

REPORT OF
COMMITTEE ON QUEBRACHO REQUIREMENTS
OF THE PETROLEUM INDUSTRY
OF THE
NATIONAL PETROLEUM COUNCIL

April 27, 1949

COMMITTEE ON QUEBRACHO REQUIREMENTS

OF THE PETROLEUM INDUSTRY

CHAIRMAN - John R. Suman
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Gulf Oil Corporation

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R. S. Shannon
Pioneer Oil Corporation

Carey R. Wagner
Drilling Specialties Company

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Mr. Walter S. Hallanan, Chairman
National Petroleum Council
Suite 601, 1625 K Street, N. W.
Washington 6, D. C.

Dear Mr. Hallanan:

Submitted herewith is the report of the Committee on Quebracho Requirements of the Petroleum Industry. This report constitutes a careful study of the requirements of the industry for this material and of the substitutes and alternative materials that can be used in its place. The findings of the Committee can be summarized briefly and in general form as follows:

1. The position of the oil industry insofar as its operations would be influenced by the availability of Quebracho is sound. The industry is in no way dependent on this product for the maintenance of the efficiency of its operations. There are sufficient other natural products or chemicals which are available for use or which could be made available with a minimum of development to meet the needs of the oil industry for this type of mud treating compound. Suitable examples of these are products from the buttonwood trees of Mexico and Yucatan, lignin derivatives, and other products of wood chemistry, complex phosphates, as well as several miscellaneous other materials.

2. Various elements of the petroleum and chemical industry have maintained in the past and are now maintaining continuous research efforts in order to meet the changing needs of the industry operations.

On the basis of the study undertaken by this Committee, it appears that there is no further need for the Committee on Quebracho Requirements to remain active.

Sincerely,

/s/ John R. Suman

John R. Suman, Chairman
Committee on Quebracho Requirements
of the Petroleum Industry

Attachment

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SUBSTITUTE MATERIALS FOR QUEBRACHO EXTRACT
IN TREATING DRILLING MUD

INTRODUCTION

At the request of the Secretary of the Interior, the National Petroleum Council appointed a committee to make a study of the requirements of the petroleum industry for quebracho, the present development, utilization and availability of substitutes; to make recommendations as to the ways and means of assuring self-sufficiency of the United States in the event of an emergency; and to report the results to the National Petroleum Council.

The Chairman of the Committee on Quebracho Requirements of the Petroleum Industry is Mr. John R. Suman, Standard Oil Company (N.J.), New York, N.Y.; the members are as follows: Mr. George S. Bays, Stanolind Oil & Gas Company, Tulsa, Oklahoma; Mr. George E. Cannon, Humble Oil & Refining Company, Houston, Texas; Mr. Harold Denton, Sun Oil Company, Beaumont, Texas; Mr. P. E. Jones, Union Oil Company of California, Wilmington, California; Mr. William M. Keck, Jr., Superior Oil Company, Los Angeles, California; Mr. Hallan N. Marsh, General Petroleum Corporation, Los Angeles, California; Mr. J. S. Morris, American Association of Oilwell Drilling Contractors, San Antonio, Texas; Mr. G. L. Ratcliffe, Baroid Sales Division, National Lead Company, Los Angeles, California; Mr. Walter F. Rogers, Gulf Oil Corporation, Houston, Texas; Mr. A. H. Rowan, A. H. and C. L. Rowan, Fort Worth, Texas; Mr. R. S. Shannon, Pioneer Oil Corporation, Denver, Colorado; and Mr. Carey R. Wagner, Drilling Specialties Company, Bartlesville, Oklahoma.

SUMMARY

It is estimated that the oil industry in the United States is currently using 20,000 to 25,000 tons of quebracho extract annually in controlling the physical properties of drilling mud.

Among the other materials which are used for the same purpose and may be considered as quebracho substitutes as far as mud treating is concerned are the soluble sodium salts of meta and pyrophosphoric acid, lignosulfonates, extract from various woods and sub-bituminous materials.

In the event of an emergency, the oil industry could employ the phosphoric acid compounds instead of 60 percent of the quebracho currently being used.

The calcium lignosulfonate compounds are effective quebracho substitutes. Kembreak, the trade name for a calcium lignosulfonate, is now being manufactured for the oil industry at an annual rate of 6,000 tons.

The raw materials used are available from the paper industry as waste products in large quantities and the manufacture of calcium lignosulfonates could be easily increased to meet the mud treating requirements of the oil industry.

Sub-bituminous products are now being mined and processed for mud treating purposes at a rate of 8,400 tons per year. These materials, sold under the trade names of Tannathin and Carbonox, are effective quebracho substitutes in a large variety of drilling muds and are available from deposits in the United States in large quantities.

Plans are now under way to construct a plant in Mexico to extract tannin from the Yucatan tree. The plant now being considered will have a 5,000-ton annual capacity. The Yucatan extract is an effective substitute for quebracho in controlling the physical properties of drilling mud.

Redwood bark contains a lignin-like material, the salts of which are effective quebracho substitutes. A total of 700 tons per month of redwood bark extract could be supplied on relatively short notice and the supply increased as the demand arose.

Laboratory and field test data indicate there are quebracho substitutes in the United States or adjoining countries in sufficient quantity to meet the demand of the oil industry in the event it was impossible or difficult to obtain quebracho from Argentina and Paraguay.

CONCLUSIONS

1. It is estimated that the oil industry in the United States is presently using a maximum of 25,000 tons of quebracho extract annually in the treatment of drilling mud.
2. There are substitute materials available in the United States and bordering countries in large enough quantities to supply the oil industry's quebracho requirement in the event it was no longer possible to import quebracho extract from Argentina and Paraguay.
3. In the event of an emergency the quebracho requirements of the oil industry could be handled by the following substitute materials.
 - a. The soluble sodium salts of meta and pyrophosphoric acid could be used instead of 60 percent of the quebracho presently employed in the treatment of drilling fluid.
 - b. Calcium lignosulfonate is an effective quebracho substitute; at the present time 6,000 tons per year are being manufactured. The manufacture of calcium lignosulfonate could be expanded to meet almost any demand of the oil industry, as it is estimated that 2,500,000 tons of the raw material are produced annually as a by-product of the paper industry.
 - c. Sub-bituminous products are effective substitutes for quebracho. At the present time 700 tons per month are being mined for drilling mud purposes. The production of sub-bituminous products for drilling mud control purposes could be increased to meet the entire requirement of the oil industry, should the need arise.

- d. Redwood bark contains a lignin-like material that is an effective substitute for quebracho extract. It is estimated that 700 tons per month of the redwood bark extract could be supplied to the oil industry on very short notice and the supply increased as the demand arose.
- e. Plans are now under way to construct a plant in Mexico to extract 5,000 tons per year of tannin from the Yucatan tree. The Yucatan extract is an effective substitute for quebracho in the treatment of drilling mud.

DISCUSSION

There are a large number of chemical compounds that can be used to reduce the viscosity and gel strength of drilling muds, chief among which are the sodium meta and pyrophosphates, tannin compounds (the chief source of which is quebracho extract), lignin compounds and lignin sulfonates.

It has been estimated by five independent investigators that the oil industry in the United States uses 20,000 to 25,000 tons of quebracho extract per year in the chemical treatment of drilling muds. The question has been raised as to the desirability of stock-piling quebracho extract, which is imported chiefly from Argentina, for use in case of an emergency, whereby importing quebracho extract would be difficult or impossible.

There are sufficient materials available in the United States which can be employed in place of quebracho extract to reduce the viscosity of drilling mud. Drilling operations would not be retarded to a great extent if quebracho were not available for use in drilling mud. A period of crew training would be necessary to acquaint the drilling personnel with the techniques of using new materials; however, this would not be a serious or difficult problem.

Kembreak

One of the materials used to reduce the viscosity of drilling mud is calcium lignosulfonate that is manufactured from waste sulfite liquor of the paper industry. The special process of manufacture produces a product containing approximately 80 percent calcium lignosulfonate of a selected molecular weight range. The material is sold to the oil industry under the trade name of Kembreak. Physically, Kembreak is a brown, non-hygroscopic, water soluble, amorphous compound, having a pH of approximately 7.0 and a specific gravity of about 1.5. Kembreak may be dissolved in water up to concentrations of 30 percent.

Kembreak has been used to replace quebracho as the dispersant in drilling mud under two different conditions. The first is that in which the drilling program calls for conversion to a calcium-base mud at some predetermined depth. The second is that in which the Kembreak is used after trouble has been encountered with salt water or some contaminant which renders the mud used unsatisfactory. The following general observations can be made as to the use of Kembreak in drilling mud:

1. The characteristics, as determined by the usual testing methods, are similar in normal converted muds, using either Kembreak or quebracho as the dispersant.
2. Properties resulting from the use of a calcium-base system are present when either dispersant is used.
3. Both quebracho and Kembreak are stable at temperatures normally encountered in drilling.
4. The filtration of a calcium-base mud dispersed with either Kembreak or quebracho may be slightly higher than the original mud before conversion. Filtration-reducing compounds may be used to lower the filtration to the desired value.
5. The amount of Kembreak required to convert and maintain a calcium-base mud is approximately the same as the quantity of quebracho required.
6. Kembreak differs from quebracho in that it is not recommended for use in normal sodium-base muds or high pH sodium-base muds prior to conversion.

Figure I shows the comparison of quebracho and Kembreak on the viscosity filtration and gel strength of a sample of natural mud from the Orange Field, Texas. It is noted that Kembreak is slightly more effective in changing the physical properties of this mud than is quebracho.

Figure VII shows that Kembreak can be used to reduce the viscosity of a mud contaminated with cement.

The present supply of Kembreak is estimated at 6,000 tons per year; however, the potential supply is unlimited for the purposes of the petroleum industry. It is estimated that 2,500,000 tons of lignin are produced annually as a constituent of waste sulfite liquor by the sulfite pulp mills in the United States and Canada. The lignin is present in waste sulfite liquor as calcium lignosulfonate or lignosulfonic acid.

The production of calcium lignosulfonate from waste sulfite liquor is secondary to the manufacture of wood pulp for the paper industry. Therefore, most manufacturers control their digestion operations to obtain the type of pulp desired without consideration for the properties of the waste sulfite liquor. Variations in the wood stock and in the time and temperature of digestion will produce lignosulfonates in different degrees of sulfonation and in different ranges of molecular weights. For this reason, it is not known that all waste sulfite liquors can be processed to produce a product as effective in drilling fluids as Kembreak.

Tannathin and Carbonox

Another material which can be used to reduce the viscosity of drilling mud is a sub-bituminous material mined in several states. The material is sold to the oil industry for use in drilling mud under the trade names of Tannathin and Carbonox.

The following general observations can be made on the use of sub-bituminous materials in drilling mud:

1. Tannathin and Carbonox have been used successfully in Texas, Arkansas, and Louisiana to control the viscosity of native shale muds. The use of this material could be expanded to other areas.
2. Carbonox has been used successfully in the preparation and maintenance of high pH starch muds, even in the presence of small amounts of anhydrite, i.e., less than two pounds per barrel. At concentrations higher than this, water may be necessary to control gel strength.
3. Carbonox has been used successfully, particularly in reducing filtration loss, in muds contaminated by salt water, up to about 25,000 ppm.
4. Carbonox and Tannathin have been used successfully to treat cement-contaminated muds.
5. In the treatment of some shale muds about 10 to 20 percent more Carbonox or Tannathin than quebracho may be required.
6. About twice as much Carbonox as quebracho is required to treat cement-contaminated muds.
7. Laboratory and field tests show that sub-bituminous materials can be used as a substitute for quebracho in many instances. However, experience with certain types of mud indicate that the substitution could not be considered complete. It is probable that field testing of sub-bituminous materials on a greater variety of muds would expand its use to types about which, at the present time, we have little or no information.

Figure II shows a comparison of Tannathin and quebracho on the viscosity of an 8 percent bentonite suspension. In this particular mud, Tannathin was more effective than quebracho, or mixture of quebracho and caustic soda, in reducing the viscosity.

Figure III shows a comparison of quebracho, Tannathin and sodium acid pyrophosphate on the viscosity of an 8 percent bentonite suspension. The Tannathin was not as effective as the phosphate compound in reducing the viscosity of this suspension.

Figure IV shows the comparison of quebracho and Tannathin on the viscosity of a natural shale mud from a well at Humble, Texas. The data show that Tannathin was more effective than quebracho, or caustic soda-quebracho mixture, in reducing the viscosity of this mud sample.

Figure V shows the comparison of quebracho and Tannathin on the viscosity of a mud sample contaminated with sodium chloride. The data show that Tannathin can be used effectively to reduce the viscosity of mud samples contaminated with sodium chloride.

Figure VI shows that Tannathin can be used to reduce the viscosity of mud contaminated with cement, but that larger amounts of Tannathin than

quebracho may be required to obtain the desired viscosity reduction.

Figure VIII shows the effect of Carbonox on the viscosity of a mud prepared from Glen Rose shale. The data plotted show that the mud viscosity can be reduced by the addition of Carbonox.

Definite specifications for the sub-bituminous material for use in drilling mud cannot be established. It is necessary to conduct laboratory tests to determine if the materials are effective in reducing mud viscosity. At the present time approximately 700 tons per month of material suitable for use in drilling mud are being mined. It is understood that the amount of sub-bituminous material produced could be increased to replace all quebracho used in drilling mud, if there were a demand for the material.

Yucatan Extract

A tree growing in Mexico produces a large amount of tannin material. The extract from this tree is known as Yucatan extract. The material is not being extracted on a commercial basis; however, a company is now being formed to manufacture Yucatan extract and the initial production rate is planned to be 5,000 tons per year. The manufacturers of Yucatan extract plan to sell the material as a substitute for quebracho in the treatment of drilling mud. Information is not available to the author as to the possible use of Yucatan extract in the leather industry.

Figure IX shows the effect of Yucatan extract on the viscosity and gel strength of a drilling mud prepared from El Paso clay. The data show that Yucatan Puro is as effective as quebracho in reducing the viscosity and gel strength of this mud sample. Similar results have been obtained on samples of drilling mud from other sources.

Pecan Shell Extract

Pecan shells contain a tannin material that is as effective as quebracho in treating drilling mud. The supply of this material is limited and only about 10 tons per month are being used in drilling mud. At best, the production could only be increased four- or fivefold and should not be considered as an emergency substitute for quebracho by the oil industry.

Redwood Bark Extract

Redwood bark contains a lignin-like material that can be substituted for quebracho in many instances. It is understood that approximately 700 tons per month of the redwood extract could be supplied to the oil industry on very short notice.

Sodium Phosphate

The soluble sodium salts of meta and pyrophosphoric acid are very effective in reducing the viscosity and gel strength of drilling muds and have been used for that purpose for at least 15 years. Data on the effect of these materials on the properties of drilling mud is well known by the oil industry.

It is estimated that if the need arose, sodium meta or pyrophosphate could be used in place of 60 percent of the quebracho now being used in treating drilling mud.

Chestnut Extract

Chestnut extract may be used as a substitute for quebracho in treating drilling mud. This material is not considered in this report, as its production has been mostly for the leather industry.

FIGURES

- FIGURE I COMPARISON OF QUEBRACHO AND KEMBREAK
- FIGURE II COMPARISON OF QUEBRACHO AND TANNATHIN ON BENTONITE MUD
- FIGURE III COMPARISON OF QUEBRACHO, TANNATHIN AND SODIUM ACID
PYROPHOSPHATE
- FIGURE IV COMPARISON OF QUEBRACHO AND TANNATHIN
- FIGURE V EFFECT OF QUEBRACHO AND TANNATHIN ON SALT CONTAMINATED
MUD
- FIGURE VI COMPARISON OF QUEBRACHO AND TANNATHIN ON CEMENT
CONTAMINATION
- FIGURE VII EFFECT OF KEMBREAK ON VISCOSITY OF CEMENT CUT MUD
- FIGURE VIII EFFECT OF CARBONOX ON VISCOSITY OF MUD
- FIGURE IX COMPARISON OF QUEBRACHO AND YUCATAN PURO ON VISCOSITY
OF MUD

SUMMARY OF QUEBRACHO SUBSTITUTE CORRESPONDENCE

DOMESTIC POSSIBILITIES:

1. Oregon Forest Products Laboratory -- Suggest Douglas-fir Bark from the Pacific-Northwest, 7.6 to 18.3 per cent tannin content. They are doing development work on extraction of tannin. No work done yet on application in drilling muds.
2. Mid-American Corp. -- This information derived from Mr. Jack MacDonald (from New Orleans) consulting engineer. This is a new corporation formed to buy buttonwood trees from which extract will be made. Competitive to Quebracho. Large reserves in Mexico and Yucatan Peninsula along Gulf Coast. Said to be suitable for Quebracho substitute. Can be transported either overland or by boat. They anticipate being in operation August 1949. Supply 5,000 tons at the end of one year; ultimate 20,000 tons. This compares with a Quebracho useage currently of the order of 20,000 tons in the oil industry.
3. Armour Leather Company - Newberry, Pa. -- Suggest possibility of use of their "Runaway Extract" from their tanneries as a substitute for Quebracho. This application would require some investigation to develop
4. Diamond Alkali Company - Cleveland, Ohio -- Directed attention to the use of Sodium Ligno Sulphonate in conjunction with Quebracho. This doesn't seem to bear directly on the problem at hand, although derivatives of Lignins may prove to be of interest.
5. Stanford Research Institute - Standford University, Calif. - Suggest four California sources of tannic acid: (1) redwood bark (2) tanbark oak bark (3) California bay tree (4) Australian black wattle or acacia. Not too much information in the literature concerning acreage of tannin-containing trees. Exploitation of this would require detailed evaluation survey and development work.
6. Session Oil Mills - Enterprise, Ala. -- Suggest the uses of extracts from pecan wastes. Considerable work has been done on this. Problem here is inadequate reserves.
7. Water Treatment Company - Pittsburgh, Pa. -- Sent sample of tannin material designated "Baerite #15-A" for use as Quebracho substitute.
8. Masonite Corporation - New York -- Have available large quantities of a wood pulp product which would sell for about $2\frac{1}{2}\phi$ /lb. This material owing to its availability in quantity at low cost, could be an interesting starting compound for development work with Lignins for use as Quebracho substitute.
9. Monsanto Chemical Company - Boston, Mass. -- They have offered their services in cooperative effort with oil industry for development of synthetic substitutes. They have a great deal of experience in this field. At the present time, however, there appears to be no need for getting into a program of this kind.
10. Hercules Powder Company - Wilmington, Del. -- Have offered their services in cooperative research effort for development of wood product derivatives for Quebracho substitute. This is an experienced organization in this field; however, again there appears to be no need for setting up a program of this kind at this time.

11. Armour Research Foundation - Chicago -- Suggest use of Cascalote plant. Tannin is extracted from seed pods, hence is an annual harvest, rather than product of destruction of tree as is case with Quebracho. They have been doing development work on a pilot-plant scale on a suitable concentrate. They are soliciting suggestions for the arrangement of tests of this material. This could be interesting, although the need for it does not appear urgent.

12. The Dow Chemical Company - Houston -- Chas. F. Reed writes directing attention to the work of Dixie Chemical Company. This work relates to extracts from pecan shells.

13. The F & B Manufacturing Co. - Wichita Falls, Texas -- H. A. Fonville writes concerning development of source of tannic acid from an unspecified plant which grows in Southwest Texas and Mexico. He is soliciting the interest of the Committee in the development of his idea. This may be the same plant in which Armour Research Foundation is interested.

14. Rayonier Incorporated - New York -- Suggest the use of concentrated sulfite waste liquor from paper pulp operations. There are large amounts of this material available and it is understood that it can be applied with some success in drilling mud.

15. Peyton Randolph Harris, Attorney - New York -- Suggests the use of "chestnut oak" bark. As you know, chestnut oak bark has been used successfully; the question involved here is the supply.

16. Sprinz & Sprinz - New York -- Suggests the use of the Saw Palmetto root which contains, it is said, about 22% tannin. This tree grows in Florida and other coastal states. Again it appears that an exhaustive survey would have to be made to appraise the potential supplies of this material. It does not appear to be of interest at this time.

17. West Virginia Pulp and Paper Company - New York -- Suggests their lignin product "Indulin" for consideration. As you know, some work is being done on the lignins. Their product, however, may prove to be of some interest.

FOREIGN POSSIBILITIES - OTHER THAN MEXICO:

1. "Coffette" Products, Inc.-Brooklyn - Robert Brown suggests the use of extract from coffee beans. This proposal does not appear to be of interest in view of development work which would be required and potentially easier sources of supply.

2. Sopic Corporation-New York - Suggests Myrobalams from India. This material does not answer the Committee's problem owing to its remoteness from our shores.

3. Pellew Wilson Sons & Co., Inc.-New York - Suggests Brazilian Acacia Bark. This material, of course, suffers from the same supply disadvantage that Quebracho would in the event of emergency, hence does not answer this problem.

4. Flood & Company-New York - Solicited our interest in joining with them and their Brazilian associates in the expansion of Quebracho extract plant in Brazil. This does not appear to be of interest to the Committee.

5. Otis Astoria Corporation-New York - Presented tannin substitute from Peru. Again this is not of interest since we should find substitutes within the United States insofar as the Committee's activities are concerned.

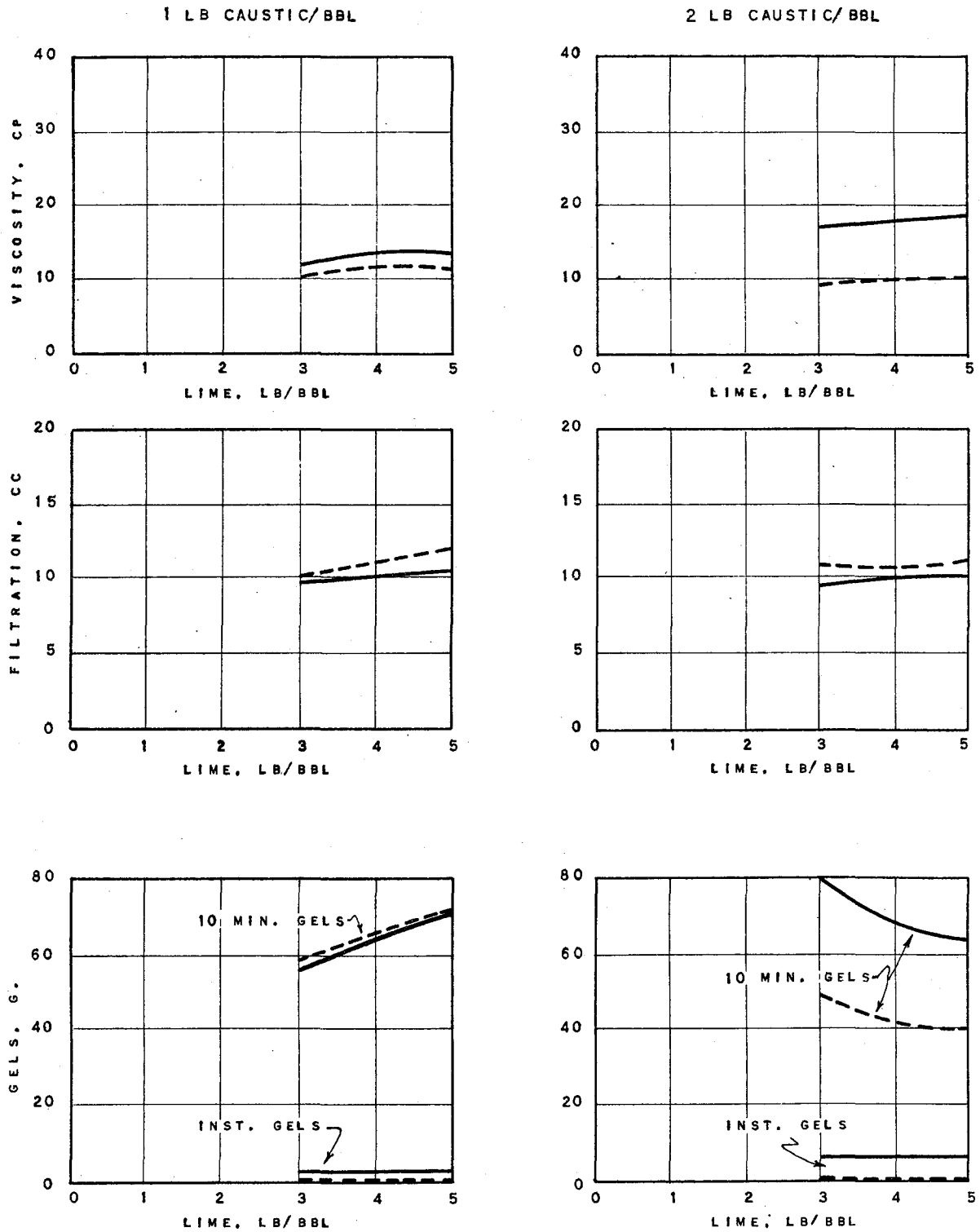


FIGURE I
COMPARISON OF QUEBRACHO & KEMBREAK

ORANGEFIELD NATURAL MUD

3 LB KEMBREAK/BBL ———
3 LB QUEBRACHO/BBL - - -

