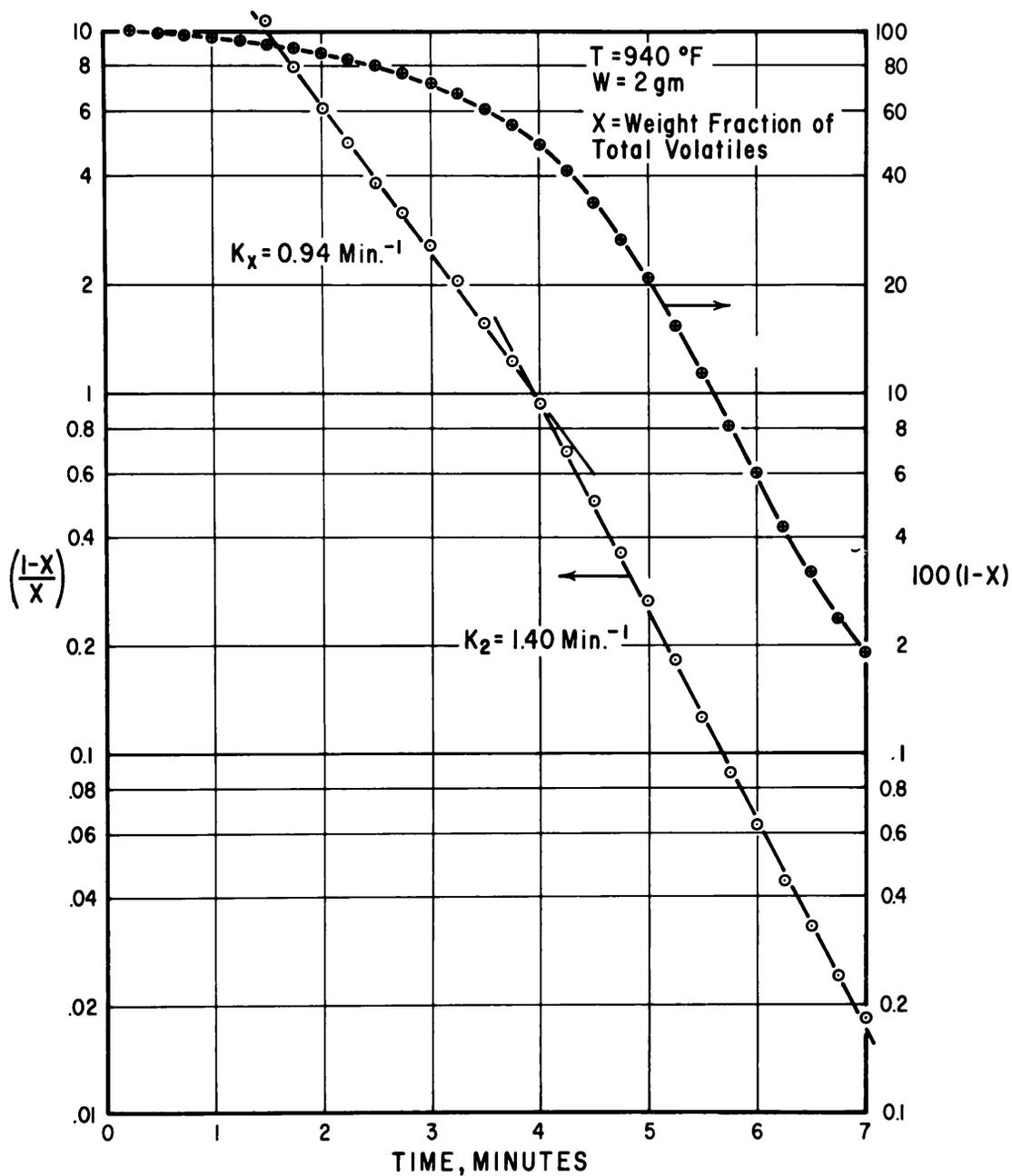


FIGURE 9.—Evaluation of reaction rate constants for Colorado oil shale devolatilization at 940°F.

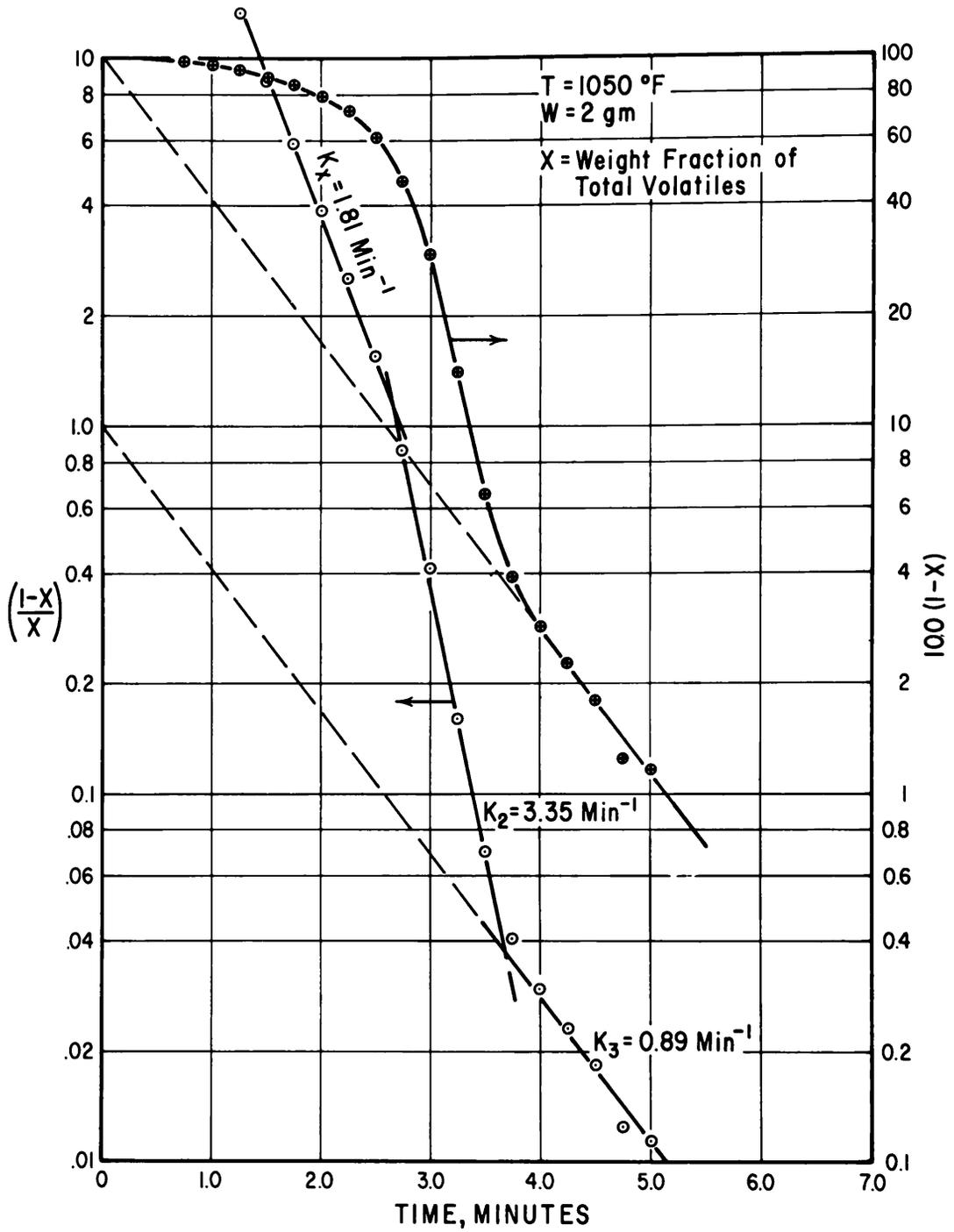


FIGURE 10.—Reaction rate data for oil shale devolatilization at 1,050°F. Note the appearance of a second point of inflection.

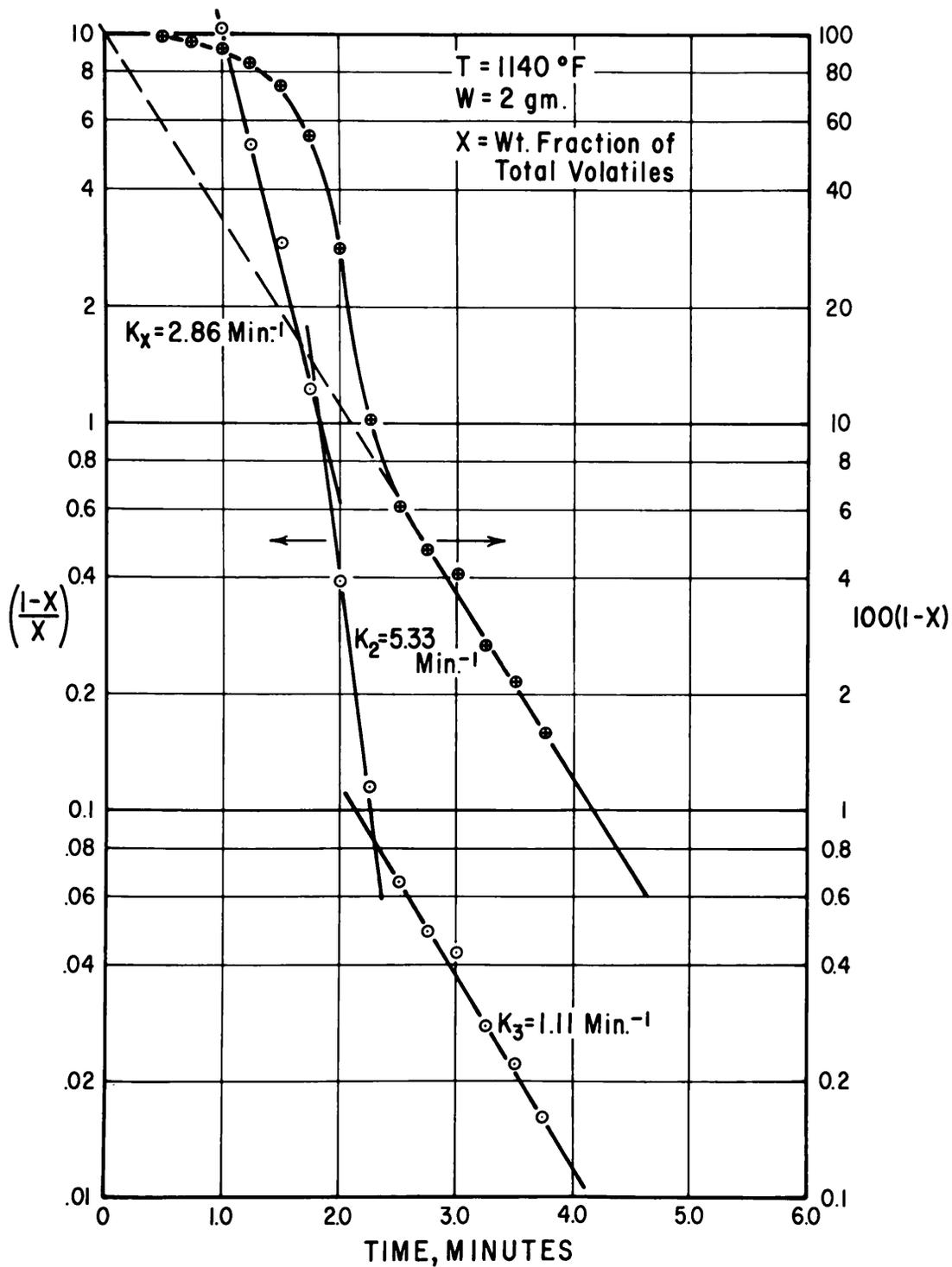


FIGURE 11.—Reaction rate data for oil shale devolatilization at 1,140°F showing three regions with different rate constants.

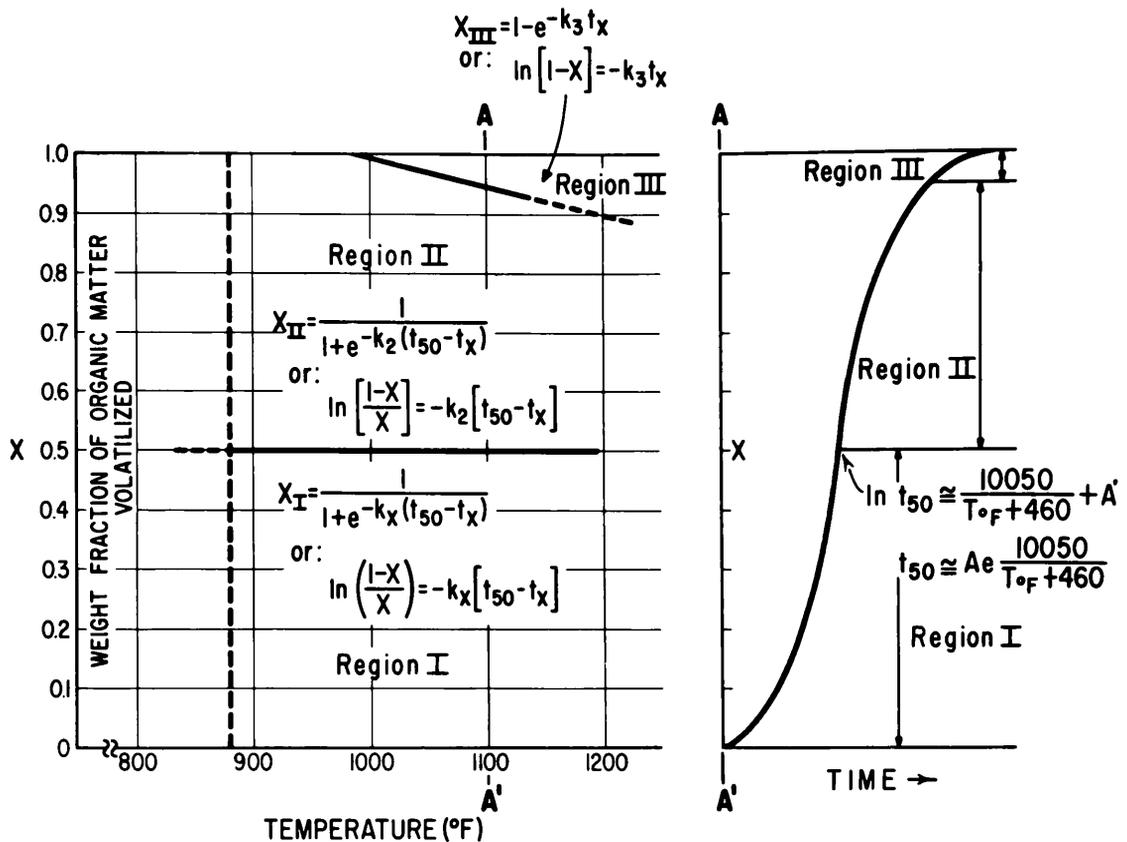


FIGURE 12.—Schematic diagram showing regions with different reaction rate expressions as a function of weight loss and temperature.

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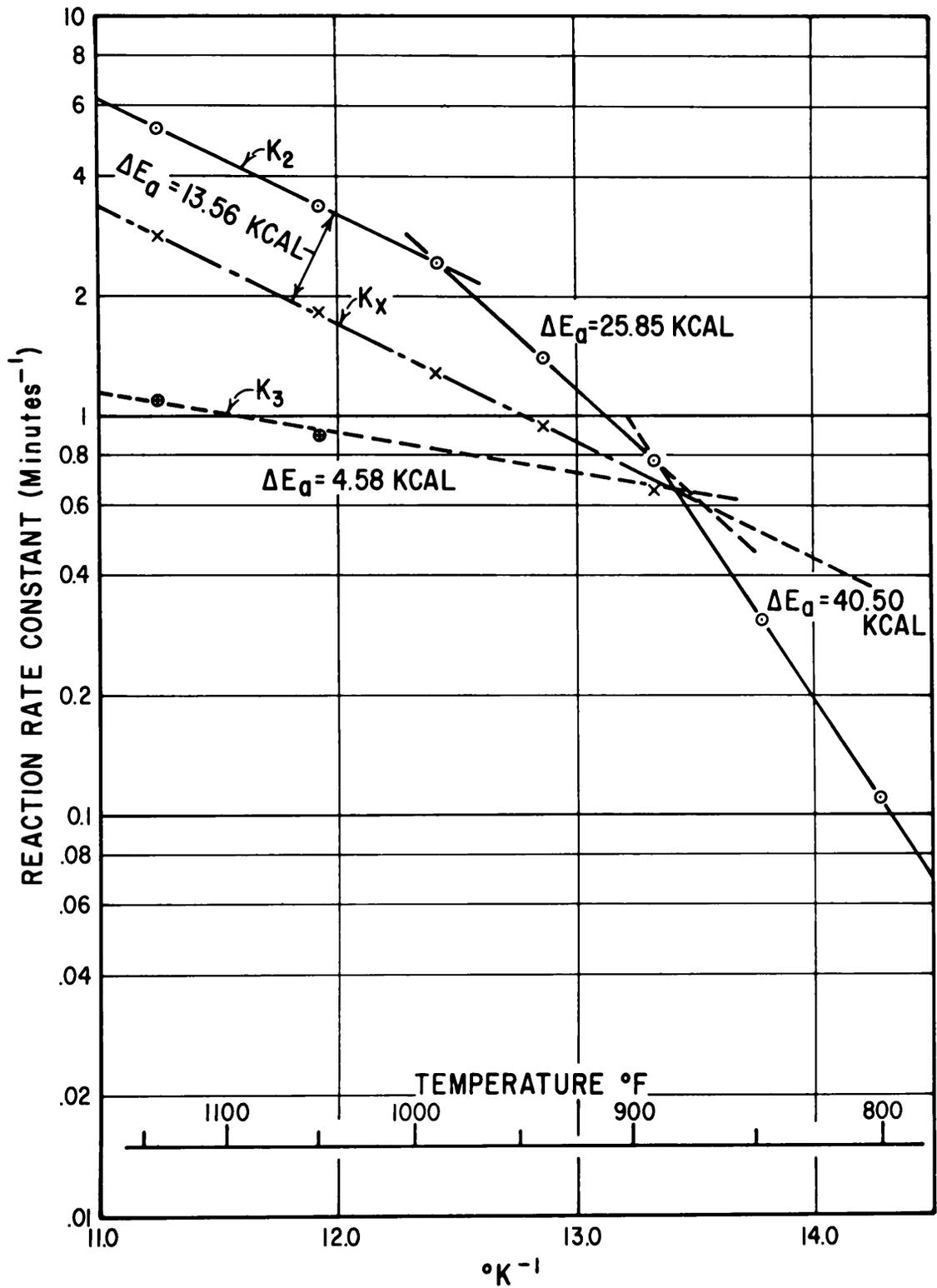


FIGURE 13.—Effect of temperature on the reaction rate constants in the devolatilization of Colorado oil shales.

CONDUCTION HEATING OF OIL SHALE FORMATIONS

HERBERT A. LESSER, GEORGE H. BRUCE, HERBERT L. STONE

ABSTRACT

A mathematical model that represents the conduction heating of a rock formation of limited permeability is discussed. Heat is introduced by the injection of a hot condensing gas into horizontal fractures through the formation. The fractures are assumed to be equally spaced; the flow of fluid is linear. The model may be used to obtain temperature histories for both fractures and formation. Application of the model in predicting in situ heating of oil shale is illustrated with four sample cases. Influences of shale thermal diffusivity, fluid pressure in the fracture and fracture spacing upon heating rate are demonstrated. In all cases considered, several years were required to heat all the formation to 700°F with 1,000°F steam. Less than 32 percent of the injected heat was utilized for heating the shale.

INTRODUCTION

The hydrocarbons contained in oil shale formations are difficult to recover because they are immobile solids and because the rock formations in which they are found have very limited permeability. These hydrocarbons, known as kerogen, can be converted through pyrolysis to recoverable liquids and gases if the formation temperature is elevated to the range 600° to 800°F. To accomplish this heating, the formation might be artificially fractured and a hot fluid injected into the fractures. If the injection and production wells are vertical and the fractures horizontal, interwell communication will be established and the hot fluid will flow from an injection well to a production well. In this process, some of the heat in the fluid will be given up and conducted into the formation. Products of pyrolysis will flow from the heated rock matrix into the fractures and be produced, commingled with the injected fluid.

The practicality of such a process is strongly influenced by the rate at which heat can be transferred from the hot fluids to the formation. An analysis of this heat conduction problem was the subject of a recent paper by these authors.¹ A brief description of the mathematical model presented in that paper is given here, together with some numerical examples. Linear flow of a condensing gas through a set of horizontal, equally spaced fractures is considered. Temperature histories for both fractures and formation are

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obtained from numerical procedures. The analysis also applies to formations containing streaks of natural permeability instead of fractures.

Heat flow problems similar to the one treated here have been studied by other workers. Thomas² has solved a radial problem in which he considers the injection of a noncondensing gas into a single, horizontal fracture and approximates the temperature profile in the fracture by a step function. The solutions to other problems, which are less similar to the present problem than the one treated by Thomas, have been reviewed by Spillette.³ In addition to these mathematical studies, a field test of an in situ shale oil recovery process using hot natural gas as the injected fluid has been reported.⁴

The first part of this paper is concerned with briefly summarizing the development of the model. Details of the calculational procedure may be found in reference 1. The second part of the paper presents results computed for a typical oil shale formation for which steam at 1,000°F is the injected fluid. Fracture spacing, horizontal and vertical thermal diffusivities, and steam pressure are varied to illustrate their effects on heating rate and heat utilization.

MODEL DESCRIPTION

Equally spaced horizontal fractures are assumed present in a formation containing immobile hydrocarbons. Except for fracture permeability or streaks of natural permeability, the rock matrix is assumed to have essentially no permeability. In figure 1 a cross-sectional view is shown of a typical fracture and adjacent formation. A condensing gas is injected uniformly along one end of each fracture, and the outlet gas (or condensed liquid) is removed at the opposite end at a lower temperature. Vertical temperature variations, horizontal pressure changes, and horizontal heat conduction in the fractures are neglected. In both the fractures and formation, the presence of oil and gas products is ignored.

In the rock matrix, horizontal and vertical heat conduction occur and the respective thermal conductivities are different and temperature-dependent. The formation density-heat capacity product is assumed constant. Absorption of heat by the endothermic cracking of kerogen is not included in the model. From the work of Sohns, et. al.⁵ it appears that the neglected heat (together with other, less important heat sinks) represents less than 25 percent of the total heat required to heat the shale to 800°F, at which temperature the pyrolysis is near completion. Neglect of this heat sink will lead to a somewhat faster calculated transport of heat into the formation than actually occurs in oil shale formations.

Initially, the formation is assumed to have the same temperature everywhere. The fractures are assumed to be full of the injected fluid at forma-

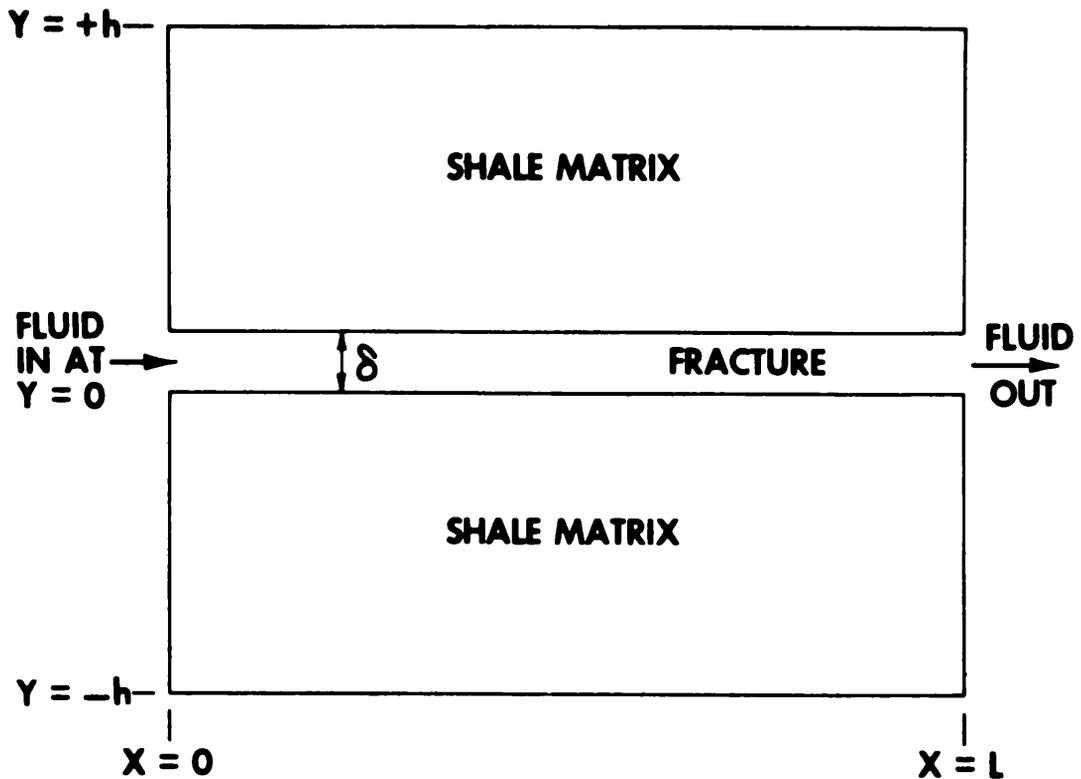


FIGURE 1.—Cross-section of typical fracture and adjacent shale matrix.

tion temperature. Gas at an elevated temperature is then injected into the fractures at some specified flow rate. Heat given up by the fluid flowing in a fracture is distributed equally above and below the fracture. No-heat-flow boundary conditions are imposed at equal distances above and below the fracture, which are shown in figure 1 as the distance $\pm h$. With these conditions, the problem is equivalent to that of a fracture near the center of a system containing a large number of equally spaced fractures. Finally, it is assumed that there is no transfer of heat between either injection or producing well and the formation; i.e., the formation is heated solely by the flow of condensing gases through the fractures.

Under the above assumptions, the temperature histories of the rock matrix and fracture may be described by a system of three partial differential equations, two functional relationships, and associated initial and boundary conditions. The partial differential equations represent the conservation of energy at each point in the rock matrix, the conservation of energy at each point in the fracture, and the conservation of mass at each point in the fracture. The functional relationships relate fluid density and enthalpy to fluid temperature and vapor quality. A formal statement of the equations and the numerical procedure used to solve them may be found in reference 1.

Temperature histories obtained from the solution to the system of equations are influenced by the parameters:

1. $(\rho C)_f$, formation density-heat capacity product,
2. $k_x(T)$, formation thermal conductivity in the horizontal direction,
3. $k_y(T)$, formation thermal conductivity in the vertical direction,
4. δ , fracture thickness,
5. $2h$, fracture spacing,
6. L , fracture length,
7. T_o , initial formation temperature,
8. T_{inj} , temperature of injected fluid,
9. S_{inj} , vapor quality of injected fluid,
10. v_{inj} , injection velocity, and
11. p , injection pressure.

In addition, the specific injection fluid used influences the results.

APPLICATION OF THE MODEL

DESCRIPTION OF EXAMPLE CASES

The mathematical model described in the previous section can be used to investigate the effect of some of the important parameters on the feasibility of in situ heating of oil shale. Some results for a typical oil shale formation are presented here, the injected fluid being steam at 1,000°F. A higher injection temperature is not used because of the possibility of carbonate decomposition.⁶ Four parameters are varied: horizontal and vertical thermal diffusivities, fracture spacing, and steam pressure. The thermal diffusivities, $\alpha_x(T)$ and $\alpha_y(T)$, are the quantities $k_x(T)/(\rho C)_f$ and $k_y(T)/(\rho C)_f$, respectively. The effects of the four parameters are illustrated by computing (1) the fraction of the formation heated to 700°F as a function of time, and (2) the fraction of injected heat conducted into the formation as a function of the fraction of the formation heated to 700°F. A temperature of 700°F was chosen because it is in the middle of the temperature range 600° to 800°F in which most of the kerogen in oil shale pyrolyzes. For the base case, additional curves are presented for 600° and 800°F. From these curves the amount of kerogen that is decomposed can be estimated if laboratory tests are made to determine the fraction kerogen which decomposes below each temperature.

Numerical results presented here by no means represent an exhaustive study of the parameters appearing in the equations. They do serve to demon-

strate the utility of the model and to establish the order of magnitude of time required to sufficiently heat a typical formation.

In table 1 are parameter values which were held constant in the four cases investigated; i.e., the values of initial formation temperature, injection temperature and flow rate, formation density-heat capacity product, formation length, and fracture width. The values of parameters which were varied from case to case are shown in table 2. Case 1 is the base case and differs from each of the other cases by the value of a single parameter. For this

TABLE 1.—*Values of constant parameters*

T_o	=	100°F
T_{inj}	=	1000°F
$(\rho v)_{inj}$	=	1000 lb/sq ft hr
$(\rho C)_f$	=	41.2 Btu/cu ft °F
L	=	500 ft
δ	=	0.02 ft

TABLE 2.—*Values of varied parameters*

Case	α_x (sq ft/hr)	α_y (sq ft/hr)	h (ft)	p (psia)
1	0.015	0.010	20	1,000
2	0.015	0.010	20	400
3	0.030	0.020	20	1,000
4	0.015	0.010	10	1,000

case, $\alpha_y = 0.010$ sq ft/hr, the fracture spacing is 40 feet and the steam pressure is 1,000 psia. (k_x and k_y are treated as a single parameter with $k_x = 1.5k_y$. This relationship is consistent with the data of Thomas⁷ for oil shale at 104°F. Although k_x and k_y are usually temperature-dependent, there is no general agreement for oil shale as to what this dependency is. Hence, they are taken to be constant in the examples presented here.) Case 2 is obtained by reducing the steam pressure to 400 psia, Case 3 by doubling α_y to 0.020 sq ft/hr, and Case 4 by halving the fracture spacing to 20 feet. To obtain the density and enthalpy functions at the two prescribed pressures, 400 and 1,000 psia, second degree equations were fit by the method of least squares to data from Keenan and Keyes.⁸ A separate fit was done for each phase with resulting curves fitting the data very well.

The solution of the model equations can be used to plot the temperature distribution in the formation at a given time. Curves describing the temperature distribution above the fracture after injection times of 0.57, 2.85 and 5.71 years are shown for the base case in figures 2 through 4. The temperature distribution below the fracture is simply the reflection of the distribution above the fracture. In figure 2 the 200° and 400°F isotherms are fairly flat over wide regions. This result may be attributed to the long time during which an appreciable length of the fracture is at the steam saturation temperature of 544.61°F. Even after 2.85 years have elapsed, only a small amount of the formation has been heated to 700°F (fig. 3). By 5.71 years, only superheated steam is present in the fracture, and about half of the formation has been heated to 700°F or higher (fig. 4). The temperature profiles in the fracture are shown in figure 5 for the same three times used for figures 2 through 4.

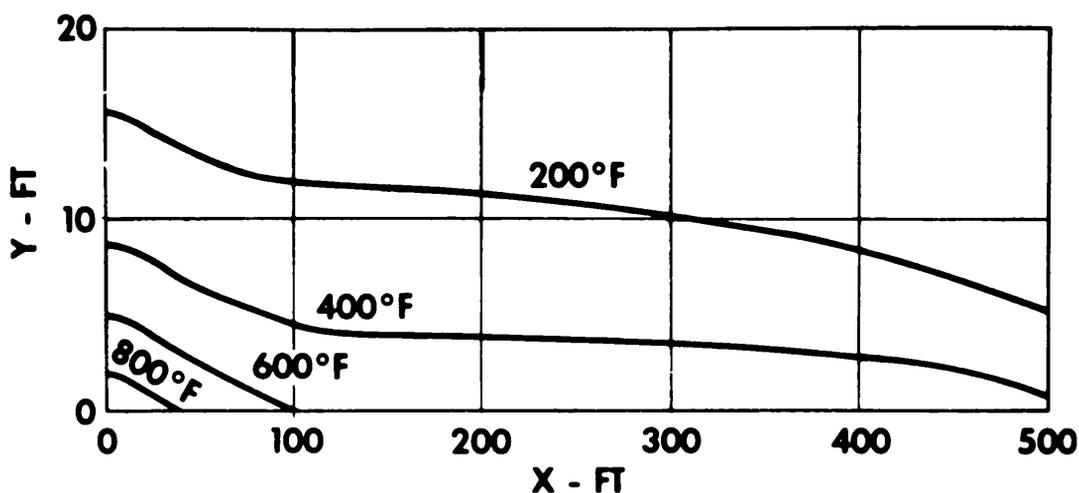


FIGURE 2.—Formation isotherms after injecting steam for 0.57 year (Case 1).

In figure 6 are curves showing, as functions of time, the fraction of the formation heated to specified temperatures. The slow rate at which the formation gains heat may be attributed to the low thermal diffusivities characteristic of oil shale formations. Results shown in figure 6 indicate that almost 10 years are required to heat the entire formation to 700°F. At that time, less than three-fourths of the formation has reached 800°F. These curves can be used to estimate shale oil recovery if it is known how much kerogen pyrolyzes below each of the three temperatures. In figure 7 the cumulative heating efficiency for each of the four cases is shown as a function of the fraction of the formation heated to 700°F or higher. For the

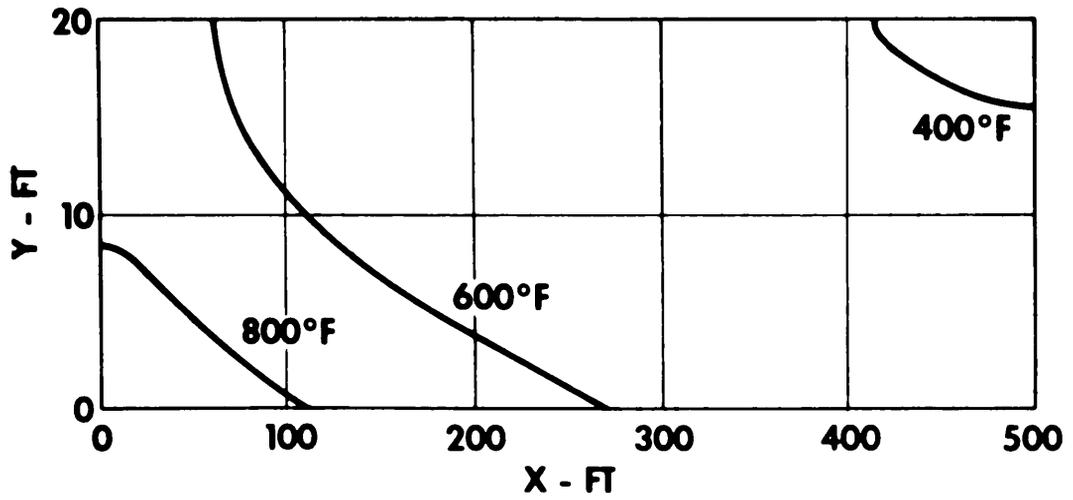


FIGURE 3.—Formation isotherms after injecting steam for 2.85 years (Case 1).

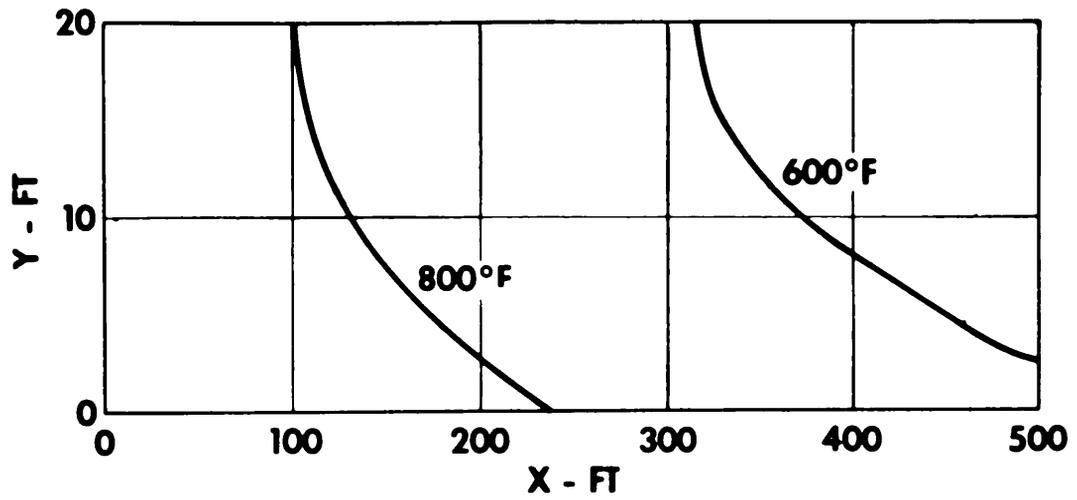


FIGURE 4.—Formation isotherms after injecting steam for 5.71 years (Case 1).

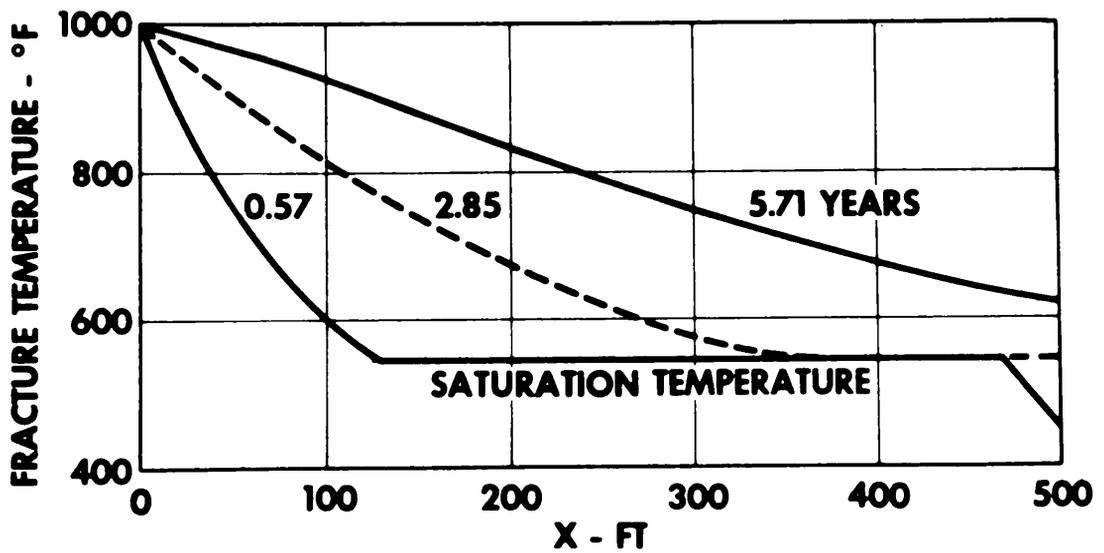


FIGURE 5.—Temperature distribution in the fracture (Case 1).

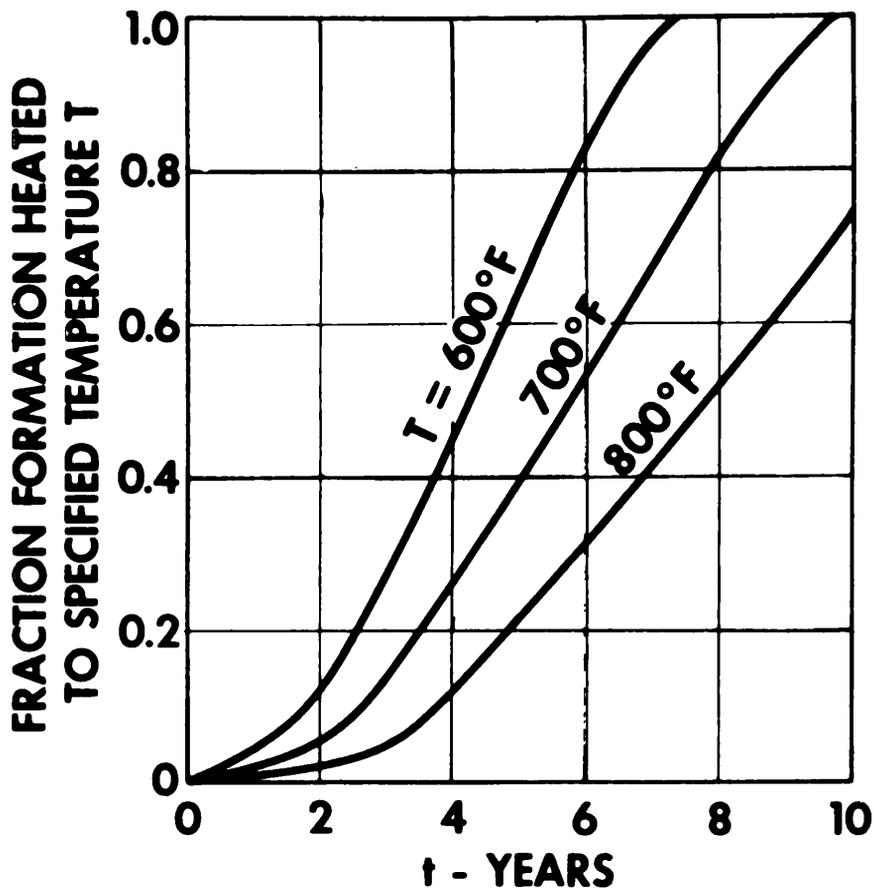


FIGURE 6.—Fraction of formation heated to specified temperature (Case 1).

injection process under study, the heating efficiency is rather low. Once the outlet temperature reaches the saturation temperature, an appreciable amount of heat begins to be produced at the production well. Thereafter, the cumulative utilization of heat decreases rapidly. For Case 1, only 25.4 percent of the heat injected is utilized over the 9.8-year period required to heat all the formation to 700°F or higher.

If an injection pressure of 400 psia is used instead of 1,000 psia, the heating process is slowed (Case 2). This behavior results from the lower steam saturation temperature which causes a long period of heat transfer with a smaller temperature gradient at the fracture. In figure 8 the fraction of formation heated to 700°F or higher is depicted as a function of time for each of the four cases. Comparison of curves 1 and 2 shows that the lower heating rate at the lower pressure results in more time (11½ years) being required to heat all the formation to 700°F or higher. The 600° and 800°F curves are not shown; however, they are spaced about the 700°F curves like those shown in figure 6. Figure 7 shows that the heating efficiency for the low pressure case is lower than for Case 1. Pressure changes affect

the numerical results by their effect on the density and enthalpy functions. An ideal heat transport agent (for heating the formation to 700°F) would have a saturation temperature above 700°F and a large heat of vaporization at that pressure. Unfortunately, steam has a low heat of vaporization at a saturation temperature of 700°F .

Doubling the thermal diffusivities of the formation leads to a more rapid rise in formation temperature. This effect is illustrated by the curves shown in figure 8 where the curve designated Case 3 was computed for diffusivities twice those used in computing the curve designated Case 1. The time required to heat all the formation to 700°F or higher is lowered to 8.1 years from the 9.8 years of Case 1. The curves of figure 7 show that this diffusivity increase also leads to more efficient utilization of injected heat.

If the distance to the reflection boundaries used in calculating Case 1 is shortened from 20 to 10 feet, a dramatic improvement in formation heating rate results. Results of this calculation are shown as Case 4 in figure 8. Only 4.1 years are required to heat all the formation to 700°F compared to 9.8 years for Case 1. This change in fracture spacing results in nearly the same heat utilization curve as was obtained for Case 3. An explanation of this result is given in Appendix C of reference 1.

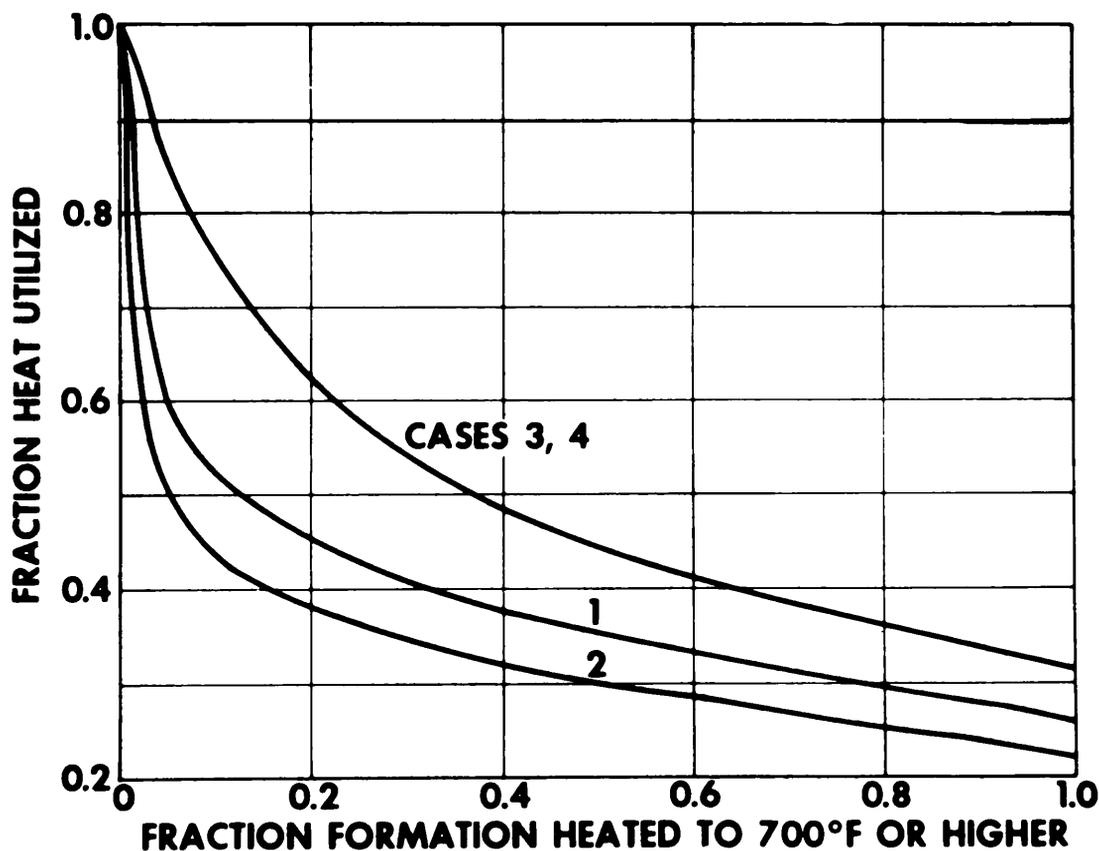


FIGURE 7.—Utilization of injected heat.

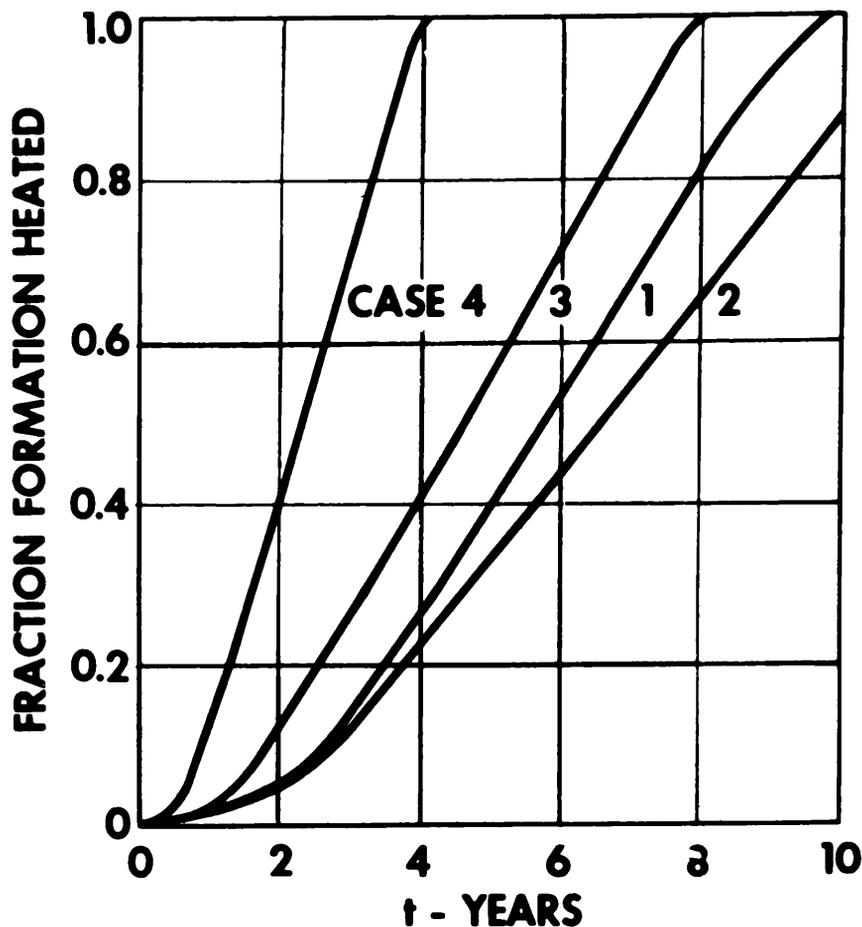


FIGURE 8.—Fraction of formation heated to 700°F or higher.

The heating efficiencies for all four cases could be improved by reducing the steam injection rate, but more time would then be required to achieve the desired amount of heating. Efficiencies could also be increased by the use of heat exchangers to transfer thermal energy from the production stream to the boiler feed stream.

These numerical examples serve to demonstrate the general effect on formation heating of one-at-a-time variations in steam pressure, thermal diffusivities, and fracture spacing. Results of the type obtained provide a means for estimating the recovery of shale oil or other immobile hydrocarbons from formations that are either fractured or have streaks of high, natural permeability. Optimal parameters will be determined by economics—cost of drilling wells, inducing fractures, generating steam, etc., vs. the value of produced hydrocarbons.

CONCLUSIONS

A mathematical model has been developed¹ for computing the temperature history of an impermeable formation heated by the flow of hot, con-

densing gases through horizontal permeability streaks in the formation. To demonstrate the application of the model in predicting oil shale heating, four cases have been solved to obtain (for typical oil shale formation parameters) estimates of the effectiveness of the heating process. With injected steam at 1000°F, 4 to 11½ years were required to heat all the formation to 700°F, a reasonable target temperature for oil shale formations. In all cases, less than 32 percent of the injected heat was utilized for heating the shale. The long time required for heating and the low heating efficiency are results of the low thermal diffusivities characteristic of oil shale formations.

NOMENCLATURE

- C_f = formation heat capacity
 h = distance from fracture to no-heat flow boundary
 k_x = thermal conductivity in the x-direction
 k_y = thermal conductivity in the y-direction
 L = fracture length
 p = fluid pressure
 S = vapor quality
 S_{inj} = vapor quality of injected fluid
 T = temperature
 T_0 = initial temperature of formation and fluid
 T_{inj} = temperature of injected fluid
 t = time
 v = fluid velocity
 v_{inj} = fluid velocity at point of injection
 x = horizontal distance from injection well
 y = vertical distance from fracture
 α_x = thermal diffusivity in the x-direction
 α_y = thermal diffusivity in the y-direction
 δ = fracture thickness
 ρ = fluid density
 ρ_f = formation density

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H-OIL UPGRADING OF SHALE OIL FEEDS

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INTRODUCTION

The estimated recoverable reserve¹ of a thousand-billion barrels of oil from the Green River formation shale in Colorado, Utah, and Wyoming periodically rekindles interest, particularly on the part of crude-deficient, domestic oil companies. Recent announcements of a semi-works-scale plant and future plans for a 30,000 to 60,000 barrels per day unit to obtain oil from shale have stirred current interest.

Oil shale is a fine-grained, compact, sedimentary rock (marlstone) which contains an organic substance, kerogen. Kerogen is only slightly soluble in known petroleum solvents but is converted to shale oil when subjected to temperatures above 700°F.

The conventional method to recover oil from shale involves room and pillar underground mining and above-ground retorting. Shale oil thus obtained must be upgraded prior to processing by conventional petroleum refinery operations.

SHALE OIL CHARACTERISTICS

Conventional crude shale oil resembles petroleum in that it is composed of hydrocarbons plus sulfur, nitrogen, and oxygen derivatives of hydrocarbons. Shale oil differs from petroleum in other characteristics. Shale oil contains larger amounts of non-hydrocarbons, particularly nitrogen- and oxygen-containing organic compounds, which may be the major constituents in the higher boiling fractions. Shale oil hydrocarbons are highly unsaturated, resembling the products of thermal cracking of petroleum.² Crude shale oil produced by conventional retorts contains about one weight percent sulfur and two weight percent nitrogen. Inspections of a crude shale oil sample are compared in table 1 with those for oil from the Athabasca Tar Sands and vacuum bottoms from West Texas and Kuwait.

Hydrogenation provides one method to upgrade shale oil and to overcome the major refining difficulties caused by nitrogen and sulfur compounds. The ability of the H-Oil process to upgrade shale oil by hydrogenation has been demonstrated in pilot plant equipment.

Hydrocarbon Research, Inc., Trenton, New Jersey.

The H-Oil process was developed jointly by Hydrocarbon Research, Inc. (HRI) and Cities Service Research and Development Company. The original application envisioned for the H-Oil process was the upgrading of hydrogen-deficient petroleum residua, but the ability of the process to upgrade other feedstocks was soon realized. Other heavy hydrocarbon feedstocks successfully upgraded by the H-Oil process include coal tar, shale oil, and oil extracted from Athabasca Tar Sands. H-Oil is particularly applicable for upgrading shale oil because the catalyst is not deactivated by nitrogen and sulfur and the process is operable with shale oil feed containing suspended fine solids.

Since the H-Oil process has been described in detail elsewhere^{3 4 5 6 7}, only a brief resumé is presented. The H-Oil process features an ebullating catalytic system in which the upward velocity of the gas and liquid maintains the expanded bed of catalyst in continuous random motion. This hydrogenating system can handle any high-boiling liquid that is pumpable. Advantages of the H-Oil system relative to fixed bed systems are:

1. Extraneous inert solids introduced with the liquid feed pass through the reaction space and are discharged with the product. In a 30-barrel-per-day, pilot-plant unit, tar sands oil which contained several percent of fine sand was handled without any process difficulties.

2. Isothermal conditions are maintained throughout the reaction space in

3. Hydrogen distribution problems are eliminated throughout the reactor by the random motion of the catalyst.

4. Catalyst can be either intermittently or continuously added and withdrawn to maintain constant catalytic activity within the reaction bed. This prevents down time and eliminates the necessity for "swing" reactors to permit changing the catalyst.

5. There is no tendency for pressure drop to increase as a result of accumulated foreign materials. Tarry deposits do not accumulate on the catalyst. Removal of inorganic matter by filtration, as required at times in a fixed-bed system, is not necessary.

6. Active, rugged catalysts of a relatively small particle size are employed. Catalytic poisoning effects by porphyrin complexes, nitrogen, sulfur, and oxygen in the feed have been mitigated and catalyst life is sufficient to make catalyst regeneration usually uneconomic.

These features make the H-Oil process a versatile system applicable for upgrading shale oil feed.

EXPERIMENTAL RESULTS

Experimental results discussed below are based on single-stage operation; however, a two-stage system is shown in the simplified schematic flow diagram (fig. 1), since there are inherent advantages in a two-stage process.

Inspections for two shale oil feeds are presented in table 2: charge stock A comprises the entire shale oil feed, charge stock B represents shale oil bottoms with an IBP of 601°F.

In single-stage operation with extinction recycling of 650°F+ oil from charge stock A, the liquid was reduced in pour point from +75 to +10°F while the viscosity was reduced from 153 to 33 SSU at 122°F. Results are presented in table 3 for charge stock A with extinction recycling of 950°F+ (Case 1) and 650°F+ (Case 2) oil, respectively. Inspections are given for the total liquid product and for the individual fractions. H-Oil process yields related to volume percent 650°F material converted for single-stage operation are shown in figure 2. Comparable results for light hydrocarbons are presented in figure 3.

Shale oil bottoms, charge stock B, was processed to yield 97 percent of the distillate products boiling below 950°F. With a consumption of 2000 std cu ft of hydrogen per barrel, the pour point was reduced from 110°F to 70°F and the viscosity was reduced from 96 SF seconds at 210°F to 45 SUS at 122°F. Product inspections are presented in table 3. Single-stage operation resulted in 60 percent nitrogen removal. No operating difficulties were experienced with 0.77 weight percent ash in the feed.

Hydrogen consumption for charge stock A as a function of 650°F conversion is shown in figure 4. Hydrogen production from the propane and lighter hydrocarbons produced during upgrading of whole shale oil is insufficient for consumption in the H-Oil process. However, off gases from shale retorting are expected to be sufficient to balance the hydrogen requirement. Hydrogen balances for an H-Oil unit processing shale oil for Cases 1, 2, and 3 are presented in table 4.

Nitrogen removal in the 650°F+ extinction recycle run (Case 2) was 77.6 percent. The relationship between conversion and nitrogen removal for both single- and two-stage operations is presented in figure 5. Single-stage data are based on laboratory results. Two-stage results are predicted from correlations derived from extensive work on petroleum feedstocks. For a plant processing 50,000 barrels per day of shale oil, the stoichiometric maximum quantity of ammonia produced from the whole shale oil is 192 tons per day. Based on 77.6 percent nitrogen removal, the ammonia production is 149 tons per day. For two-stage operation, the production is predicted to be 168 tons per day.

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ECONOMICS

Economics for upgrading whole shale oil (Case 2) and shale oil bottoms (Case 3) are presented in table 5. Compressors are steam driven by steam produced during cooling of the reactor effluent. Pumps are motor driven. Cooling water requirements are minimized by using air coolers to condense the steam from the turbines driving the compressors. Product streams are fuel gas and "synthetic crude."

Investments are on-site for the H-Oil process and include equipment to deliver ammonia-free fuel gas and synthetic crude. Costs are incremental and include only the H-Oil processing step.

These costs can be readily incorporated into an overall shale oil processing scheme. No credit is taken for co-produced ammonia.

ACKNOWLEDGMENTS

The authors express appreciation to the managements of Hydrocarbon Research, Inc., and Cities Service Research and Development Company for permission to publish experimental data on H-Oil treatment of shale oil.

TABLE 1.—*Inspection on charge stocks*

<i>Source</i>	<i>Shale oil</i>	<i>West Texas vacuum bottoms</i>	<i>Kuwait vacuum bottoms</i>	<i>Oil from Athabasca Tar Sands</i>
Gravity, °API	18.9	10.5	7.1	6.4
Sulfur, W %	0.8	3.1	5.2	4.6
Ramsbottom carbon, W %	3.6	15.4	17.5	15.8
Vanadium, ppm	4	38	78	120
Nickel, ppm	2	22	26	70
Nitrogen, W %	1.92	0.38	0.38	0.38
Ash, W %	0.04	0.02	0.03	2.6
Hydrogen/carbon atomic ratio	1.6	1.50	1.45	1.47

TABLE 2.—*Inspections on shale oil feed*

<i>Charge stock</i>	<i>A</i>	<i>B</i>
Gravity, °API	18.9	6.0
Sulfur, W %	0.8	0.6
Nitrogen, W %	1.92	2.5
Carbon, W %	84.21	84.98
Hydrogen, W %	11.24	10.19
Oxygen (by diff.) W %	1.79	1.56
Ash, W %	0.04	0.77
Ramsbottom carbon, W %	3.6	13.2
Pour Point, °F (upper)	75	110
Viscosity, SF sec. at 210°F	153*	96
Benzene insolubles, W %		1.0
IBP, °F	432	601
IBP-975°F (IBP-650°F)		
Gravity, °API	(29.2)	12.6
Sulfur, W %	(0.78)	0.6
Aniline Point, °F	(88.)	103
Pour point, °F		80
Volume percent	(32)	57.0
975°F+ (650°+)		
Gravity, °API	(14.0)	-1.3
Sulfur, W %	(0.69)	0.6
Ramsbottom carbon, W %		25.5
Volume percent	(68)	43.0

*SUS at 122°F

TABLE 3.—*H-Oil processing of shale oil feeds, summary of yields and inspections*

<i>Charge stock</i>	<i>A</i>		<i>B</i>
	<i>Whole shale oil</i>		<i>Shale oil bottoms</i>
<i>Case number</i>	1	2	3
Yields, % on feed			
H ₂ S, NH ₃ , H ₂ O, W %	4.2	4.2	4.0
C ₁ -C ₃ , W %	2.9	5.8	8.1
C ₄ -180°F, V %	6.2	11.6	8.5
180-400°F, V %	15.7	26.4	14.4

TABLE 3. (cont.)

<i>Case number</i>	1	2	3
400-650°F, V %	53.8	70.5	33.4
650°F+ (650-950°F), V %	30.2	(40.7)
950°F+, V %			8.6
Total C ₄ +liquids, V %	106.0	108.5	105.6
Hydrogen consumption, SCF/Bbl	1320	1930	2000
Inspections			
Collected liquid			
C ₄ +gravity, °API	36.3	43.7	28.4
Sulfur, W %	0.02	0.02	<0.07
Nitrogen, W %	0.60	0.43	1.08
Pour point, °F	60	10	70
Viscosity, SUS at 122°F	36	33	45
IBP-400°F			
Gravity, °API	51.6	53.8	52.6
Aniline Point, °F	124	124	120
Nitrogen, W %	0.28	0.16	0.24
Paraffins, V %	45	47	44
Olefins, V %	3	2	4
Aromatics, V %	16	15	16
Naphthenes, V %	36	36	36
400-650°F			
Gravity, °API	34.1	34.6	28.7
Diesel Index	45	47	30
Nitrogen, W %	0.46	0.50	0.67
Sulfur, W %	0.02	0.02	<0.07
650°F+ (650-950°F)			
Gravity, °API	25.1		(18.1)
Diesel Index	40		(25)
Sulfur, W %	0.02		(<0.07)
Nitrogen, W %	0.56		(1.12)
950°F+			
Gravity, °API			5.9
Sulfur, W %			<0.07
Ramsbottom carbon, W %			11.7
Nitrogen, W %			1.7

TABLE 4.—*Hydrogen balance*

<i>Case number</i>	1	2	3
Items			
H-Oil capacity, barrels/day	50,000	50,000	16,000
Chemical hydrogen consumption, SCFB	1320	1930	2000
Chemical hydrogen consumption, MMSCFD	66	97	32
20% allowance for losses, MMSCFD	13	19	7
Total hydrogen consumption, MMSCFD	79	116	39
Hydrogen production from H-Oil C ₃ -MMSCFD	43	86	42
Percent hydrogen deficiency	46	26	0

TABLE 5.—*Economics for H-Oil upgrading of shale oil*

<i>Feedstock</i> <i>Case number</i>		<i>Whole shale oil</i> 2		<i>Shale oil bottoms</i> 3	
Feed rate, Bbl/SD		50,000		16,000	
Investment, \$		12,800,000		5,800,000	
Costs	Unit cost	Req't	\$/yr.	Req't	\$/yr.
Hydrogen, SCF/Bbl	30¢/MSCF	1,930	9,554,000	2,000	3,168,000
Catalyst			1,120,000		448,000
Power, KW	0.9¢/KWH	11,000	784,000	3,700	264,000
Fuel, MM Btu/hr	31¢/MM Btu	100	246,000	34	83,000
Cooling water, gpm	1.0¢/M gal.	5,500	26,000	1,800	9,000
Labor, men/shift	3.35\$/hr.	4	119,000	3	89,000
Supervision & overhead			190,000		143,000
Maintenance & supplies	4.3% inv.		552,000		250,000
Insurance & local taxes	2% inv.		256,000		116,000
Depreciation	18-yr. st. line		713,000		322,000
Incremental total cost			13,560,000		4,892,000
Incremental cost, \$/Bbl feed*			0.82		0.93
Ammonia Production, tons/day			149		49

*Profits are not included

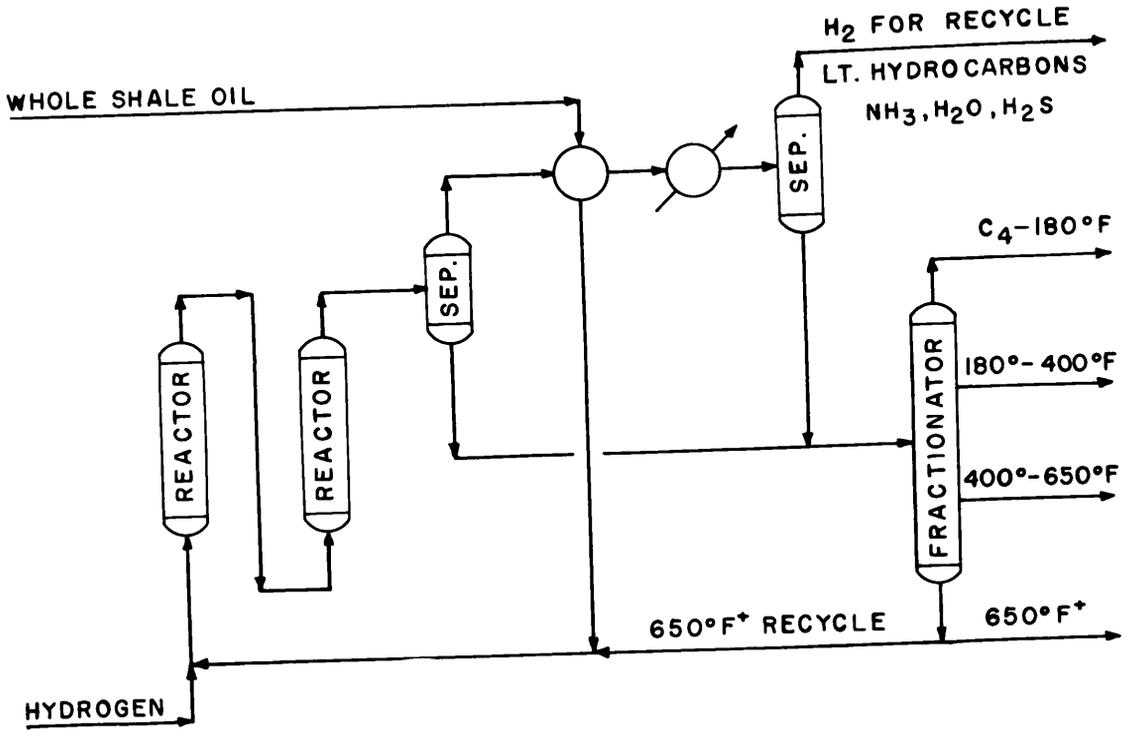


FIGURE 1.—H-Oil upgrading of shale oil. Schematic flow diagram.

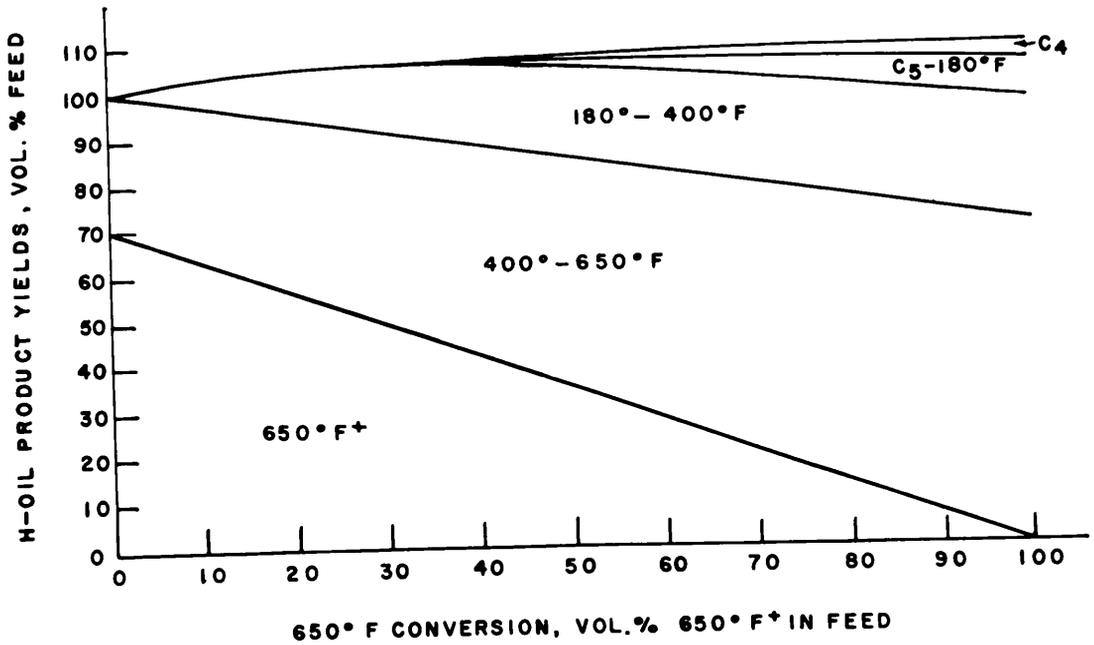


FIGURE 2.—H-Oil upgrading of whole shale oil. Yield distribution vs. conversion. Single stage data.

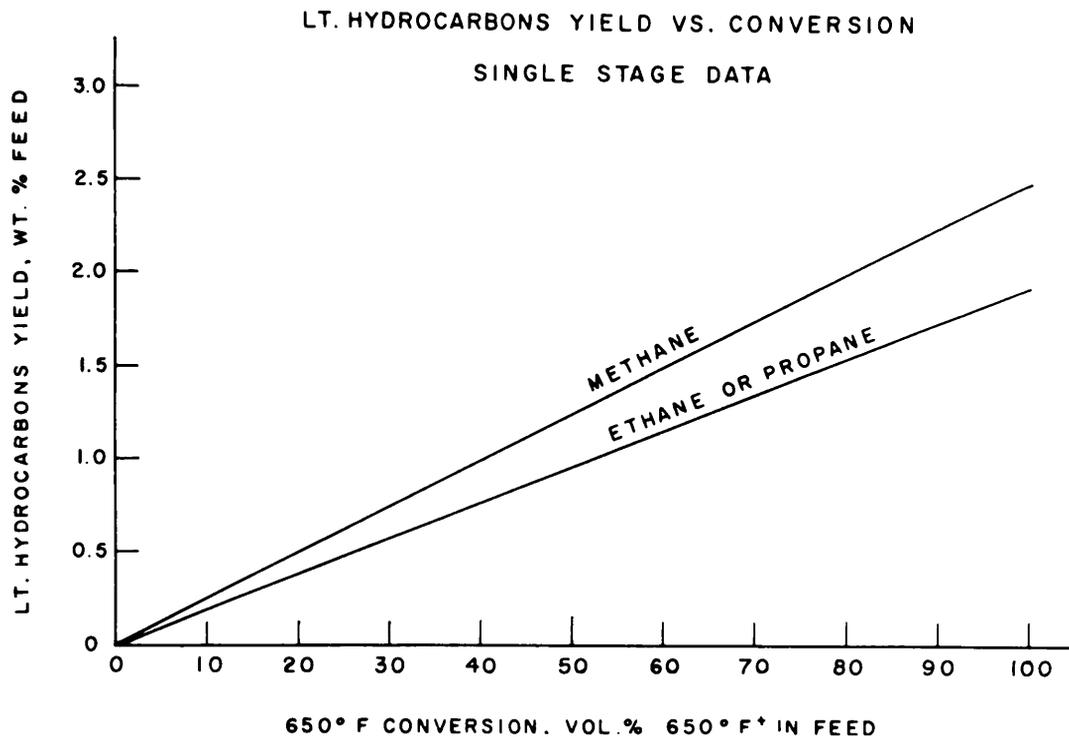


FIGURE 3—H-Oil upgrading of whole shale oil. Lt. hydrocarbons yield vs. conversion. Single stage data.

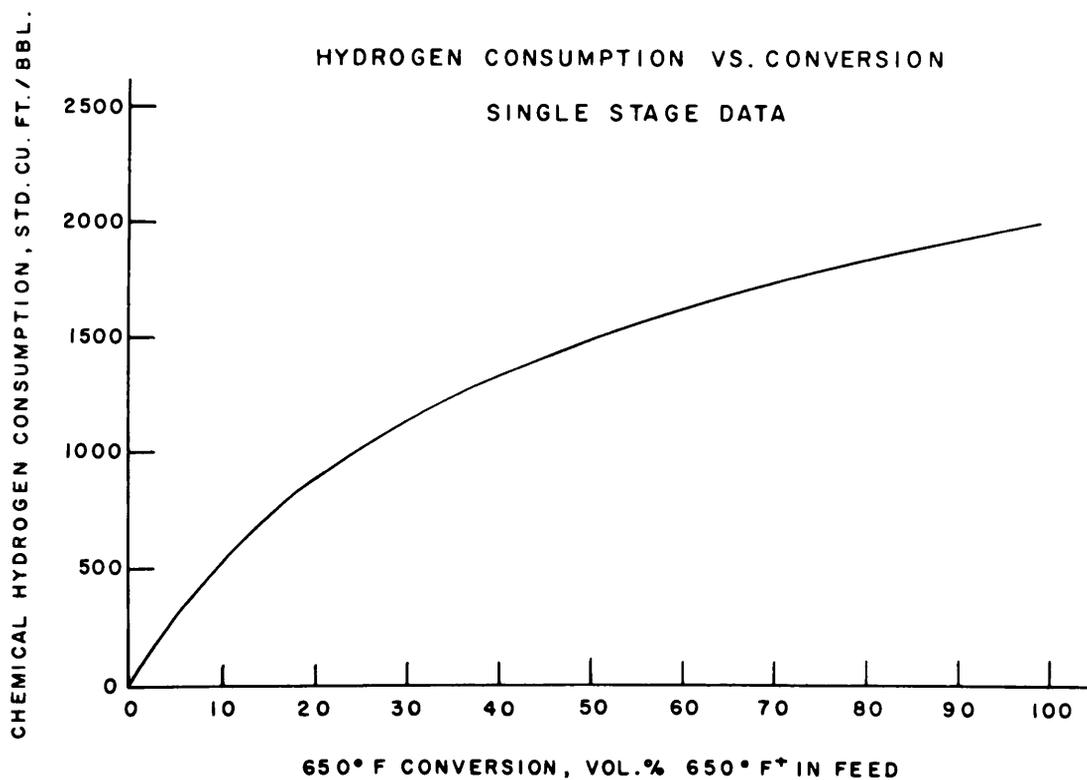


FIGURE 4.—H-Oil upgrading of whole shale oil. Hydrogen consumption vs. conversion. Single stage data.

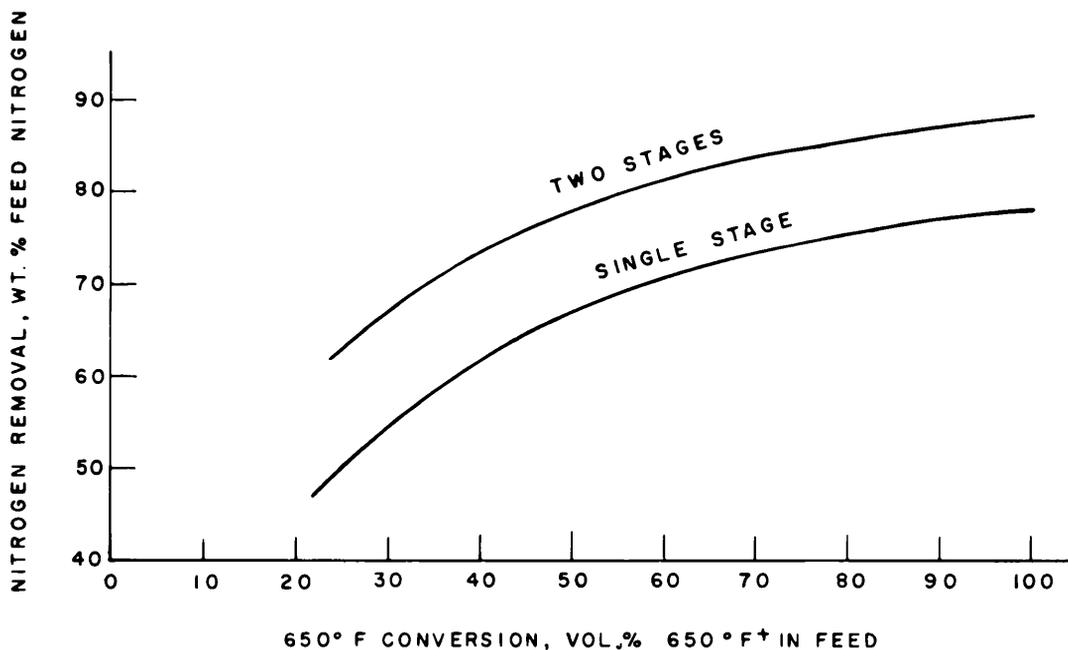


FIGURE 5.—H-Oil upgrading of whole shale oil. Nitrogen removal vs. conversion.

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HYDROTORTING—USE OF HYDROGEN FOR IMPROVED RECOVERY OF SHALE OIL

WARREN G. SCHLINGER and
DALE R. JESSE

INTRODUCTION

The past two to three years have witnessed a renewal of research efforts directed toward the development of economically attractive methods for recovering shale oil from the vast oil shale reserves in Colorado, Utah and Wyoming. The patent and technical literature has disclosed and described numerous techniques for achieving these goals. Several investigators^{1 2 3} have reported on the advantages of using hot hydrogen-containing gases as a retorting fluid instead of air. Use of hydrogen permits recovery of shale oil in yields far in excess of the Modified Fischer Assay.⁴ It has been demonstrated that yields in excess of 120 to 125 percent of the Fischer Assay can be realized.

BACKGROUND

The recovery of the shale oil generally consists of three major phases; (1) mining and transporting the crude oil shale to the primary processing site, (2) extraction of the shale oil from the large fraction of ash and foreign material in the raw shale and (3) refining the crude shale oil to marketable products. Each of these steps is a major operation and contributes significantly to the cost of obtaining finished products from oil shale.

The following discussion will be directed primarily toward the second of these phases, however, some discussion as to how the second and third phases can be combined will be presented.

In nearly all methods for extracting the shale oil, heat is supplied by combustion of a portion of the carbonaceous material in the shale to break down thermally and to distill the organic matter contained in the natural shale. A number of retorts have been proposed and demonstrated employing a wide range of flow conditions. However, almost without exception, heated air has been employed to burn the residual organic material left on the shale after a major portion of the original organic material or kerogen has been decomposed and removed by the hot combustion gases.

It is well known that the Fischer Assay⁴ procedure does not measure the total hydrocarbon content of oil shales. Instead it is intended to be a labora-

Texaco Inc., Montebello Research Laboratory, Montebello, California.

tory evaluation test for estimating the maximum oil recoverable in a conventional air retort system. The spent shale from the assay typically contains 5 percent organic and free carbon. This carbon represents nearly 12 gallons per ton of material that could be recovered as liquid hydrocarbon under more suitable retorting conditions.

Tests will be described in which, by use of hot hydrogen, the oil shale was almost entirely stripped of its organic material. In these tests hydrogen at pressures ranging from 1000 to 2000 psig was employed in a recycle system. By controlling the temperature of the recycle gas, complete and efficient retorting is realized. All but a few tenths of a percent of the organic carbon in the shale can be converted to distillate hydrocarbons. Yields of oil ranging from 105 to 115 percent of Fischer Assay can be repeatedly obtained. A typical yield obtained by hydrogen retorting or "hydrotorting" is shown in table 1. For comparative purposes the oil yield from a conventional retort employing air as the retorting fluid is also included in the table.^{5 6}

TABLE 1.—*Oil yield comparison air vs. hydrogen as retorting fluid*

	<i>Air Retort</i>	<i>Hydrotort</i>
Raw shale Fischer Assay, gals/ton	31.6-33.3	33.4
Product oil yield, gals/ton	30	37.1*
Product oil basis Fischer Assay volume percent	90-95	111
*C ₆ + liquid product		

The effectiveness of hydrogen as a retorting medium is further emphasized by the state of the spent shale. After the hydrotorting is completed, the spent shale has no cohesive strength and is easily crushed to a dust resembling conventional cement. Figure 1 is a photographic comparison of the raw and spent shale. The majority of the particles will pass through a 200-mesh sieve; this spent shale is apparently composed of the original particles deposited during formation of thick sedimentary oil shale deposits. Although the shale as mined is a strong coherent mass, it appears that the binder is actually the kerogen or kerogen-related components. Once these organic materials are thoroughly removed, nothing remains to cement the sedimentary particles together. Pieces of oil shale as large as 4 inches in diameter have been successfully hydrotorted.

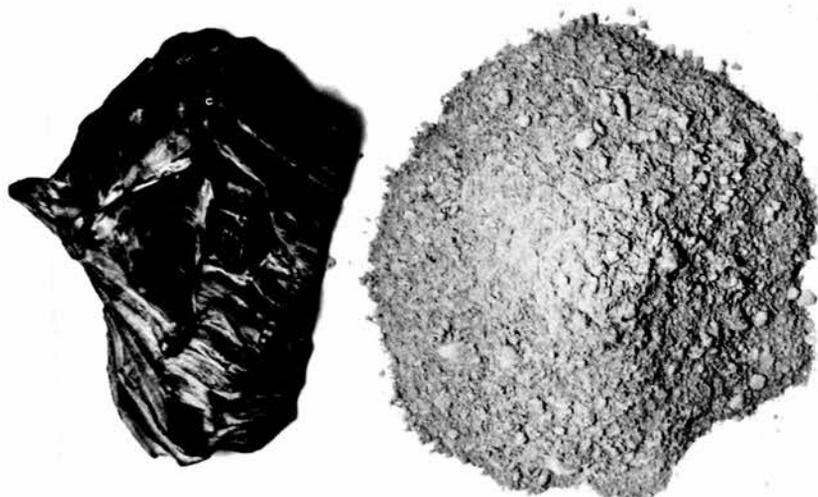


FIGURE 1.—Comparison of raw and spent shale.

PROCEDURE

Numerous tests have been conducted to evaluate the hydrotorting procedure. Two types of equipment have been employed. One series of tests was conducted in an experimental unit as shown in figure 2. The retort in this pilot unit consisted of a section of 6-inch pipe about 12 feet long in series with a catalyst case about 4 feet long fabricated from 3-inch pipe and containing about 15 pounds of catalyst.

In order to obtain more reliable data a larger unit was fabricated. This second unit containing a 20-foot 10-inch diameter retort was assembled without a catalyst case and is shown in figure 3.

In both systems tests were made under batch conditions. The retort was first loaded with oil shale without any crushing or grinding in excess of that required to reduce the maximum size chunks to about 4 inches in diameter. Once the system was purged of air and pressured with hydrogen, the recycle compressor was started and the heaters were fired. As the upflow of hot hydrogen passed through the shale bed, a hot zone moved through the shale and its progress was followed by noting the temperature changes of suitably located thermo-couples. After the top bed thermocouples reached 900°F to 1000°F, the whole system was kept hot for an additional 2-6 hours. The heater was then turned off and the cool hydrogen was passed into the shale bed until the bed reached 100°F to 150°F. After depressuring the system, the shale vessel bottom flange was removed and the spent shale discharged. The liquid product, including a substantial amount of water was collected in the high pressure separator.

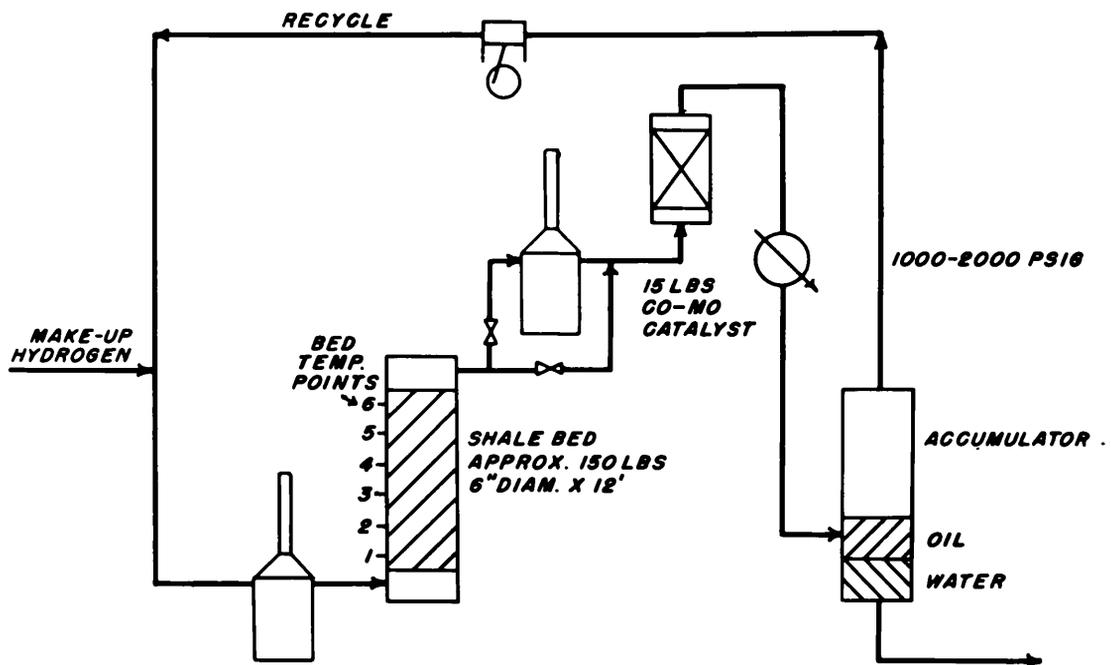


Figure 2. Flow Scheme - Catalytic Hydrotorting.

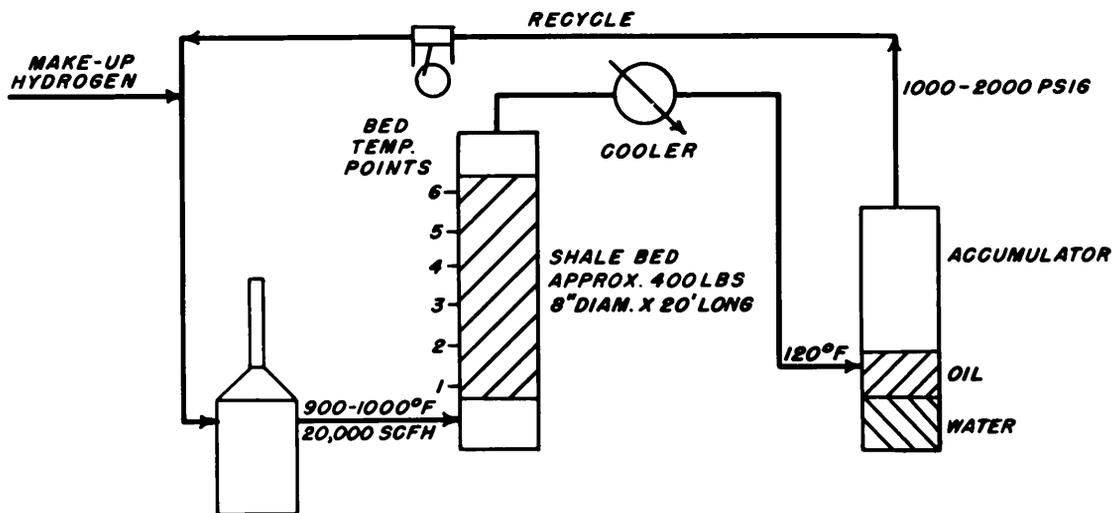


Figure 3. Flow Scheme - Non-catalytic Hydrotorting.

During the test period, make-up hydrogen was added to keep the system at the selected operating pressure. Measurement of the recycle gas composition before and after the test run provided quantitative information on the production of non-condensable gases. Hydrogen consumption was estimated by using mass spectrographic gas analyses and a material balance on the argon present in the make-up stream.

DISCUSSION

A comparison of the quality of oil produced from various retorting procedures is shown in table 2. Oil produced by the Fischer Assay, a conventional air retort, and hydrotorting with and without catalyst are included.

As shown in the table, oil shales for the comparisons were obtained from different areas and had varying assays. However, it is not believed that the differences in assay values significantly affect the properties of the recovered shale oil. There are, however, marked differences in the oil quality. As indicated by the characterization factor,⁷ the non-catalytic hydrotort oil

TABLE 2.—*Properties of shale oil Fischer Assay—air retort—hydrotort*

	<i>Fischer Assay</i>	<i>Air retort</i> ^a	<i>Hydrotort</i>	
			<i>Non-catalytic</i>	<i>Catalytic</i>
Gravity, °API	24.1	20.7	24.5	34.2
Viscosity, SUS at 100°F	73	223	61	—
Viscosity, SUS at 122°F	—	—	—	41.2
Viscosity, SUS at 210°F	36	46	34	—
Sulfur, wt %	0.98	0.77	0.56	0.12
Nitrogen, wt %	1.80	2.01	1.88	0.77
Carbon, wt %	85.23	—	85.44	—
Pour point, °F	75	90	65	80
Hydrogen, wt %	11.38	—	11.12	—
Conradson carbon, wt %	2.33	4.57	4.28	0.03
Characterization factor (K)	11.42	11.45	11.37	11.9
ASTM DISTILLATION				
IBP	192	402	160	166
10%	336	536	278	—
20%	430	622	354	—
30%	518	692	430	—
40%	600	764	506	—
50%	655	814	568	—
60%	685	836	634	—
70%	705	865	682	—
80%	Cracked	889	712	710
90%	—	Cracked	Cracked	—
Fischer Assay, Oil shale charge, gal/ton	33.4	32.5	33.4	42.9

is more aromatic than the corresponding air retort oil. The increased aromaticity of the untreated hydrotort oil probably results from the added liquid material obtained from components that typically undergo condensation reaction to form coke in non-hydrogen atmospheres.

Figure 4 shows the viscosity-temperature relationship of the oils obtained from oil shale by the various processes.

The catalytically treated oil shows further increases in gravity and characterization factor and substantial decreases in sulfur, nitrogen, and carbon residue. In a batch type operation the catalytic treatment is inefficient since the bulk of the shale oil tends to pass over the catalyst bed in a very short period of time at a relatively high space velocity. Further decreases in sulfur and nitrogen would be expected in a more uniform or continuous operation.

A complete material balance based on the non-catalytic batch operation is presented in table 3. The hydrogen requirement for this operation is

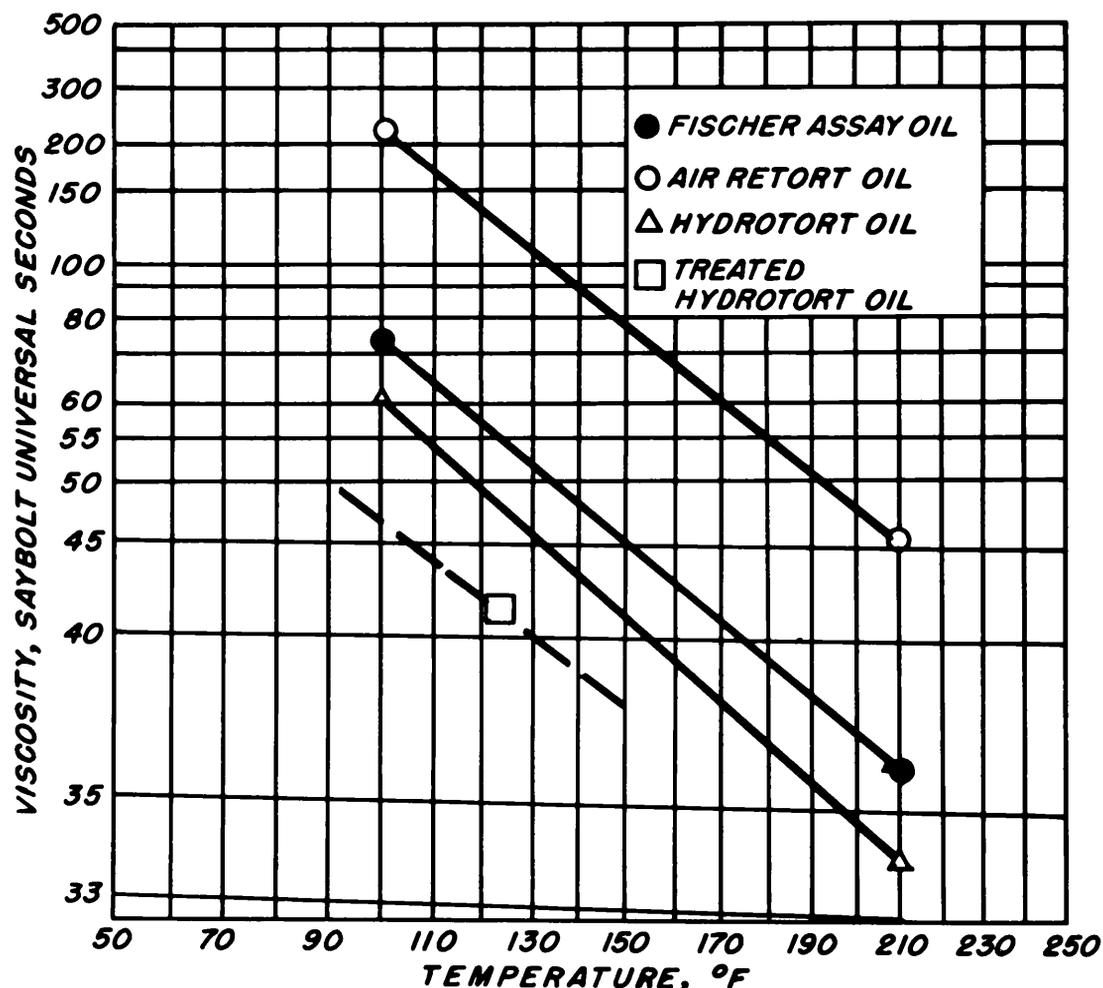


Figure 4. Viscosity-Temperature Relationships for Several Shale Oils.

relatively large. A little more than 1600 SCF of hydrogen are required for each barrel of oil produced, and an additional 500-1000 SCF are required for the catalytic treatment.

TABLE 3.—*Batch hydrotorting of oil shale material balance*

<i>Feed Streams</i>	<i>Lbs.</i>	<i>Gals.**</i>	<i>SCF**</i>
Raw Shale*	2000.000		
Hydrogen (as 100%)	8.467		1594
Total	2008.467		
<i>Product streams</i>			
Spent shale	1659.700		
C ₆ + oil product	279.200	37.1	
Water	25.000	3.0	
Hydrogen sulfide	0.886		10
Ammonia	2.863		64
Methane	19.836		470
Ethane	10.494		132
Propane	7.690		66
Butylenes	0.440		3
Butanes	2.000		13
Pentanes	0.358		2
Total	2008.467		

*Fischer Assay: 33.4 gallons per ton oil; 3.0 gallons per ton water.

**Basis 1 ton raw shale charge.

The hydrogen required for the hydrotorting phase and catalytic treatment of the oil from 1 ton of 33.4 gallons per ton shale could be supplied by partial oxidation^{8,9} of about 4 gallons of the least desirable portion of the liquid product. In addition it is estimated that the dry gas production is sufficient to supply the fuel needs of the process.

The dry gas produced consists primarily of methane. During the tests shown herein, the average bed temperature was 975°F; by altering the hydrotort temperature, and/or introducing components such as CO or CO₂ into the retorting gas the dry gas production and thus hydrogen consumption can be changed markedly.

Table 4 presents a comparison of the elemental composition of the raw and spent shale. The analysis includes both organic and inorganic material

such as water of hydration and carbonates. The organic carbon content is typically less than 1 per cent.

TABLE 4.—*Raw oil shale and spent shale properties*

	<i>Raw oil shale</i>	<i>Spent shale</i>
Carbon, wt %	19.520	7.230
Hydrogen, wt %	1.965	0.265
Nitrogen, wt %	0.430	0.060
Sulfur, wt %	0.290	0.205

CONCLUSIONS

Hydrogen stripping or hydrotorting presents an effective method for recovering oil from oil shale. Other recovery schemes fall far short of the oil yields obtained when employing hydrogen-rich gases at elevated pressures. This efficiency is in part due to the suppression of coke production by the hydrogen. In addition, less net thermal energy is needed for extraction since the endothermic decomposition of inorganic carbonates can be avoided by close temperature and composition control of the recycle gas.

ACKNOWLEDGMENTS

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PRESENT TRENDS IN ESTONIAN-RUSSIAN WORK ON OIL SHALE

WŁADISŁAW J. CIESLEWICZ

NATURE OF ESTONIAN OIL-SHALE DEPOSITS AND THEIR COMMERCIAL EXPLOITATION

Estonian oil-shale industry had a very inauspicious start. The story is told that at the beginning of the last century an Estonian peasant built a new house for himself, using blocks of kukersite shale. The first time he lit the stove, made also of the same material, everything—the stove and the house—went up in smoke.

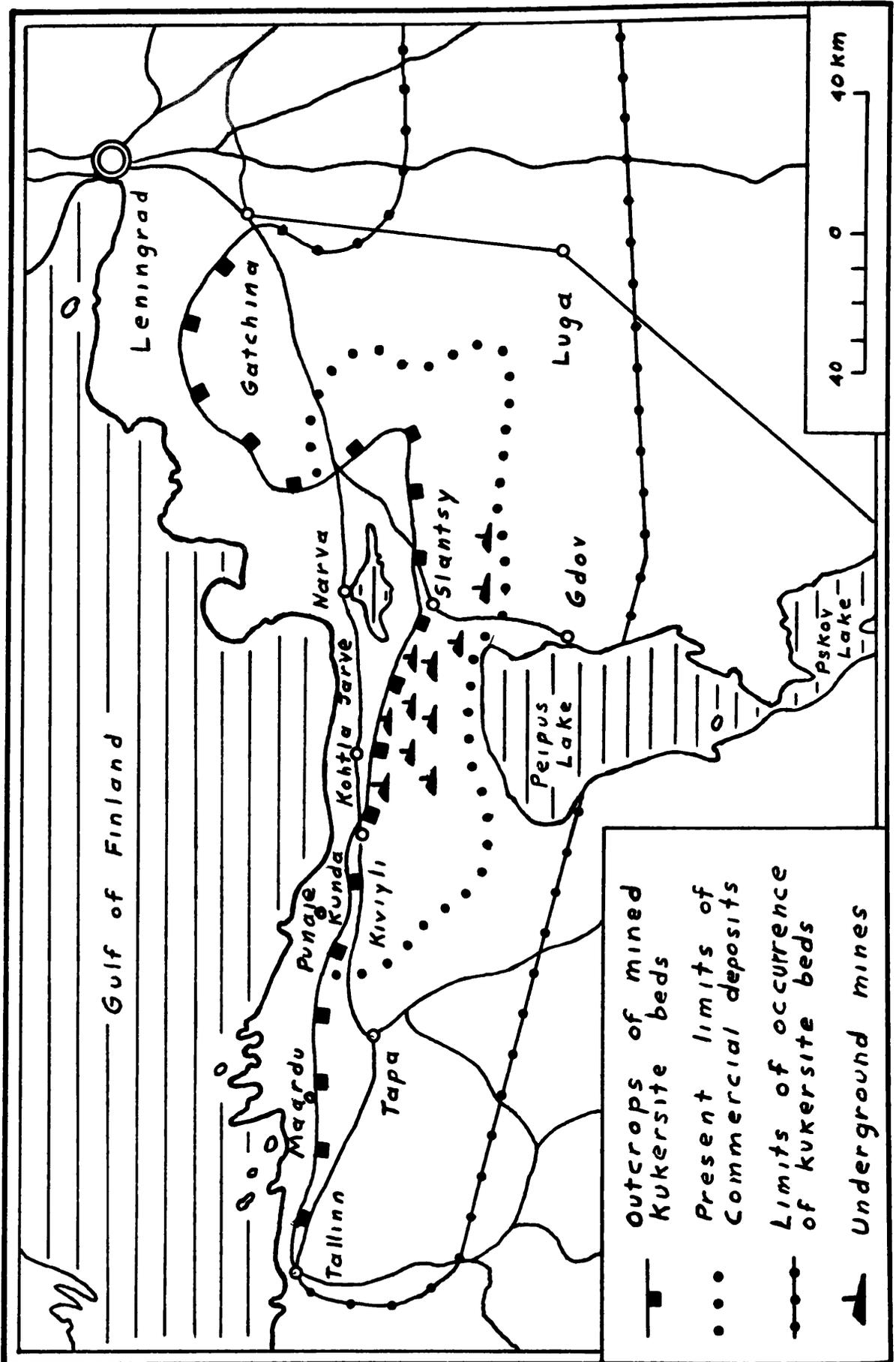
The hapless peasant did not know of course that Estonian oil shale contains up to 35-40 percent kerogen, of which more than 80 percent consists of volatile components. On retorting, this organic matter gives rise to tars (70 percent) and a vapor-gas mixture. Used as fuel, kukersite yields 2,000-2,500 k cal/kg (Rostovtsiev, 1965).

Large-scale commercial exploitation of the oil shale started after the Second World War when Russian Bolsheviks seized and subjugated the Baltic countries. The Estonian oil-shale basin lies near Leningrad, Russia's second largest city and a great industrial center. The Baltic region of Russia has always been deficient in fuel and hydroelectric power, and in the post-war years Russia has used oil shale of occupied Estonia to meet these two demands.

Kukersite oil shale is found in thick calcareous Late Ordovician beds of marine origin which lie throughout the basin at depths varying from 0 to 300 m. Shale layers with thicknesses from 0.6 to 0.7 m and up are considered commercial. Shale beds with an aggregate thickness of 3 m are also common throughout the basin (Baukov, 1958).

The Russians have developed more than 10 large underground mines and several open-pit mines whose total annual output in 1966 reached 25 million metric tons. As of 1957 40 percent of all oil shale mined was burned as raw fuel at industrial plants and power plants throughout the Pre-Baltic region. The new Pre-Baltic electric power plant at Narva, which has an annual output of 1.5 million kilowatts, is also run on oil shale. As raw fuel for needs of the Pre-Baltic region, the kukersite shale costs about 20 percent less per heating unit than coal which must be transported from the

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remote Donets or Kuznetsk basins. The remaining 60 percent of oil-shale output as of 1957 was retorted at gas generating stations and chemical processing plants (Pravda, July 25, 1958).

The two largest oil shale processing complexes are located at Kohtla Jarve and at Kiviyili, right in the mining area. Another gas generating combine, retorting about 1 million tons of oil shale per year, is at Slantsy on the Russian-Estonian border. Gas generated at these three centers is piped to Leningrad in Russia, also to Tallin and Narva in Estonia. In 1965 the gas works of Kohtla Jarve and Slantsy, using in part the reconstructed compartment kilns, produced municipal gas at the rate of 3 million cubic meters every 24 hours. An additional 140 km of pipelines was laid in 1965 to carry oil shale gas from Kohtla Jarve to Tallin.

Since 1958 the Leningrad area is also being supplied with cheaper fuel brought in by pipelines from natural gas and oil fields in northern Caucasus. The construction of another such pipeline, this time from the Second Baku area, is scheduled for completion by the end of the current five-year plan (1970). These new sources of cheap natural gas and oil pose a serious threat to Estonian oil shale industry. Moreover, Russia's political commissars, after 50 years of socialist economy, finally came to the conclusion that, in the long run, production based on profit and incentive, that is on capitalism, is the only viable economic system. Consequently, they are reluctant to continue state subsidy of oil shale industry and are demanding profitable operations.

CURRENT OIL-SHALE RESEARCH AND DEVELOPMENT

To this end, in the last decade or so, an extensive and continually expanding research program has been organized. The reduction of mining and processing costs, and the finding of new uses for oil shale and for the by-products of oil shale processing, are the two general objectives. Several research organizations are involved in this work. The most important among them is the Oil Shale Institute at Kohtla Jarve. This organization is—according to Russian claims—the largest oil shale research center in the world. The Oil Shale Institute was established 15 years ago and is directed by Professor E. Pietukhov. Among the scientists working at the Institute are Academicians* Hugo Raudsepp and Agu Aarna; Doctors S. I. Feingold, A. S. Fomin, A. V. Korzhevnikov, and M. Ia. Gubergrits (Ogoniok, February 2, 1964). Another prominent name among Russian oil shale scientists is Nicolai Sieriebriannikov, the chief engineer (manager) of the Kohtla Jarve works where the Oil Shale Institute maintains many of its laboratories and runs several pilot plants. Many investigations on oil shale are also conducted at the

Tallin Polytechnic Institute and in a number of research institutes in Leningrad. The above-mentioned organizations are credited with development of several new methods and many adaptations of processes and technologies used in petroleum industry, but not directly applicable to oil shale processing. Several different institutes of the Academy of Science and of the Ministries of Fuels and of Mining are also working on problems of oil shale industry. The principal research and development aims are as follows:

MINING

A. *Modernization of underground mines*

Because of antiquated methods, the costs of mining kukersite shale are disproportionately high and the progress in reducing these costs is slow. Between 1959 and 1965 (last seven-year plan) the mining cost per ton of shale went down only 13.7 percent. The Oil Shale Institute and various mining institutes are carrying out considerable research work to bring about further improvement. A cursory review of a recent publication describing 14 different mining research projects shows concentration of effort on the following problems: development of cutters, loaders, and other machinery specially designed for oil-shale mining to replace coal and ore mining machines used until now: studies of room and pillar methods; mechanical ore dressing including separation in heavy media; wet jigging and screening; improvements in blasting techniques; express methods of ore-grade control on conveyors; and automation techniques.

A new and fully mechanized mine is now being developed near Kohtla Jarve. When completed, this mine will cover an area of 50 square miles and have 30 miles of conveyor belts: it will produce 33,000 metric tons of shale per day mined by room and pillar method. Surface buildings and installations will be made to constitute self-containing units to facilitate servicing and repairs. Three more mines of this type are planned (the magazine: *Soviet Union*, no. 187, September, 1965). Modernization of older mines is gradually taking place; notably, hand sorting of shale is being replaced by mechanical separating in heavy medium (magnetite suspension) (Ogoniok, August 28, 1966). The Russians claim that as a result of improvements already made, the monthly output per miner at Kohtla Jarve reached 117 tons (Ogoniok, February 2, 1964).

B. *Development of open-pit mining*

Although large-scale open-pit mining operations started only several years ago, they already account for about 30 percent of the oil shale mined. The

*Members of the Russian Academy of Science.

largest open-pit mine is located in Kohtla Jarve area. Specially built draglines, the ESh-15/90 with 15 m³ bucket and 90 m boom, are employed. In 1963, which was the first year of ESh-15/90 operation, the dragline working in the pit Estonslaniets #1 moved 2010 thousand cubic meters of dirt (Rostovtsiev, 1965; Arumae, 1965).

PROCESSING

A. *Development of large retorts of new design and reconstruction of older gas retorts*

The retort with the new design is the so-called UTT-500. It employs a solid heat exchanger, has a throughput rate of 500 tons of shale per day, and is cheaper to build because it uses up only 40 to 50 percent of the metal required for the older type tunnel and shaft kilns. UTT will be used especially at the oil-shale chemical processing plants, but will eventually replace older gas retorts as well.

It was developed by the Kzhizhanovskii Institute of Energetics and has been extensively tested during the last 6 or 8 years on a semi-commercial pilot plant at Kiviylü. The UTT-500 is very flexible and can work either on the tar regime or on the gas regime. Under the tar regime the oil shale is semi-coked at relatively low temperatures (480°C-520°C), and tar is the principal product (15-20 percent per dry shale). Under the gas regime, at retorting temperatures of 650°C-750°C, fuel gas is the main product (120 m³/ton of shale). Finally, if high temperatures are maintained during gas regime, pyrolysis of volatile components may be also achieved, resulting in still higher gas yields (Doilov, 1965).

Russians look upon this new retort as a major breakthrough in their technology of oil shale processing. This is true if one considers that many of their older retorts such as the Pinch type GGS-1 and GGS-4 had prior to their reconstruction in 1961-1963 a shale throughput of only 33 and 37.5 tons per day, respectively (Halling, 1965).

The Russians claim that by installing batteries of UTT-500 in large enough numbers they will be able to cut by half the processing costs of any given plant. The new UTT design is highly praised by everyone concerned, and there is a general clamor for its immediate use. Some UTT-500 are already in commercial operation. However, I have found no information to date indicating that UTT installation on a large scale has actually begun. This appears to be caused by bureaucratic delays in allocation of funds and materials for UTT construction and by technical difficulties in applying the results of research. It is generally true that Russian research is far ahead of Russian technology.

In 1961-63 the older Pinch type compartment retorts at Kohtla Jarve gas generating stations were reconstructed and converted from vertical to horizontal-transverse flow of heat carrier (gas). This insured better heat distribution in the shale charge and made possible an increase of shale throughput of each retort by 40 percent (Halling, 1965). Modification of fluid regimes of these retorts is planned in order to secure further increase in retorting rates (to 80 tons per day). The condensing systems will also be improved. Generated gas will go through supplementary cooling to 15°C-20°C, and electrofilters will be installed. This will reduce losses of very light tars that escape with fuel gas in quantities of 1-2 g/m³ of gas (Piik and Vakher, 1965).

Looking to the future, the Russians have also started the development of a much larger retort than the UTT-500. It will presumably employ solid heat exchangers and will be able to process 1500 tons of shale per day. Working on this giant retort are the Teploelektrprojekt of Leningrad (a fuel technology institute) and the Academy of Science (Pravada, December 24, 1964). The Russians hope that this retort, when developed, will eventually process all shale mined. The power plants and industrial plants, which now burn shale as raw fuel, will be supplied with fuel oil instead. Burning of fuel oil in place of raw shale will reduce both the cost of operation and the excessive air pollution. Moreover, shale gas and shale crude, produced at these throughput rates, will become really competitive with natural gas and oil.

B. Development of the so-called energy-chemical or power-chemical method of oil shale processing

This new approach emphasizes production of quality tar and not solely the generation of gas. The tar obtained is used as raw material for production of a wide variety of shale-petrochemicals. To this effect the Russians have begun to change the regimes of their gas generators. The generator gas itself is now more extensively used in the processes of organic synthesis. In the last few years the Oil Shale Institute has perfected the technology for utilizing retort gas in production of ammonia.

Basic to this whole concept of energy-chemical utilization of oil shale is, of course, the new UTT-500. It was, in fact, designed especially for energy-chemical processing. The information gathered from several fragmentary descriptions gives the following general picture of the UTT retorting process. Oil shale of different grades crushed to small size is fed into the retort, together with ash of spent shale heated up to 850°C. The shale is then semi-coked at low temperatures. These were variously reported as 350°C-500°C and 480°C-520°C. The gaseous fraction is very high in hydrocarbons

(70 percent) of which up to one-half are olefins. The tars, likewise, have high concentrations of light olefins and aromatic hydrocarbons, especially benzene. On the other hand, the content of undesirable acidic components (CO_2 and H_2S) in the gas is low, thanks to chemical sorption of these components by heated ash used as solid heat exchanger. Plants working under the chemical (tar) regime make maximum use of both the gaseous and the liquid fractions for production of oil shale chemicals. The gas is cleaned and transferred to organic synthesis plants where olefins (ethylene and propylene) are removed from it. The latter are used principally in the production of detergents, also polyethylene, acetone, phenols, and a few other products. The remaining gas is used for the production of ammonia fertilizers and carbamide.

At several plants at Kohtla Jarve and Kiviylil the oil shale is also retorted for shale gasoline, 'kukersol' as the main product. The Russians claim that from high-grade shale oil (30-45 percent kerogen) they get 50 gallons of shale crude per ton (Baukov, 1958). This is twice the amount which we expect to obtain from Colorado shale. However, in spite of this high yield, at this time the kukersite crude is not competitive with natural petroleum and its production is not emphasized. Light gas oils are used for lubricants, detergents, and other products. The shale-lubricants allegedly are superior in quality to those obtained from natural petroleum.

The Oil Shale Institute has developed a new method of preparing medium tars obtained in semi-coking for their distillation. This method, which is now employed in the industry, consists of thermal settling and washing off of chlorides. The distillates are used as fuels or processed to electrode carbon. The latter was found superior in quality to electrode carbon prepared from petroleum tars. Heavy tars with high degree of impurity so far have been excluded from processing. They are merely diluted with distillates, decanted, and used as heavy gas oil. The residuum is used only in part as an admixture to oil shale burned in gas generators; the bulk is taken to the dump. However, studies are being made on processing of heavy tars and slurries to electrode coke (Ekonomicheskaja Gazeta, June 25, 1963; Aarna, 1965, Ioonas, 1965; Pietukhov, 1965; Magazine: Iunost', June, 1966). Considerable quantities of phenols are obtained from benzene water and from tar water (Aarna, 1965). Some data showing yields of several specific products obtained in processing oil shale in UTT retorts are given elsewhere in this paper (table 2). Reported yields of products obtained in older tunnel and compartment ovens working under gas regime are as follows:

per ton of processed shale:	municipal gas	400 m ³
	benzene	25 kg

sulfur	3 kg
tar	50 kg

the tar contains:	phenols	1 kg
	naphthalene	1.5 kg
	anthracene	0.3 kg

Under the new energy-chemical concept of shale utilization, more than 30 different chemicals are now produced from oil-shale gas and tar besides the municipal gas, gasoline, kerosene, diesel fuel, lubricants, and asphalts. Among these products are toluene, xylene, butyl alcohol, phenols, phenol formaldehyde tars, acetone, detergents, ammonia, pesticides and herbicides, drying oils for the printing industry, tanning agents, aniline dyes, improved flotation agents, plasticizers, polyesters, fibers, foam plastics, synthetic rubber, special glues, paints and varnishes, ion exchange resins, and electrode coke. As methods and technologies are perfected, new plants are being added to the Kohtla Jarve and Kiviylu complexes. Some of the plants recently put into operation are those producing pesticides, lubricants, detergents in semi-finished form (paste), electrode coke, and ammonium (Pravda, March 28, 1964).

SOME RECENT RUSSIAN STUDIES ON PROCESSING OF OIL SHALE

A number of investigations carried out during 1963 and 1964 seem particularly pertinent to our own studies and therefore deserve special mention.

Pietukhov, Aranovich, and Nudel'shtrekher (1965) studied the influence of temperature on the composition of gas during processing of shale in the UTT-500 retort. They analyzed 105 representative samples of gas obtained under temperatures ranging from 457°C to 547°C. Since nitrogen is not an inherent component of the gas obtained by semi-coking of oil shale in the UTT retort, the calculations were based on assumption of a nitrogen-free gas. The data from about 100 observation-pairs were tabulated, subjected to mathematical correlation analysis, and the results were plotted in the form of graphs to show a number of correlations (graph 2. following page).

The results indicate strong influence of temperature on the composition of gas. Nitrogen content drops off very sharply as temperature increases. This is in part due to the fact that at higher temperatures the generation of gas intensifies, thus increasing internal pressure of the retort. This in turn cuts

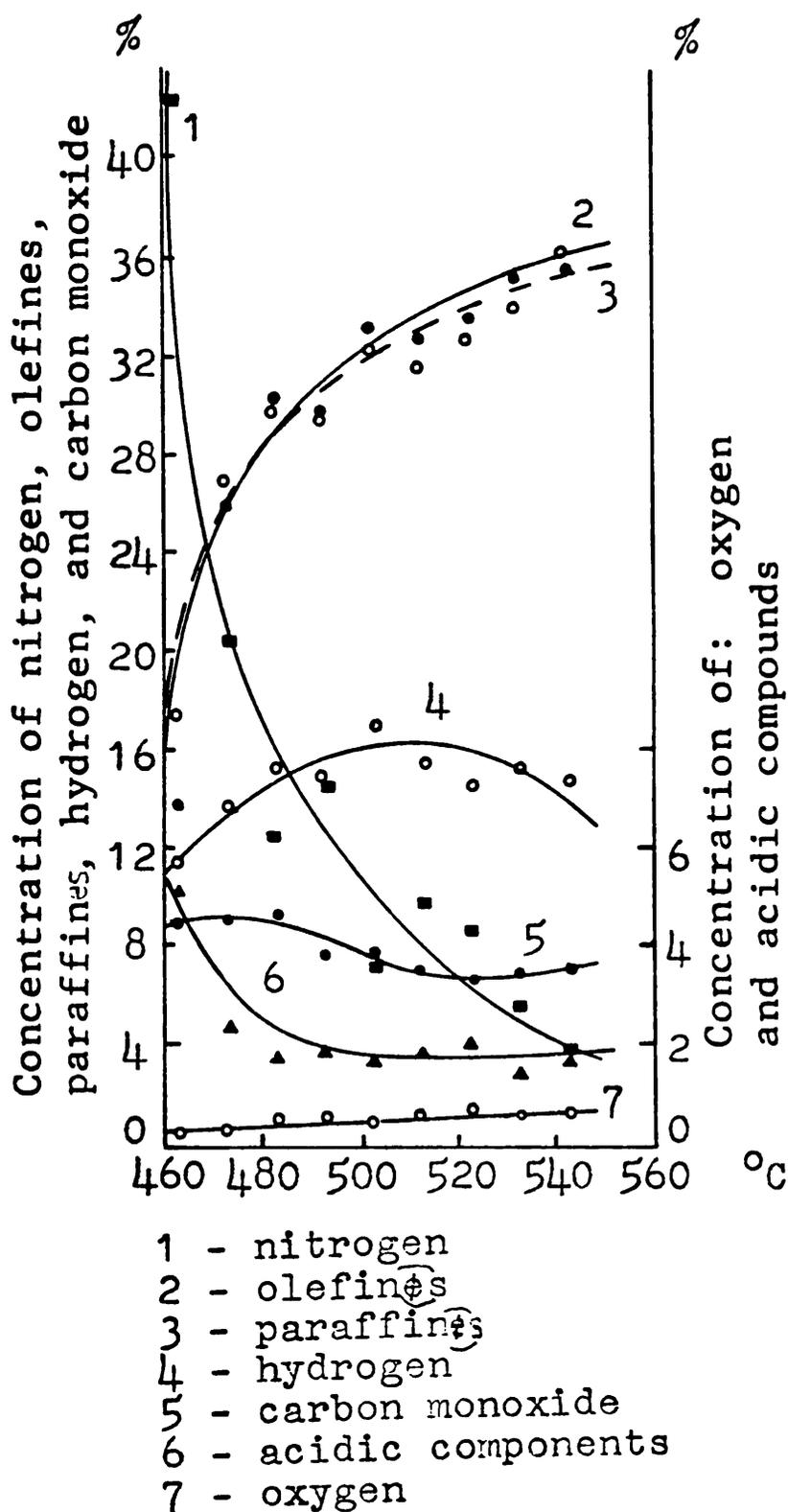


FIGURE 2.—Relationship between content of individual components in gas and temperature of semi-coking (in UTT-500); % of total gas volume.

off more effectively the inflow of nitrogen-bearing flue gases which enter the reactor from the furnace, together with the solid-heat exchanger (heated shale ash). The gradual decrease of hydrogen content past its peak values at 500°C-510°C is due to increased "dilution" of the gas with hydrocarbons. The latter evolve from the shale at a faster rate than does hydrogen, once the temperature rises above 500°C. The drop in carbon monoxide concentration at higher temperature regimes can be also explained—at least in part—by "dilution." By comparison with gases generated in other retorts, the UTT gas is very low in acidic components. This is due to chemical sorbtion of these components by the solid-heat exchanger. The concentration of hydrocarbons increases from 16 percent of the total gas volume at 460°C to about 36 percent at 550°C. However, the molecular ratio: olefins/paraffins remain nearly the same (1.00 ± 0.15), regardless of temperature.

Tables and graphs also show a strong influence of temperature on the total gas output. Over the temperature range from 462°C to 542°C, the yield of paraffins and olefins, expressed in cubic meters/ton of shale, increases five to six times. Hydrogen content records a smaller increase, namely from 3.74 m³/ton of shale at 462°C to 10.00 m³/ton at 542°C. The last figure amounts to less than half of the molecular output of lower olefins. The foregoing quantitative relationship between paraffins/olefins, as well as total hydrocarbons/hydrogen, indicates that dehydrogenation of paraffins plays only a minor role in the formation of the corresponding lower gaseous olefins. Instead, the breaking of C-H bonds of higher hydrocarbons, and the resultant formation of both paraffins and olefins seems to be the principal reaction. This corroborates previous findings of Aarna (1956) that solid-heat exchangers do not cause much dehydrogenation.

The application of pyrolysis to oil-shale processing has several disadvantages. In the first place, the entire shale charge must be heated to a high temperature (about 700°C) which takes extra time and therefore reduces throughput rate; secondly, coke yield increases at the expense of tar; and finally, it subjects the entire apparatus to excessive heating. In an effort to avoid these disadvantages Doilov and Mil'k (1965) worked out a scheme for applying thermo-oxidizing pyrolysis to oil-shale processing.

In refining of petroleum this process results moreover in higher yields of the main product, unsaturated hydrocarbons. However, it is much more difficult to apply the same process and with comparable results to the processing of oil shale. For one thing, the composition of the products of oil shale retorting is much more complex; the boiling ranges are greater; also, the shale oil tars are unstable and have the tendency to form coke. Doilov and Mil'k set up an experimental oxidizing pyrolyser to be operated as part of a single technological unit with the UTT-500 retort. To prevent coke

formation, the oil shale, under this scheme, was retorted at normal tar regime (500°C). Generated vapor-gas mixture directly from the standpipe of the combustion chamber of the retort was run through a condenser, where the heaviest tar components were eliminated. In this particular series of experiments the excluded tars accounted for about 25 percent of the total primary tar. Only tars with specific gravity of 0.89-0.91 were allowed to go into the pyrolyser. On entering the pyrolyzer the mixture had a temperature of 350°C and was still in the vapor-gas phase without undergoing preliminary heating. The vapor-gas mixture was then subjected to oxidizing pyrolysis. The latter took place under optimal conditions of temperature and pressure. These were determined by Mil'k in earlier studies (1963).

Comparison of results obtained by retorting oil shale under tar regime, gas regime, and 'multi-stage' regime with application of oxidizing pyrolysis, are shown in table 1.

Doilov and Mil'k tabulated these results also in terms of total yields per dry shale, and prepared a number of graphs showing different relationships. Complete reproduction and discussion of these data exceed, however, the limited scope of this paper. In general, both higher olefin concentrations in the gas and higher total olefin yields were obtained by thermal pyrolysis process, rather than by retorting in a 'single-stage' pyrolysis in the retort (gas regime). Highest total olefin yield calculated per dry shale reached 59 kg/ton. It was obtained under the following conditions:

temperature of pyrolysis—	700°C
oxygen consumption	—80-85 m ³ /ton of tar
contact time	—1-1.5 sec

Above 700°C the amount of olefins produced strongly decreases, mainly because of the decomposition of the lighter members of the series. Over the same temperature range (700°C-825°C) the decomposition of ethylene is much more limited—its yield decreasing only from 36.7 to 32.9 kg/ton.

Phenols have many industrial applications, and they are therefore considered an important product in energy-chemical processing of oil shale. In connection with introduction of new retort design (UTT) and improvements of older retorts, the Oil Shale Institute studied the influence which design and regimes of retorts have on yield of light tar phenols. In these tests samples of primary tar were taken from 19 retort units of 7 different types currently in use at Kohtla Jarve and Kiviylu complexes. Some of the retorts were sampled at different times in order to detect the effect which changes made in their operational-industrial regimes have had on the phenol production. Broad diesel fraction with boiling points up to 325°C was used as the phenol

TABLE 1.—Gas characteristics

Tar regime	Gas regime		Multi-stage variant (oxidizing pyrolysis)							
	1	2	3	4	38	20	5	9	10	40
Temperature, °C	650	730	600	700	725	765	825	705	710	700
Contact time, sec.	—	—	1.6	1.4	1.3	0.9	1.2	1.0	1.0	1.4
Oxygen consumption per tar, m ³ /ton.	—	—	80	80	92	84	80	110	140	192
Gas composition, % of volume:										
C ₂ H ₄	12.7	17.0	22.3	27.0	22.8	23.0	18.6	24.4	23.8	20.7
C ₃ H ₆	7.6	7.2	10.2	8.8	7.7	5.8	1.3	6.5	5.2	6.5
C ₄ H ₈	5.1	4.3	2.3	0.3	1.2	0.5	0.3	0.9	0.5	0.5
C ₅	—	—	0.3	1.2	—	0.2	—	0.3	—	—
Σ C _n H _m	25.4	28.5	35.1	37.3	31.7	29.5	20.2	22.1	29.5	27.7
CH ₄	21.0	20.0	30.0	29.2	20.0	24.1	20.4	27.4	28.3	22.2
C ₂ H ₆	11.5	9.7	3.5	1.9	3.1	2.8	0.5	1.8	2.0	2.1
C ₃ H ₈	2.8	2.3	1.0	0.3	0.7	0.3	—	0.3	0.1	0.4
C ₄ H ₁₀	1.3	0.9	—	—	0.6	1.4	1.2	—	—	—
C ₅	—	—	0.5	0.3	1.1	2.8	0.4	0.4	0.4	0.6
Σ C _n H _{2n+2}	36.6	32.9	35.0	31.7	25.5	31.0	22.7	29.9	30.7	25.3
H ₂	19.2	20.2	5.9	12.9	12.0	16.0	32.7	14.1	14.4	11.7
CO	8.6	7.3	12.7	11.3	14.1	16.8	16.6	17.0	19.1	21.2
CO ₂ +H ₂ S	6.5	7.5	9.3	5.5	8.8	7.0	6.7	6.2	5.0	11.8
O ₂ +N ₂	3.7	3.7	2.0	1.3	7.9	0.7	1.3	0.7	1.3	2.3

source. Details of procedure as well as several tables and graphs are given by Aarna and Efimov (1965). I shall reproduce here data based on two such samplings of the UTT-500 retort and some figures taken from different tables to show comparison of results obtained from seven units, each representing a different retort type.

The study indicated that the concentration of light phenols in the tar increases under more rigorous regime, that is when retorting temperatures are high and the contact time of the vapor-gas mixture with the shale bed is long. However, under such regime the yield of tar is lower, which means of course that the total phenol yield itself decreases. Most satisfactory results on both accounts were obtained with UTT retorts and with tunnel ovens. Feeding of shale crushed to small-size fraction was also helpful, increasing the tar yield and at the same time preventing excessive semi-coking. Because of lesser danger of coke formation, the contact time of vapor-gas mixture with the shale bed could be increased resulting in bigger yield of light phenols. For similar reasons, retort designs, which favored uniform distribution of heat exchanger, gave higher yields of light phenols permitting maintenance of higher throughput rates that otherwise would reduce the yield of these products. Both UTT and gas generators with transverse flow of heat exchanger (gas) favor such good distribution. On the otherhand, the yield of total phenols from UTT-500 was much below that which has been expected (table 3). This is apparently due to specific nature of thermal decomposition processes of fine grained oil shale in retorts which use spent shale as heat exchanger. Light phenols actually form at the expense of heavier phenols when the latter undergo thermal decomposition (Soo, Orav. and Nurkse, 1965). Studies of condensation systems of gas retorts were also made to determine losses of light phenols. It was found that the amount of phenols with low boiling points, which escape with fuel gases without being captured in the condenser, do not exceed 0.1 percent of the total phenol yield. Consequently, their recovery would have little effect on the yield of light phenols. However, other components of the light tar fraction escape in substantial quantities (Aarna and Efimov, 1961; Piik and Vakher, 1965).

Increased demands for electrode coke created greater need for heavy oil shale tars essentially free of ash (not over 0.05 percent of ash). This requirement is difficult to satisfy—especially with employment of new, high-efficiency retorts (UTT-500). Many different studies have been carried out in this connection on economic methods of purifying heavy tars. Ioonas, Leeper and Sieriebriannikov (1965) worked out a method of extracting maximum impurity-free distillate from heavy tars and residues by means of coking. In a vat-type retort constructed to a laboratory scale, they coked heavy impure tar obtained from a gas retort (GGS-4). In order to determine

TABLE 2.—*Relationship between regime of retorting and yield of light phenols in using UTT-500*

	<i>Sampling Date</i>	
	<i>March</i>	<i>April</i>
	<i>17</i>	<i>22-25</i>
	<i>1964</i>	<i>1964</i>
Working moisture of shale, %	13.6	12.0
Content of organic substance per dry weight of shale, %	32.8	31.0
Oil-shale throughput, ton/24hrs	525	491
Technical yield of tar per dry shale, %	17.6	16.0
Temperature of vapor-gas mixture on leaving retort, °C	470	528
Final temperature of cooling of vapor-gas mixture in condenser, °C	28	22
Specific gravity of tar at 20°C	0.9670	0.9660
Fractional composition of tar, % of volume:		
beginning of boiling, °C	69	71
boiling point (boils away by) 200°C	20	29
boiling point (boils away by) 250°C	29	40
boiling point (boils away by) 300°C	40	52
Content of total (undifferentiated) phenols in tar, % of weight	18.5	13.0
Yield of broad diesel fraction with boiling points up to 325°C, % of total weight of primary tar	41.04	47.74
Content of total phenols in broad diesel fraction, % of weight	10.71	7.68
Fractional composition of phenols, °C		
10% of volume boils away	247	224
20% of volume boils away	278	253
30% of volume boils away	287	282
40% of volume boils away	294	291
50% of volume boils away	—	297
boiling away by 300°, % of weight	60.9	69.4
Specific gravity of phenols (measured at 20°C) with low boiling points	1.0821	1.0727
Yield of light phenols calculated per tar, % of weight	2.68	2.55
Yield of light phenols calculated per organic substance content of retorted shale, kg/t	14.4	13.2
Content of light phenols in daily tar output of retort, tons	2.14	1.76

TABLE 3.—*Yields of total and light phenols from different type retorts*

<i>Retort unit and type</i>	<i>Yield per total organic substance in the shale, kg/ton</i>		<i>Fraction of light phenols per total</i>	
	<i>tar</i>	<i>total phenols</i>	<i>light phenols</i>	<i>%</i>
Tunnel oven #3, at Kiviylü	760	180	11.5	6.4
Gas generator GGS-5 (with central feed of heat exchanger)	487	150	7.5	5.0
Gas generator GGS-5 (with transverse flow of heat exchanger)	532	141	10.2	7.2
Pilot gas generator, enlarged	688	179	15.1	8.5
UTT-500 (solid heat exchange)	537	99	14.4	14.6
Compartment retort	179	33	6.1	18.5

possible catalytic action of ash in the tar, they also run parallel experiments on samples of filtered tar.

As the yield of distillate increases, its viscosity, specific gravity and flash point also increase. The distillates are essentially free of impurities. It was also found that by using gas or steam in coking, the yield of distillates can be increased by 10-15 percent. The yields of distillates obtained by coking of residues ranged from 23 to 47 percent per dry residue, depending on scheme of condensation of vapor-gas mixture and on the method and place of collecting the residue. The engineers of the oil shale processing complex at Slantsy have prepared a design for a semi-commercial plant for processing heavy tars and residues by coking. Further tests are planned prior to plant construction.

Oftentimes in processing of oil shale it is necessary to determine the degree of decomposition of organic matter (called the degree of kerogen decomposition) at any particular time during the retorting process and prior to its termination. The scientists of the Oil Shale Institute developed a method which now makes this possible. The method is based on the observed fact that a relative carbon enrichment and hydrogen impoverishment of the nonvolatile organic residue take place during the retorting process. A quantitative study was made of this enrichment-impoverishment process as it occurs during semi-coking of the kukersite shale. The details of procedures

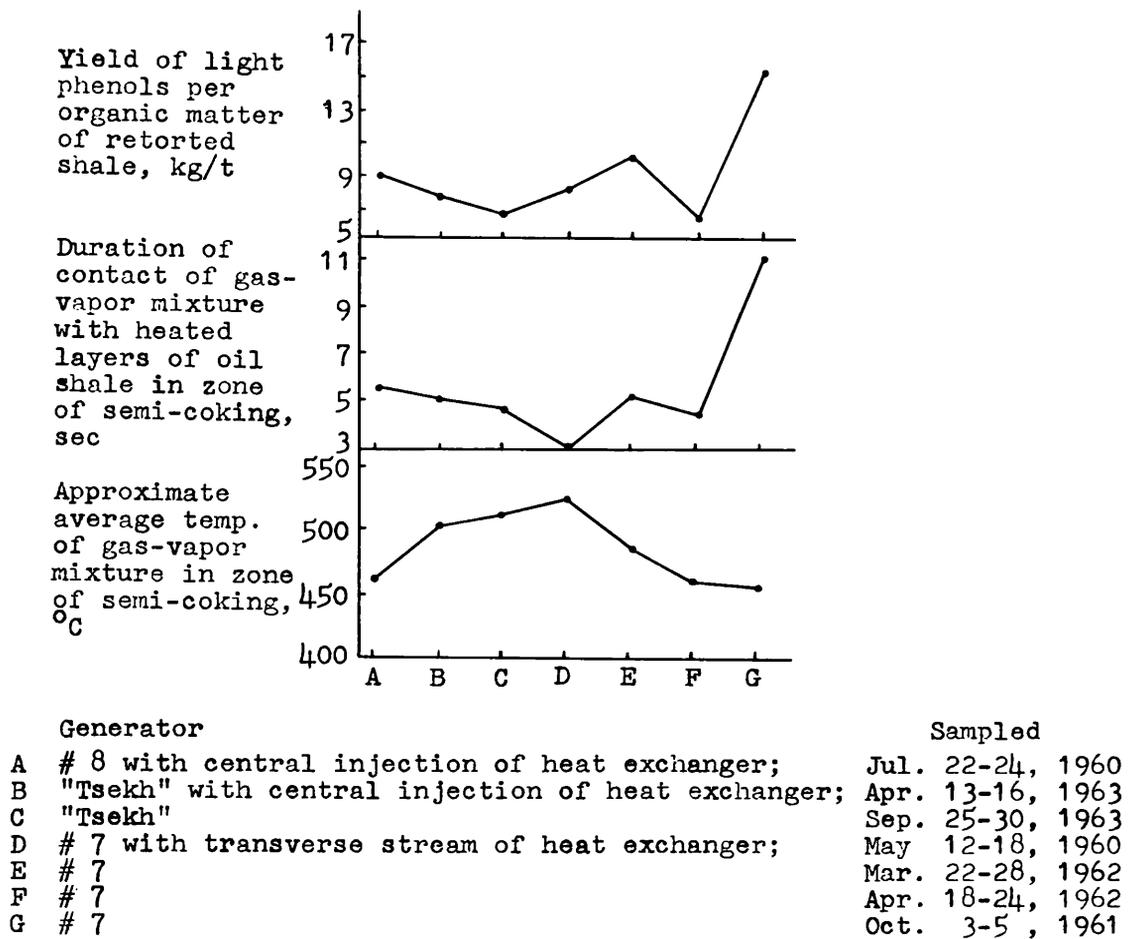


FIGURE 3.—Relationship between yield of light phenols and technological parameters of gas generators.

and methods of calculation are described by Aranovich (1965). As a result, a relationship has been discovered between the C/H weight ratio and the degree of kerogen decomposition. This relationship gives a curve of equal sided hyperbole which can be accurately expressed by the equation:

$$C/H = \frac{150}{100-x} + 6.5$$

where: x = degree of kerogen decomposition.

In another series of experiments an attempt was made to determine C/H changes in the solid residue obtained in retorting of oil shale fines with solid heat exchanger. The new curve had the same general character, but it was displaced along the axes of both coordinates. This displacement is due

TABLE 4.—Character of distillates obtained by coking of heavy tar

No. of expt.	S.g. d_4^{20}	Moisture %	Viscosity at 50°C, °VU*	Flash point, °C	Ash content, %	Fractional composition, % volume		
						up to 200°C	up to 300°C	up to 360°C
2	0.954	1.2	2.09	40	0.023	10	44	70
3	0.969	1.5	2.73	51	0.042	8	36	60
9	0.979	1.6	2.28	27	0.043	11	40	67
10	0.978	1.7	2.20	25	0.046	11	43	75
8	0.992	3.0	3.34	58	0.012	5	35	59
7	1.002	18.4	5.17	72	0.016	2	27	54
5	1.008	11.0	7.60	112	0.030	—	23	53
6	1.006	6.7	8.11	116	0.011	—	20	50
12	0.999	3.4	5.09	101	0.013	2	32	60
11	0.998	2.9	5.55	100	0.026	1	28	58

*Viscosity is given in degrees of "VU"; I was unable to identify these units.

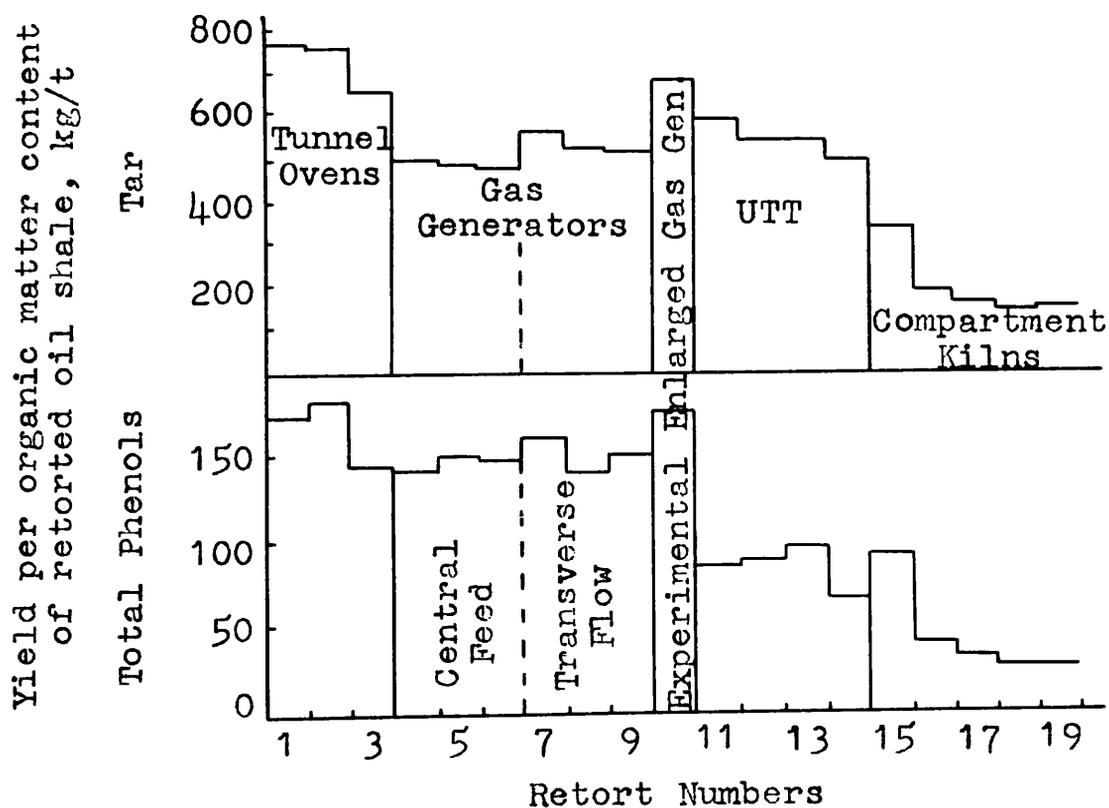
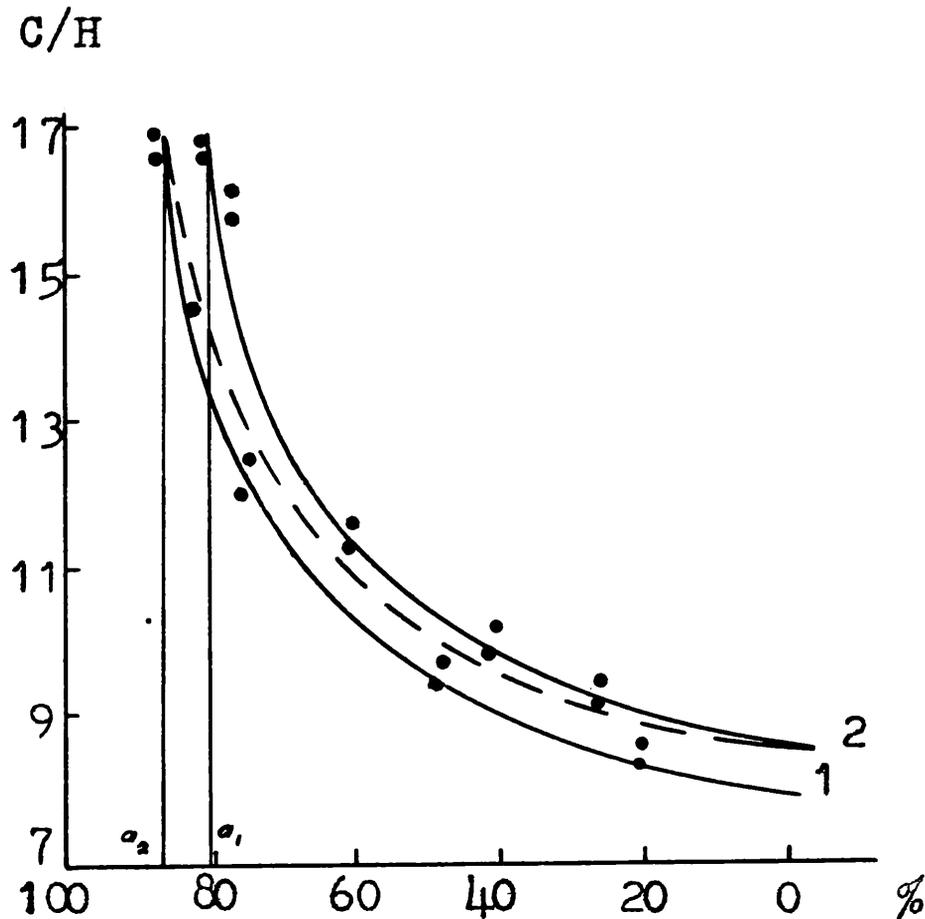


FIGURE 4.—Yield of total phenols from oil shale retorts.



Relationship between C/H in semi-coke and degree of kerogen decomposition

- 1 - For pure oil shale
- 2 - For oil shale in presence of ash

FIGURE 5.—Relationship between C/H in semi-coke and degree of kerogen decomposition. Curve 1-for pure oil shale; curve 2-for oil shale in presence of ash.

to capture of some volatile components by the solid heat exchanger (heated oil shale ash) and to the presence of some organic carbon and hydrogen in the ash itself.

Corrosive action of waste waters of oil shale processing often creates serious problems. In order to facilitate planning of preventive action, a method was devised for extracting carboxylic acids present in these waters and determining both qualitatively and quantitatively their composition (Mietsik, Rokhumagi, and Lisman, 1965).

In this particular study, average samples of waste waters were taken from the compartment kilns of Kohtla Jarve and from tunnel kilns of Kiviylil

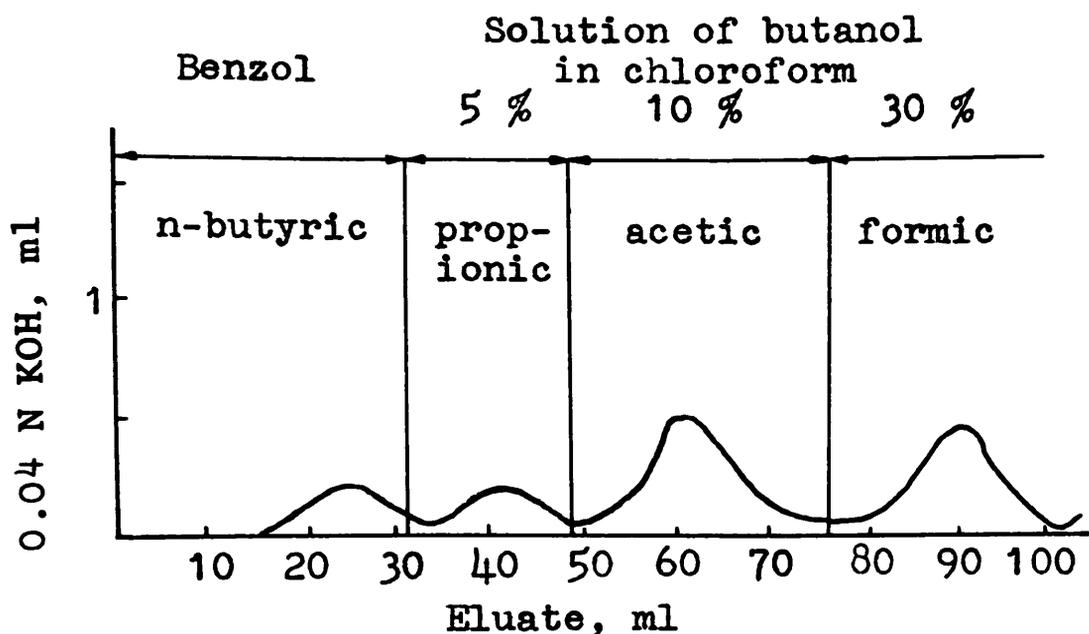


FIGURE 6.—Separation of a mixture of carboxylic acids with a known quantity of KOH used in titration.

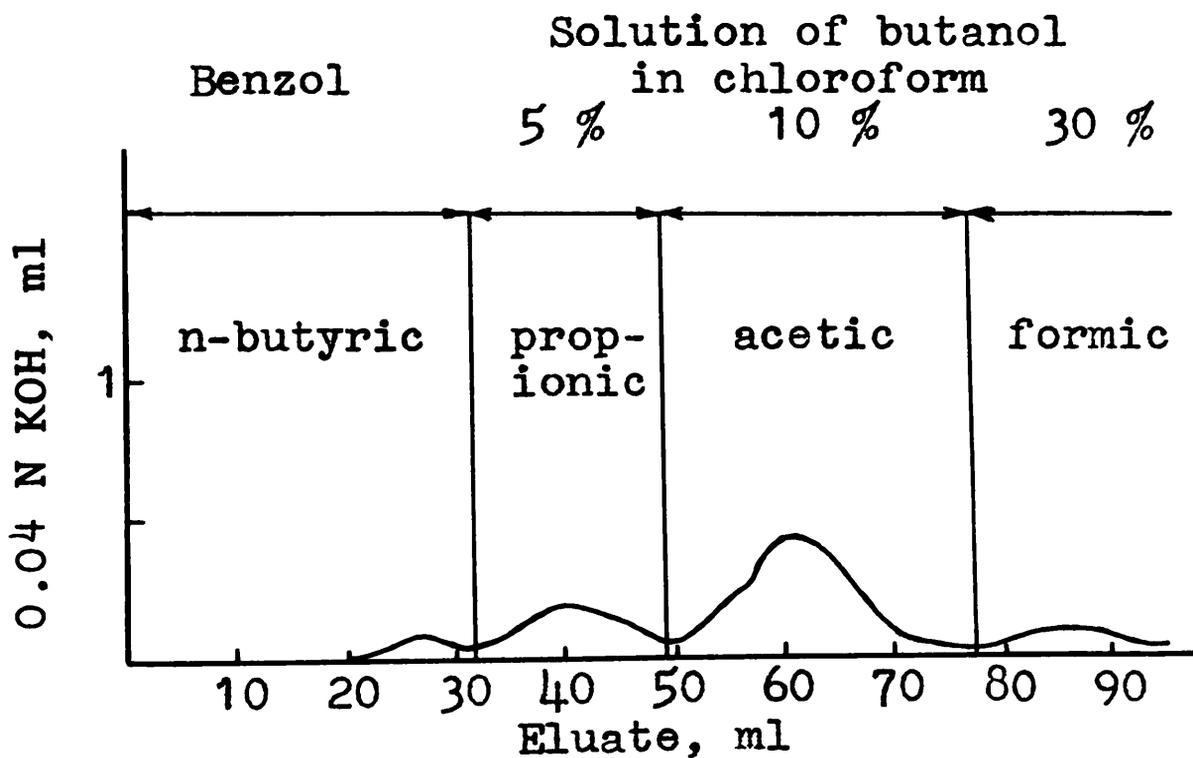


FIGURE 7.—Chromatogram showing separation of carboxylic acids extracted from tar water after sprinkling in tar separator "Teizen" (Retort GG-5).

oil shale processing complexes. The new method made it possible for the first time to extract all four carboxylic acids detected in the waste water. It has been also found that the amount of volatile carboxylic acids in the tar water increases when 'Teizen' type sprinklers are employed with tar separator. Distributive chromatography was used very effectively to obtain separation of the carboxylic acid mixture into its individual components.

C. *Full utilization of by-products and waste materials*

This is part of the so-called complex utilization of the kukersite. The Oil Shale Institute has developed a new method of preparing medium tars for distillation. These were previously burned as raw fuel. The Institute is now working on processing heavy tars and even slurries to electrode coke (Ioonas, 1965). The shale ash is rich in calcium carbonate and in micro-elements, and as such it is a very good fertilizer for Russia's dominantly acidic soils as well as for soil enrichment in general. Agricultural studies and experiments conducted with oil shale ash led to the discovery of a plant growth stimulator. The Russians claim that its application has doubled the crop of alfalfa and considerably increased the turnip crop. The first fertilizer plants, working the smaller size fractions of the ash from the dumps, have already been established at Kohtla Jarve. Another waste-product processing plant has been erected at Punai Kunda and is producing 850,000 tons of Portland cement annually—also using ash as raw material (Izvestia, November 12, 1965). In planning stages, or already under construction, are other plants which will manufacture building blocks, rock wool and other insulating materials from the ash. The clinker from spent shale that has been heated to 2,000°C will be used as special purpose building material.

D. *In situ gasification*

The Chemical Institute of the Estonian Academy of Science has been working since 1958 on in situ gasification of low-grade kukersite shale left behind in the mines after removal of high-grade shale by room and pillar method has been completed. The Institute operates a pilot plant in one of the oil shale mines at Kiviylü (Pravda, April 11, 1958). I have no information at this time on the present status of this work.

Absolutely no mention has been made so far of applying nuclear blasts to in situ retorting.

Future Outlooks of Estonian-Russian Oil Shale Industry

Any attempt to arrive at true dollars and cents figures for costs of Russian oil shale products would be an utterly meaningless exercise in arithmetic. This is true of most state-socialist economic ventures anywhere. It suffices

to say that the kukersite shale industry has not been profitable and has had to be subsidized by the state throughout most of the postwar period. That much has been admitted—post-factum, of course—by Russia's present governor in occupied Estonia, V. Klauson (*Pravda*, December 24, 1965). However, Klauson claimed that the oil shale industry is now operating in the black. In 1964 the Kohtla Jarve mining-processing complex allegedly made a profit of 6.3 million rubles, and the Kiviylil complex 1.5 millions. Whether or not this is true, it is indeed hard to say. Other information is available, however, which indicates that the shale oil industry may now be in fact on the threshold of profitable operations. The Economic Institute of the Estonian Academy of Science conducted, under the direction of economist professor D. Kuznietsov, a study of the oil shale industry. In a report published in 1964 the Institute concluded that "under present conditions in Estonia the oil shale industry—from the standpoint of both capital expenditure and operating costs—is the most economic source of raw materials for the petrochemical industry." The study also came out strongly in support of the new energy-chemical and complex utilization as the only economic approach to oil shale processing (*Ekonomicheskaja Gazeta*, June 13, 1964; see also Kuznietsov, 1959).

The Russians are apparently encouraged by the results of energy-chemical and complex-utilization, also by their breakthrough in the new retort design (UTT-500) as well as the success of gas retort improvements. Their confidence in the economic future of the oil shale industry is shown by their willingness to make further large investments in this field. Thus the current five-year plan ending in 1970 calls for an increase of 30 percent in the oil shale output over the 1965 levels (22 million metric tons). The oil shale processing facilities at Maardu, about 100 miles west of the Kiviylil—Kohtla Jarve area, are now being greatly expanded. The operations at the only other Russian oil shale processing center—namely that of Syzran on the Volga in the Kuibyshev-Saratov area—are also increasing and are being changed from gas generation to gas and chemical processing (Efimov and Sieriebriannikov, 1965). It is significant that the oil-shale deposits mined at Syzran are of much lower grade than the kukersite shale (Baukov, 1958). The Russians are also planning to establish a new energy-chemical oil shale processing complex at the site of Bukhtaminsk Reservoir and Power Plant now under construction in Kazakhstan, right in the area of kenderlyk oil-shale deposits (Efimov and Help, 1965). This despite the fact that Kazakhstan now has abundant supply of gas and oil from newly developed fields. Also significant is the fact that Russian geologists continue to look for oil shale deposits. They have made two recent discoveries. One deposit has been found in southern Ukraine (at an unspecified location). It is estimated at

600-700 million tons and has allegedly higher grade shale than the Estonian kukersite (Trud, July 1, 1965). The other deposit, not so large, was located near the town of Stolin in the region of Pripet Marshes of eastern Poland, now under Russian occupation (Izvestia, August 5, 1965). Both of these discoveries aroused considerable interest.

PERTINENCE OF RUSSIAN WORK AND EXPERIENCE WITH OIL SHALE TO OUR STUDIES OF COLORADO OIL SHALE

Any attempt to draw an analogy between economics of the prospective Colorado oil shale industry and the existing Estonian oil shale industry must take into account a number of fundamental differences which exist between them. We can list these differences as relative advantages and disadvantages of each.

Advantages of the Colorado shale:

1. The fact that Colorado shale industry will develop under free enterprise rather than the socialist system.
2. Increasing depletion of our natural gas and oil reserves coupled with increasing costs of finding and producing crude petroleum. This situation is steadily improving the competitive position of Colorado oil shale. The very opposite is true of Estonian oil shale industry. In Russia reserves of natural gas and oil are rapidly increasing, and the completion of pipelines will soon make cheap gas and oil available in plentiful supply.

Advantages of the Estonian oil shale:

1. Established industry with vast facilities and considerable operational experience versus one that will have to start from scratch.
2. Kukersite shale is of higher grade than Colorado oil shale.
3. Plentiful water supply versus lack of water as in the case of the Colorado oil shale.
4. Serious underdevelopment of Russian petrochemical industry, insuring Estonian shale-chemicals of good markets for years to come.

Admittedly, because of these great differences, the economic lessons which the Russians have learned in their operation of the Estonian oil shale industry do not seem very applicable to our studies of economic prospects of the Colorado shale. However, we might take a closer look at Russia's new energy-chemical and complex-utilization of oil shale processing to see if this approach might not offer us some economic advantage. These two fields—the chemical processing and the waste product utilization, are the areas where the Russians are doing a lot of research, developing new methods, and

adapting many petrochemical technologies to shale-chemical processes. This information and the Russian experience with the successful new solid-heat exchanger large-capacity retort should be quite useful to us.

*This paper is based on material actually referred to in the text. The remaining select bibliography is compiled merely for readers' information.

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BIOGRAPHIES

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V. Dean Allred received his Ph.D. in Fuel Technology at the University of Utah in 1951. Prior to joining Marathon in 1956, he had worked for the Houdry Process Corporation, Marcus Hook, Pennsylvania; the Catalytic Construction Company, Philadelphia; and Union Carbide Nuclear Company, Oak Ridge National Laboratories, Oak Ridge, Tennessee.

At present, Dr. Allred is a Research Associate at Marathon Oil Company's Denver Research Center.

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Mr. Alpert received a B.Ch.E. degree from the Polytechnic Institute of Brooklyn in 1952 and a Master's degree from Rutgers University in 1955. He also did graduate work at Columbia University. He was employed by Hydrocarbon Research, Inc., in 1952 to carry out development work on projects for the petroleum and chemical industries. Mr. Alpert is responsible for the preparation of technical reports and correlation and evaluation of pilot plant data.

GEORGE H. BRUCE

Mr. Bruce is a research associate with Esso Production Research Company. He has been with Humble's Production Research Division and the present company since receiving his B.S. degree in physics from the University of Texas in 1949.

WLADYSLAW J. CIESLEWICZ

Mr. Cieslewicz came to the United States from Poland in 1949. He earned a B.A. degree in economics, an M.A. in Russian, and an M.S. in geology from American universities. He has spent one year in central Chile studying gold placers. In addition, he has done extensive translation work and reviews of Russian scientific literature for the U.S. Geological Survey and various oil companies. He is now a part-time instructor in Russian and German at the Colorado School of Mines.

THEODORE S. CROSS

Theodore "Ted" S. Cross, who is presently on leave from Pacific Power & Light Company for graduate work at the University of Wyoming, started working on the oil shale project with Noel Melton of the United States Bureau of Mines in August 1965 in the Green River area.

Mr. Cross graduated with a B.S. degree in electrical engineering from the Massachusetts Institute of Technology in 1956, and in the same year received a B.S. degree in mathematics from St. Lawrence University. He joined Pacific Power & Light Company shortly after graduation as a member of the engineering department for the Wyoming Division.

He has been a member of the Institute of Electrical and Electronics Engineers since 1956. He is a registered Professional Engineer in Wyoming, a member of the Wyoming Society of Professional Engineers, and a member of the National Society of Professional Engineers.

JOHN R. DONNELL

Mr. Donnell was born in Norwood, Massachusetts, in 1919. He has a B.S. degree in geology from the University of Alabama. He studied further at Stanford University in the field of geology. Most of his work has been in investigations of oil shale. He has had experience in mapping areas underlying coal deposits in Colorado and Kentucky and areas of potential interest for oil and gas. He is presently with the U. S. Geological Survey in Denver.

JOHN R. DYNİ

Mr. Dyni is presently employed as geologist by the Conservation Division, U. S. Geological Survey in Denver. His academic training includes a B.S. degree from Wayne State University in 1953, and an M.S. degree in geology from the University of Illinois in 1955. Mr. Dyni was employed as engineering geologist by the U.S. Corps of Engineers, Kansas City, Missouri, from 1955 to 1958. Since 1958 Mr. Dyni has been associated with the Geological Survey in Denver, and his work during this period has dealt primarily with the geology of the leasable minerals on Federal lands in the Rocky Mountain area.

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Mr. Ely is a senior partner in the law firm of Ely and Duncan, Washington, D.C. He is a member of the bar of the United State Supreme Court, of the highest courts of California and New York, and of the District of Columbia.

Mr. Ely served as assistant to the Secretary of the Interior and chairman of the Technical and Advisory Committee of the Federal Oil Conservation Board, 1929-33, and has been in private practice since.

His firm specializes in natural resources law with particular attention to mining, petroleum, water resources, and electric power. Recently Mr. Ely drafted mining laws for the Kingdom of Saudi Arabia, the Malagasy Republic, and Turkey, and has been consulted by a number of other foreign governments in preparation of petroleum laws.

He drafted the federal regulations for unit operation of oil and gas fields on the public domain, and was counsel to the Governor of Oklahoma in the negotiation and drafting of the Interstate Oil Conservation Compact.

Mr. Ely is currently special counsel to the Colorado River Board of California in interstate negotiations, and chief counsel for California (Special Assistant Attorney General) in the United States Supreme Court litigation over the Colorado River. He has been counsel in other Supreme Court litigation involving the Columbia, Sacramento-San Joaquin, St. Lawrence, and Niagara Rivers.

STANFORD FEIGELMAN

Mr. Feigelman received the degree of B.S. in chemical engineering from Pennsylvania State University in 1951. He then joined the Atlantic Refining Company's Research and Development Department. In 1954 he joined the U. S. Navy. In 1957, after his tour of duty with the Navy, he rejoined Atlantic's R & D Department and began work on the development of the HDA hydrodealkylation process.

In 1961, Mr. Feigelman joined the staff of Hydrocarbon Research at the laboratory in Trenton, New Jersey. He supervised the development of the Hy-C hydrocracking process and contributed to the correlation and data analysis of the H-Oil process.

WALTER E. HEINRICHS, JR.

Walter E. Heinrichs, Jr., graduated from the Colorado School of Mines in 1940 as a Geological Engineer with a geophysics major. In 1955 he received the School's first Van Diest Award for outstanding work during the first fifteen years following graduation.

After graduation from Mines, he worked with National Geophysical Company and Seismograph Service Corporation for four years. A two-year term in the U.S. Navy was spent with the Office of Naval Petroleum Reserves in Alaska and Washington, D. C., as an Assistant Geologist. This service

included participation in the early Gulf Coast off-shore aerialmagnetometer experiments.

Following this, he was with the U.S. Bureau of Reclamation as Assistant Chief Geophysicist and with Newmont Mining Corporation. He was also Acting Manager of Mining Exploration, United Geophysical Company, and its affiliate, Pima Mining Company, Tucson, Arizona. From 1954 to 1958 he was Manager of Minerals Exploration Company for Union Oil Company of California. In 1958 he formed Heinrichs Geoexploration Company, of which he is President and General Manager serving the minerals industry as consultant, specializing in geophysical and geological surveys.

KATHERINE C. HELLWIG

Katherine C. Hellwig is a Special Projects Engineer with Hydrocarbon Research, Inc., in Trenton, New Jersey. Mrs. Hellwig previously was a staff engineer in the Research Planning Division of the Cities Service Research and Development Company in New York and a research engineer with Petroleum Chemicals, Inc., in Lake Charles, Louisiana.

Mrs. Hellwig served as an assistant professor of engineering at McNeese State College, while engaged in part-time consulting. She joined Ethyl Corporation in Baton Rouge, Louisiana, as a chemical engineer where her assignment included process evaluation and commercial plant process design. Later she transferred to process development as a project leader in charge of bench-scale and pilot plant operations. Mrs. Hellwig holds the B.S.Ch.E. (1951) and M.S.Ch.E. (1954) from the University of Texas.

GEORGE R. HILL

Dr. Hill is Dean of the College of Mines and Mineral Industries at the University of Utah. He was appointed an instructor in chemistry at Utah in 1946, became an assistant professor in 1947, and associate professor in 1950. He became organizer and head of the Department of Fuels Engineering at the University in 1951.

Following graduation from Brigham Young University with an A.B. degree in 1942, he earned a Ph.D. degree at Cornell University in 1946.

Dr. Hill's employment history includes an appointment as Project Director of the Air Force Combustion Research, Light Atom Research and Surface Chemistry Research sponsored by the ONR and AEC, Project Director of Air Force Office of Scientific Research High Energy Fuel Research. Project Director of the Office of Coal Research of the U. S. Department of

the Interior, and Project Director of Equity Oil Shale Research. He has published over 30 technical articles.

ROBERT J. HITE

Mr. Hite received his B.A. degree in geology from Wichita State University (1954) and completed two years of graduate work at the University of New Mexico (1954-56). From 1956 to 1964 he was employed as geologist with the Conservation Division, U.S. Geological Survey. He is currently associated with the Geologic Division of the Survey in Denver. Mr. Hite's professional work includes geologic quadrangle mapping in southeastern Idaho and northern Utah, studies on the phosphate deposits of the Phosphoria Formation, and extensive studies on the evaporite and potash deposits of the Paradox basin.

WILLIAM D. HOWELL

Howell is a project engineer in the Petroleum Engineering Research Group, Bartlesville Petroleum Research Center of the Bureau of Mines. He obtained his B.S. degree in petroleum engineering from Texas A & M in 1958, is a registered professional engineer in the State of Oklahoma, and has authored several technical papers concerning the application of radioisotopes in the petroleum industry. His current research efforts are in well stimulation research.

DALE R. JESSE

Mr. Jesse is currently a Research Chemical Engineer at Texaco Inc.'s Montebello Research Laboratory. Since joining Texaco in 1962 he has worked on hydrogenation process development, as well as oil processing. He received his B.S. degree in 1958 and M.S. degree in 1960, both from the University of Southern California. Prior to 1962 he was associated with Union Carbide Chemical Company and Rexall Chemical Company.

HERBERT A. LESSER

Dr. Lesser, a senior research engineer with Esso Production Research Company, is currently in the Reservoir Analysis Section conducting research in numerical analysis. He received a Ph.D. degree in chemical engineering from Princeton University in 1964 after receiving his B.S. degree from Rice University.

JOHN A. LOVE

John A. Love was elected Governor of the State of Colorado in 1962 and re-elected in 1966. He was named "Colorado Man of the Year" three times by the United Press International editors of Colorado.

Graduating from the University of Denver Law School in 1941 with an LL.B., Governor Love passed the State Bar examinations and then enlisted in the Naval aviation program where he earned pilot's wings. He served in the South Pacific where he earned two Distinguished Flying Crosses and the Air Medal with several clusters for action against the enemy.

Following the war, he returned to Colorado Springs where he practiced law. He was President of the El Paso County Young Republicans in 1947 and 1948 and has served as a member of the El Paso Republican Executive Committee and the Republican state central committee.

Governor Love was elected President of the Colorado Springs Chamber of Commerce in 1954. He is a member of Rotary, the American Legion, Colorado and American Bar Associations, Colorado Springs Chamber of Commerce, Omicron Delta Kappa, Sigma Phi Epsilon, and many other professional and civic organizations.

NOEL M. MELTON

Noel M. Melton graduated from the University of Montana with a B.S. in chemistry in 1931, and did graduate work at the University of Colorado in 1933. He was employed by Stanolind Oil and Gas Co. as a research chemist and assistant petroleum engineer until 1941. He was on extended active duty as a Major in the U. S. Army from 1941 to 1946.

Mr. Melton has been associated with the U. S. Department of Interior, Bureau of Mines, Laramie Petroleum Research Center since March 1946, and has worked on various research projects related to processing oil shale and refining shale oil products. Since 1964 he has been in charge of the research project to investigate electricity as a method of increasing permeability in oil shale formations.

J. S. MILLER

Miller is a project engineer with the U. S. Bureau of Mines in Bartlesville, Oklahoma. He joined the Bureau in 1952 after graduating with a B.S. degree in petroleum from Marietta College, Marietta, Ohio. Miller has been involved in research problems in transmission and storage of natural gas. His research efforts since 1962 have been in well stimulation research.

WARREN G. SCHLINGER

Dr. Schlinger has been Supervisor of Research at Texaco Inc's. Montebello Research Laboratory since 1960. Since joining Texaco in 1953, his research work has included process studies in hydrogen generation by Texaco's partial oxidation process and development in hydrogenation and hydro-treating, as well as recovery of shale oil. Prior to joining Texaco he was a Research Fellow at the California Institute of Technology where he received his Ph.D. degree in chemical engineering in 1949. He also received his B.S. degree in chemistry and M.S. degree in chemical engineering from the California Institute of Technology.

HERBERT L. STONE

Dr. Stone is research supervisor of the Reservoir Analysis Section of Esso Production Research Company. He received his B.S. and Sc.D. degrees in chemical engineering from Rice University and MIT, respectively. From 1953 to the present, he has worked on oil recovery methods and reservoir engineering predictive techniques for both Humble's Production Research Division and Esso Production Research Company.

IRVIN L. TAILLEUR

Mr. Tailleir was born in Mt. Vernon, Washington, in 1924. He has A.B. and M.S. degrees, both in geology, from Cornell University. He was a candidate for the Ph.D. degree at Stanford University in 1951-1953. He is now with the U.S. Geological Survey in Menlo Park, California. Experience includes aerial mapping and structural and stratigraphic studies in northern Alaska.

H. A. TOURTELOT

Mr. Tourtelot was born in Lincoln, Nebraska, in 1918. He has an A.B. degree in geology from the University of Nebraska earned in 1942. His experience includes stratigraphic studies and geologic mapping in Tertiary rocks of Mississippi and Alabama and Tertiary and underlying rocks in Wyoming plus geochemical investigations of sedimentary rocks emphasizing petrology and composition of fine-grained and organic-rich rocks. He is with the U. S. Geological Survey in Denver.

