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REPORT OF INVESTIGATIONS

**LABORATORY STUDY OF THE HOT-WATER PROCESS FOR
SEPARATING HYDROCARBONS FROM SURFACE DEPOSITS
OF BITUMINOUS SANDSTONES NEAR EDNA, CALIF.**

BY *EF*
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G. B. SHEA AND R. V. HIGGINS

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LABORATORY STUDY OF THE HOT-WATER PROCESS FOR SEPARATING HYDROCARBONS
FROM SURFACE DEPOSITS OF BITUMINOUS SANDSTONES NEAR EDNA, CALIF.^{1/}

By G. B. Shea^{2/} and R. V. Higgins^{3/}

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^{2/} Shea, G. B., Senior petroleum engineer, Bureau of Mines, Petroleum Field Office, San Francisco, Calif.

^{3/} Higgins, R. V., Associate petroleum engineer, Bureau of Mines, Petroleum Field Office, San Francisco, Calif.

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FOREWORD

In the second year of World War II, the petroleum industry in California was taxed to near capacity to satisfy the expanded war demand for petroleum products, particularly fuel oil. With discoveries of crude oil in California declining and known reserves being depleted rapidly, conditions appeared to

warrant study of the possibilities of utilizing the outcropping bituminous sandstone deposits in California for obtaining new sources of oil if the war should be prolonged. At conferences in Washington, D. C., with members of the Petroleum Administration for War and the Geological Survey, Bureau of Mines engineers emphasized the importance of determining the extent of these outcropping deposits of oil-impregnated rocks and of developing a practical process for commercial recovery of the contained bitumen to assure, if necessary, a supplementary supply of fuels. The desirability of such a study was recognized, and in July 1943 the Petroleum Field Office of the Bureau of Mines at San Francisco, Calif., in cooperation with the Geological Survey and the Petroleum Administration for War, initiated a study of the bituminous-sandstone problem. It was agreed that all mapping and geological work in connection with the study would be done by the Geological Survey, all engineering studies in developing a process for extracting the oil would be carried out by the Bureau of Mines, and that the Petroleum Administration for War would aid in final adoption of the results in the field if circumstances warranted such action.

Deposits of bituminous sandstones in California occur principally in the immediate region of the Coast Range mountains, notably at Pt. Arena, in Mendocino County, about 110 miles north of San Francisco; near Santa Cruz, in Santa Cruz County; in the Edna area in San Luis Obispo County; in the Sisquoc area in Santa Barbara County; and in the Ojai and Santa Clara Valleys in Ventura County.^{4/} In addition, oil-bearing sands outcrop near McKittrick and Maricopa, in western Kern County, and along the east edge of the Kern River oil field. Among the several prominent deposits of these source materials, those occurring near the cities of Santa Cruz and San Luis Obispo, and the town of Sisquoc are the largest.

The deposits near Edna, 3 to 8 miles south and southeast of San Luis Obispo, Calif., were mapped by the Geological Survey during the winter and spring of 1943-44, and a map with a report on the geology, general characteristics of the deposits, and reserves was published.^{5/} Later, the bituminous sandstone deposits in the Pt. Arena area in Mendocino County and those near Santa Cruz County were mapped, and a report on the Santa Cruz deposits was published.^{6/} Reports on field studies of the outcrops of oil sand in the

4/ Eldridge, George H., The Asphalt and Bituminous Rock Deposits of the United States: Second Annual Report of the U. S. Geological Survey, Part 1, 1900-1901, pp. 365-452.

5/ Page, Ben M., Williams, M. Dean, Hendrickson, Eiler L., Holmes, Clifford N., and Mapel, William J., Geology of the Bituminous Sandstone Deposits near Edna, San Luis Obispo County, Calif.: Geol. Surv. Preliminary Map 16, Oil and Gas Investigations, 1944.

6/ Page, Ben M., and Holmes, Clifford N., Geology of the Bituminous Sandstone Deposits near Santa Cruz, Santa Cruz County, Calif.: Geol. Surv. Preliminary Map 27, Oil and Gas Investigations, 1945.

McKittrick area in Kern County, Calif., and the oil-impregnated diatomaceous rock deposits at Casmalia, in Santa Barbara County, also were published by the Geological Survey.^{7/}

The bituminous sandstones from the Edna deposit were selected by engineers of the Bureau of Mines for laboratory study, and considerable progress had been made toward development of an efficient process for recovering the contained bitumen by hot-water separation when the war ended abruptly in August 1945. The ending of the war, however, did not mitigate the importance of this research, and the work continued because there is a reasonable certainty that conditions eventually will necessitate commercial development of some of the bituminous sandstone deposits in California to supplement future peacetime supplies of petroleum and its products. As a matter of fact, the unprecedented postwar demand for petroleum may cause exploitation of these deposits sooner than anticipated.

INTRODUCTION

This preliminary report presents the results of laboratory research in the adaptation of the hot-water separation process to the recovery of hydrocarbons from bituminous sandstones of the Edna deposits near San Luis Obispo, Calif. The report describes the construction and operation of the laboratory separation plant and discusses the problems involved and the results obtained in treating the Edna bituminous sandstones. The utilization of the recovered bitumen as a source of motor fuels, Diesel fuels, and fuel oils also is discussed, and data on cracking, analytical distillation, and its asphalt properties are summarized.

The studies have demonstrated that the hot-water method of separation may be applied satisfactorily to separating hydrocarbons from the Edna sandstones, although the presence of mineral salts and fine silt in the deposits complicates the operation. Certain operating problems still remain to be solved, but, unquestionably, further study and experimental work will lead to their solution. Although the work has not been advanced to the pilot-plant stage and does not permit estimates to be made of separation costs, the small-scale studies have provided much valuable information of a fundamental nature on the recovery of bitumen from the Edna bituminous sandstones by the hot-water separation method.

^{7/} Page, Ben M., Hendrickson, Eiler L., Williams, M. Dean, Moran, Thomas G., Asphalt and Bituminous Sandstone Deposits of Part of the McKittrick District, Kern County, Calif.: Geol. Surv. Preliminary Map 35, Oil and Gas Investigations, 1944.
Williams, Dean M., and Holmes, Clifford N., Geology of Oil-Impregnated Diatomaceous Rock near Casmalia, Santa Barbara County, Calif.: Geol. Surv. Preliminary Map 34, Oil and Gas Investigations, 1945.

As a basis for the studies, the authors had available the reports of Max Ball and K. A. Clark and others,^{8/} of the Scientific and Industrial Research Council of Alberta, Canada, covering many years of experimental and semicommercial studies of hot-water separation of the Alberta bituminous sandstones.

The separation of bitumen from bituminous sandstones by the action of heated water has been applied in the United States and other countries in early attempts to recover hydrocarbons from bituminous sandstones.^{2/} However, because of the lack of knowledge of the fundamental principles underlying efficient separation, displacement of the bitumen from the sand grains usually was incomplete, and considerable bitumen was retained in the sand tailings. Furthermore, the separated bitumen frequently contained large percentages of sand and water.

In 1920 the Scientific and Industrial Research Council of Alberta, Canada, undertook a study of the hot-water separation process and evaluation of the factors that affect its efficiency. This study was part of a broad research program initiated by the Canada Department of Mines and Resources to determine the possibilities of commercial development of the bituminous sandstone deposits of northern Alberta. As a result of both laboratory and pilot-plant studies in the ensuing years, a mass of information has been obtained which led to the disclosure of the fundamental principles underlying efficient recovery of bitumen from bituminous sandstones by the hot-water process and of the problems involved in their treatment.

ACKNOWLEDGMENTS

The studies were carried on under the general supervision of R. A. Cattell, chief, Petroleum and Natural Gas Branch, Bureau of Mines, and H. C. Miller, supervising engineer, San Francisco office.

Conferences dealing with the bituminous sandstone separation problem were held with P. H. Jones, Roy Wagner, and Robert F. Bauer, of the Union Oil Company of California, and the writers take this occasion to acknowledge their courtesy and many helpful suggestions.

^{8/} Clark, K. A., and Pasternack, D. S., Hot-Water Separation of Bitumen from Alberta Bituminous Sands: Ind. Eng. Chem., vol. 24, 1932, p. 1410.

Clark, K. A., Hot-Water Separation of Alberta Bituminous Sand: Can. Inst. Min. & Met. Trans., vol. XLVII, 1944, p. 257.

Clark, K. A., Bituminous Sands of Alberta: Oil Weekly, Aug. 13, 1945, p. 46.

Ball, Max, Development of the Athabaska Oil Sands: Can. Inst. Min. & Met., Trans., vol. XLIV, 1941, p. 58.

^{2/} Ellis, E. C., Bituminous Sands of Northern Alberta: Report No. 632, Canada Department of Mines, 1926. See pp. 173-236 for review of processes that have been proposed and/or tried for separating oil from bituminous sandstones.

Frank G. Schrader and Wallace K. Wong, formerly of the Bureau of Mines, rendered valuable assistance in the laboratory.

Special thanks are due to J. S. Ball, W. J. Wenger, W. I. R. Murphy, P. L. Cottingham, K. E. Stanfield, Mrs. R. L. Hubbard, and W. S. McAuley, who, under the supervision of H. P. Rue, supervising engineer of the Petroleum and Oil Shale Experiment Station, Laramie, Wyo., determined the cracking data and asphalt properties of the separated bitumen.

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PHYSICAL CHARACTERISTICS OF EDNA BITUMINOUS SANDSTONES

The Edna bituminous sandstones consist mainly of subrounded to rounded grains of quartz and feldspar with minor constituents of chert that range in texture from medium to coarse and are varyingly impregnated and cemented with bitumen. The following statement from the Geological Survey's recent report^{10/} on the deposit is descriptive of the enrichment:

The bituminous outcrops range in quality from rich, black, completely saturated tar sand, which in warm weather gives rise to small asphalt seepages, to slightly bituminous sandstones, to which traces of organic matter impart a light-brown color. The most widespread variety is intermediate in quality and dark brown in color. Judging from surface exposures, no single deposit consists solely of bituminous sandstone of one grade, and in some exposures there is a gradation from clean, white sandstone to completely saturated sandstone within a distance of 25 feet. The rich, high-grade tar sand, which is rarely seen except in excavations, is somewhat plastic and may be molded by hand. Where it is exceptionally rich, it appears to consist of sand suspended in asphalt rather than asphalt-impregnated sand. The moderately rich sandstone is hard and tough, whereas the lean pale-brown rock is generally soft and friable.

Published analyses^{11/} of bituminous sandstone samples obtained from quarries in the Edna deposit indicate a bitumen content ranging from 9 to 16 percent by weight. Recent Bureau of Mines analyses of four samples of several tons of material from the quarry shown in figure 1 indicate bitumen contents of 9, 11, 13, and 14 percent. These variant results are somewhat surprising in view of the fact that the samples were taken from a 1-ton sample of the rock that had been carefully selected from what appeared to be a moderately rich bitumen-impregnated ledge. Because of these results, a 200-pound portion of a 1-ton sample was crushed (1 inch by 3/4 inch, and smaller),

^{10/} See footnote 5.

^{11/} California State Mineralogist's Report No. VII, 1887, p. 52; No. X, 1889-1890, p. 571; No. XV, 1915-1916, p. 678; No. XVIII, 1922, p. 275.

carefully mixed, and quartered in accordance with standard ore-sampling procedure until a small representative sample was obtained. Three analyses of the quartered sample showed bitumen contents of 11.0, 10.8, and 11.3 percent - an average of 11 percent, or 26 gallons of bitumen per ton of sandstone.

The average depth from the face of the quarry from which the 1-ton sample was taken did not exceed 4 feet. Although higher bitumen contents may be found in samples obtained from points farther removed from the exposed faces of the quarries, it is believed, in the light of the earlier analyses, that an average of 11 percent is indicative of the degree of enrichment of a large part of the deposit.

The water content of the sandstone ranged between 1 and 3 percent by weight and probably is present as a film around the sand grains.

The specific gravity of three samples of Edna bituminous sandstone was found to be about 2.0. The specific gravity of samples from different sections of the deposit undoubtedly vary somewhat with the bitumen content, but the significance of the information did not warrant making many determinations. Consequently, in all calculations in which tons were converted to cubic yards, the specific gravity of the rock was assumed to equal 2.

The porosity of the bitumen-free sand, based on determinations made on a quarry sample, was calculated to be 36 percent. Following is a screen analysis of a sample of the sand after the extraction of bitumen:

Sieve opening, inches	0.0016	0.0058	0.0029	0.0017
Tyler sieve No.	48	100	200	325
Weight retained on, percent ..	42	38	10	4
Weight through, percent	-	-	-	6

Characteristics of Separated Bitumen

A sample of bitumen was extracted with benzol from the bituminous sandstone, and after removal of the silt in the bitumen-benzol solution by centrifuging, the benzol was eliminated by evaporation, leaving pure bitumen.

The calorific value of the extracted bitumen was found to be 17,900 B.t.u. per pound, and its viscosity was 183 seconds Saybolt furol at 210° F. The specific gravity was 1.001 at 60° F., and the sulfur content was 3.2 percent.

Reserves

Within the area mapped by the Geological Survey in the Edna area, it is estimated there are 282,880,000 short tons of bituminous material to a depth of 250 feet.^{12/} As the deposits are known to continue downward below 250 feet, in part of the deposit the estimate could be increased by assuming that the material could be mined to greater depths. Material covered by more than 50 feet of overburden was not estimated.

^{12/} See footnote 5.

On the basis of approximately 1/2 barrel (26 gallons by analyses) of bitumen per ton, the deposit contains 141,440,000 barrels of bitumen.

PRINCIPLES OF HOT-WATER SEPARATION OF BITUMEN FROM BITUMINOUS SANDSTONE

The separation of bitumen from bituminous sandstone by hot water is based upon the principle of displacing the bitumen from the sand grains by the water. Whether the oil is completely displaced depends on the properties of the water. Laboratory studies have disclosed that certain alkaline solutions are more effective than pure water in displacing oil from sand surfaces, and that complete displacement of the bitumen takes place when the bituminous sandstone is neutral or slightly alkaline.^{13/} To be effective as a displacing medium, therefore, the water must be sufficiently alkaline to neutralize the acidity that may be present in the bituminous sandstone. Complete displacement also depends on thorough disintegration and mixing of the sandstone with the displacing medium. Observations of displacement of oil from sand surfaces by an aqueous solution of sodium carbonate have shown that the solution quickly envelopes each grain once it finds access to the silicate surface.

The hot-water process consists, broadly, of three operations:

1. Heating and mixing the bituminous sandstone with water and enough alkaline reagent to form an alkaline pulp, in which the bitumen is displaced from the sand grains by the water. Efficient separation also depends on the occlusion of enough air in small bubbles in the pulp to form an oil froth.
2. Separating the oil froth from the sand by submerging the pulp in hot water. The oil froth floats to the surface of the water and the sand grains, freed of bitumen, sink to the bottom.
3. Removing the water, sand, and silt from the oil froth by dilution of the bitumen with a light oil and settling.

HOT-WATER SEPARATION OF EDNA BITUMINOUS SANDSTONES

The fundamental principles of separating bitumen from the Alberta bituminous sandstones, as determined by Clark and others,^{14/} were applied in treating the Edna bituminous sandstones. The presence of soluble mineral salts in the Edna sandstones, consisting largely of iron and calcium sulfates with some sodium and aluminum sulfates, made it necessary to water-wash the sandstones to remove these troublesome impurities. These salts were found to have a detrimental effect upon the recovery of bitumen, as they reacted with the alkaline reagents used in pulping the bituminous sandstone and precipitated insoluble gelatinous iron and calcium hydroxides, which formed slimes with the fine silt released in the pulping operation. The slimes were deposited on the sand bed in the flotation cells and impeded separation of the bitumen; in fact, the slimes were found to contain up to 50 percent

^{13/} Clark, K. A., and Pasternack, D. S., Work cited in footnote 8.

^{14/} See footnote 8.

Figure 1. - Bituminous sandstone quarry, Edna area, California.

Figure 3. - Multiple-cell flotation unit.

Figure 2. - Flow sheet of laboratory hot water separation plant.

bitumen. It appears that fine bitumen particles became entrapped in the precipitate and were prevented from floating to the surface of the water.

Preliminary tests showed that washing the bituminous sandstone with hot tap water removed nearly all of the soluble iron and calcium salts and thereby eliminated one of the more troublesome problems in treating the Edna sandstone. Hydrolysis of the ferrous sulfate made the bituminous sandstone distinctly acid, which precluded the separation of any bitumen in the washing process. The removal of the salts reduced the quantity of reagent necessary to maintain alkalinity in the pulping operation.

As stated by Clark, "Pulping appears to be the key operation of the process. It is during pulping that the oil is displaced from the surfaces of the sand grains, and if the displacement is complete the way is clear for obtaining a high yield of separated oil as froth of low sand content. Incomplete displacement results in oil being retained in the sand tailings and in oily sand being lifted into the oil froth."

Description of Laboratory Separation Plant and Operating Procedure

Figure 2 is a flow sheet of the laboratory hot-water separation plant designed to treat the Edna bituminous sandstones. Capacity of the plant is approximately 25 pounds of bituminous sandstone per hour.

Disintegrating and Water-Washing the Bituminous Sandstone

The bituminous sandstone is charged into a revolving screen drum (9.5 inches in diameter by 18 inches in length), which is partly submerged in a tank of hot water (fig. 2). A hinged screen door on the surface of the drum permits loading the sandstone. As the drum revolves, the hot water, aided by the abrasive action of the lumps of sandstone and the rolling action of several iron balls (1-1/2 inches in diameter) inside the drum, disintegrates the lumps of sandstone to particle sizes small enough to pass through the 6-mesh screen. The balls also aid in forcing the particles of bituminous sandstone through the screen into the hot water.

The disintegrated sandstone receives a preliminary washing as it falls through the water to the bottom of the tank and is removed slowly by a screw conveyor.

The partly washed bituminous sandstone falls from the end of the screw conveyor into the first unit of a multistage countercurrent washer (see fig. 2), where it is slowly churned through the wash water by a screw conveyor into the second and, similarly, into the third unit of the washer. The washed sandstone is discharged from the third unit onto a screen, where some of its contained water is drained off before it is transferred to the pulper.

The hot wash water enters the system near the top of the third washer unit and flows, countercurrent to the movement of the bituminous sands, through the three units, thus becoming progressively enriched with soluble salts. The water overflows through an outlet in the verticle chamber of

each unit and into a surge and trap tank, where particles of sand carried by the water settle out. The water is then pumped to the inlet near the top of the next unit. The overflow from the first unit is pumped into the tank containing the revolving screen disintegrator. The wash water, now greatly enriched with soluble salts from the bituminous sandstone, flows through the tank and overflows to a waste pipe at the opposite end of the tank. Virtually no silt is removed in water washing.

Each unit is steam-jacketed, and the temperature of the wash water is maintained at 175° F.

Although the washer effectively removes the soluble salts from the sandstone, experience has shown that the pumps require considerably more attention than is desirable and could be eliminated by adapting gravity flow from one unit to another.

The Pulping Process

To form a frothy alkaline pulp in which the bitumen is displaced from the sand grains, the washed bituminous sandstone is heated and mixed in a rotary pulper with a light-gravity fuel-oil diluent and aqueous solutions of sodium carbonate and/or sodium silicate. It was found that the addition of a "light oil" diluent to the pulp facilitated displacement of the bitumen by solvent action and flotation of the froth by reducing the viscosity and specific gravity of the bitumen. The pulper consists essentially of a 5-gallon cylindrical container mounted to revolve on an inclined axis and is belt driven at 30 revolutions per minute by means of an electric motor through reduction gears at the lower end of the axle. A charge of bituminous sandstone (usually 10 pounds) is placed in the pulper together with the diluent and reagents and heated to 210-212 degrees by means of three large Bunsen burners beneath the pulper. The temperature of the material in the pulper is regulated by a bimetallic thermostat inserted in a piece of 1-inch pipe, which also serves as a baffle rod to facilitate pulping. The thermostat is connected to a solenoid that operates an off-and-on valve in the gas line to the burners, thereby controlling the temperature within the indicated limits. The third burner, which burns continuously, acts as a pilot-light for the other burners.

This type of pulper made it possible to study visually the effect of different reagents, temperatures, and procedures of disintegrating the sandstones and forming the optimum pulp. Thus, it was possible to discontinue many experimental techniques as unsatisfactory without making long extraction tests. Also, by observing the action that took place inside the pulper during certain tests, new procedures were suggested, which later were tried, and some were found to warrant detailed study.

Experience has shown that after the temperature of the charge plus reagents and diluent reached 210° F., 7 minutes of heating and mixing were required to displace the bitumen from the sand grains and form a frothy pulp.

Selection of Diluent Used in Pulping

In pulping, the use of a light-gravity diluent containing substantial quantities of aromatic compounds is an important aid to the efficient separation of the bitumen from the Edna bituminous sandstone. The Edna bitumen contains aromatic compounds, and optimum solubility of the bitumen is obtained when a diluent is used that likewise contains considerable quantities of the aromatic compounds. Solubility depends to a large extent on the existence of a similarity between components of a solution.

It has been found that when a diluent containing a large percentage of aromatics is used, the tendency of dispersed bitumen to be present in the plant water is greatly reduced, and bitumen recovery is thereby increased. In the first separation tests, kerosine, which contains only small percentages of aromatic compounds, was used as a diluent in the pulping operation. Much of the dispersed bitumen present in the plant water in those tests may be ascribed to inadequate solubility resulting from the use of a diluent containing a small quantity (2.8 percent) of aromatic compounds. Consequently, in most of the separation tests a No. 3 fuel oil (gravity 33° A.P.I.) containing 23 percent aromatics was used as a diluent in pulping.

Quantity of Diluent Used in Pulping

Best results were obtained when the equivalent of one-third barrel of diluent per barrel of contained bitumen in the sandstone was added in pulping the charge. The use of larger proportions of diluent in pulping resulted in perceptible wetting of the sand grains and consequent loss of diluent to the sand tailings.

Alkaline Reagents Used in Pulping

In most of the separation tests, aqueous solutions of sodium silicate, sodium carbonate, or a mixture of the two chemicals were used to neutralize acidity of the bituminous sandstone in the pulping operation. Of the two reagents, sodium silicate is more effective than sodium carbonate in displacing the bitumen from the sand grains, but because it is less alkaline than sodium carbonate, more of it is required to neutralize the acidity of the pulp. The use of both sodium silicate and sodium carbonate in pulping is a compromise wherein the less expensive carbonate accomplishes most of the neutralization, and the sodium silicate, which is an excellent detergent, effectively breaks the oil films around the sand grains. When sodium carbonate was used alone, more silt remained in the diluted bitumen and more bitumen was lost to the slimes than when sodium silicate was used alone.

The pH of the Pulp

Numerous pulping tests showed that optimum results were obtained when the sandstone was pulped at pH 8. At this alkalinity, displacement of the bitumen was complete, and separation of the oil froth in the flotation cells was rapid. Furthermore, at pH 8 less bitumen was lost to the slimes, and considerably less sludge or "cuff" (an emulsion of water, silt, and oil) was

formed in the gun barrel settling tank (see page 15) than when the alkalinity of the pulp was below pH 8.

When the pH of the pulp was 8 to 8.5, the cuff was readily resolved by retreatment in the pulper; but when the pH was below 8, some of the cuff had to be cycled more than once to obtain satisfactory recovery of the bitumen.

It was found, also, that if the pH of the pulped charge was below 8, greater quantities of water and silt were retained in the diluted bitumen (end product).

The quantity of reagents required to neutralize the acidity and obtain an alkalinity of pH 8 in pulping the Edna bituminous sandstone ranged between 1 and 5 pounds of sodium silicate and 1 to 3 pounds of sodium carbonate per ton of bituminous sandstone. In many of the runs these reagents were introduced into the pulper as concentrated solutions, because it was not desirable to add any more water to the charge in the pulper. After pulping was completed, the alkalinity of the charge was determined by means of a pH meter.

Quantity of Water Used in Pulping

The consistency of the pulp, as controlled by the quantity of water used in pulping, has a discernible effect upon the efficiency of the process. Tests have shown that washed bituminous sand from the multiple-stage washer (fig. 2) under optimum conditions contains about 10 percent water by weight. Other things being equal, if no additional water was added in pulping the sand, a viscous (dry) pulp was obtained. Increasing the water content to 15 percent resulted in a medium fluid pulp, and 20 percent water resulted in a very fluid (wet) pulp.

For efficient separation as well as ease of handling, medium viscous pulps obtained when the water content was increased to 15 percent resulted in the most desirable conditions. The diluted bitumen from a very fluid or wet pulp did not float as readily as from a medium fluid pulp. When wet pulp was processed, globules of slowly floatable diluted bitumen were observed in the sand bed on the bottom of the flotation cells. Furthermore, some tests showed that the ash content of the end product obtained from a wet pulp was higher than that from a medium pulp.

Flotation of the Oil Froth

The oil froth is separated from the sand grains by introducing the pulp into hot water (210° F.) in the multiple-cell flotation unit shown in figure 3. The charge is dumped from the pulper into a hopper, which automatically delivers the pulp at a predetermined rate into the first compartment of the multiple-cell unit. A diagrammatic drawing of the unit is shown in figure 4. It consists essentially of four flotation cells in series and a trough in which a conveyor screw operates. The cells are 10 by 10-3/8 inches, and the first cell is 9 inches deep; the second, 10 inches; the third, 11 inches; and the fourth, 12 inches. The floor of the cells is the top of a steam chest, 11, which heats the water in the cells. Steam enters the chest at inlet 6

1, pulp inlet; 2, scrapers; 3, chain drives; 4, drive shaft; 5, bitumen discharge; 6, steam inlet; 7, glass windows; 8, trough for overflow of bitumen; 9, adjustable openings; 10, impellers; 11, steam chest; 12, steam outlet; 13, screw conveyor; 14, sheet metal trough; 15, sand-tailings discharge.

Figure 4. - Diagrammatic drawing of multiple-cell flotation unit.

and discharges at outlet 12. In each cell is an impeller, 10, with four oblique blades (9-3/4 inches long by 2 inches wide), which is chain-driven at 9 revolutions per minute from a shaft, 4. The pulp enters the first cell through chute 1, where it is mildly churned and "rolled" by the impeller blades. Most of the aerated oil froth quickly separates from the sand in the first cell and collects on the surface of the water. Additional churning of the sand and flotation of the oil takes place in the remaining three cells. The sand is discharged through the openings in the cell partitions by the blades of the rotating impellers. The rate of movement of the bitumen-freed sand from one cell to another is controlled by adjustable gates, 9, operated by screws that extend to the top of the cells. The sand tailings from the fourth cell are discharged into trough 14 and carried out by the screw conveyor, 13. The mechanics of separation are observed through the window, 7, in each cell.

Originally, impellers with vertical blades rotating at 18 r. p. m. churned the sand in a circular path, which resulted in considerable crowding and abrasion of the grains, causing some of the bitumen particles to be ground too fine to float readily through the slimes to the surface of the water. Also, considerable water and silt were worked into and retained by the large particles of bitumen that floated to the surface of the water when the sand was agitated vigorously. This condition was eliminated by using oblique blades and reducing the rotating speed from 18 to 9 r. p. m. The rolling effect on the sand caused by the oblique blades created more favorable conditions for flotation of the bitumen. The change in the speed of the impellers also reduced the amount of churning and decreased the quantity of water and silt retained permanently by the bitumen in the froth. The reduced speed also had the advantage of requiring less power to actuate the impellers.

The oil froth that collects on the surface of the water in each cell is removed by means of revolving horizontal scrapers, 2, which skim off the froth into trough 8. The froth flows from trough 8, through outlet 5, into a steam-jacketed conduit.

The pH of the Water in the Cells

The results of flotation tests, during which the pH of the water in the cells was varied between 5 and 9, show that flotation of the oil froth is influenced by the pH of the water. The rate of flotation is slow at pH 5 and increases with increase in the alkalinity of the water. At pH 9, the froth tends to contain more water than when the pH of the water is 8 or less. At pH values lower than 8 the froth appears to be more difficult to desilt. Best results were obtained when the cell water was maintained at pH 8.

Removal of Silt from Water in Flotation Cells

Very little silt is removed from the sand in washing out the water-soluble iron salts in the first step of the operation. The silt is freed only when the bitumen is displaced from the sand grains by chemical solutions in the pulping operation. The silt separates from the pulp in the flotation cells and becomes suspended in the water, although some is carried over with

the froth. In some runs, in order to maintain a minimum of suspended solids in the water in the flotation cells, the silt-laden water, which also contains small particles of suspended bitumen, was withdrawn in a small continuous stream and discharged into a settling tank. A treating chemical was added to the water to flocculate the silt without altering the pH of the water, but it proved to be unsatisfactory in facilitating the settling of the fine silt from the cell water. When freed of the larger silt particles, the water was returned to the flotation cells. (See fig. 2.) As 10 percent of the bitumen-free sands was fine enough to pass through a 200-mesh screen (half of which passed through a 325-mesh screen), that portion is difficult to separate from the bitumen, and, once separated, it is difficult to settle.

Removal of Water, Sand, and Silt from the Separated Bitumen

The oil froth contains varying quantities of water, sand, and silt, which must be removed to obtain a suitable product for refining. A typical analysis of the froth shows that it contains 6 percent sand and silt, 21 percent water, and 73 percent diluted bitumen. In order to facilitate settling of the water and mineral matter entrapped in the froth, the specific gravity and viscosity of the bitumen is reduced by adding more diluent as the froth flows from the trough, 8, into bitumen outlet 5 (fig. 4). A small reciprocating type pump driven by a direct-current electric motor was built for adding the diluent to the froth at a uniform rate. The rate of feed of diluent is controlled by the speed of the motor, which is governed by a resistance in series with the armature of the motor. The steam-jacketed conduit carries the froth and diluent into a screw mixer, where thorough mixing facilitates solution of the bitumen in the diluent. The froth-diluent mixture enters the top of the inner barrel of the mixer, is circulated downward and through the openings at the bottom of the inner barrel by the action of a revolving screw, thence upward through the annulus between the inner and outer barrel, and again down through the inner barrel. The slow motion of the close-fitting screw in the barrel of the mixer results in mixing by intimately contacting the diluent and the froth with a minimum of turbulence. Small propellers were first used instead of a screw, but the high speed necessary for circulation emulsified part of the water, oil, and silt, which prevented their separation. Thus, the water and silt content of the diluted bitumen was increased. Best results were obtained when the screw was used instead of propellers to circulate and mix the diluent and froth. The mixer was maintained at a temperature of 180° F. by means of a water bath.

The diluted bitumen overflows through the outlet pipe near the top of the mixer. The overflow from the mixer enters a cone-bottom settling tank containing hot wash water, which is maintained at a temperature of 180° F. by an electric immersion heater. A 5-gallon glass jar with a cone bottom was used as a settling tank in many runs in order to observe the settling characteristics of the water, sand, and silt.

In some runs emulsion-breaking chemicals were added to the diluted bitumen in the screw mixer to minimize emulsification of the oil and water and to aid in settling the fine silt.

In adding minute quantities of treating chemicals to the oil stream entering the screw mixer, it was desirable to feed them continuously. As no equipment was readily available that would feed 1 part chemical to 1,000 to 30,000 parts of oil into an oil stream flowing at the rate of 0.5 gallon per hour, a special feeder was designed consisting of an ordinary glass syringe mounted on a board. The piston of the syringe was pushed by a screw that was turned by a flexible shaft connected to a line shaft through a gear-reduction unit. The end of the syringe needle was placed in the inlet oil stream to the screw mixer, causing the chemical to be swept continually from the needle into the oil stream.

Additional mixing of the diluted bitumen was obtained by means of a mixing paddle in the settling tank that revolves at one revolution per minute.

The sand and most of the water and silt settle out from the diluted bitumen as an oily sludge. The partly settled oil rises and overflows through an outlet pipe near the top of the tank. The volume of the settling tank and the rate of flow through it are such that the diluted bitumen does not remain in the tank long enough to allow all the silt and water to settle; therefore, it is sent to a final settling tank, where virtually all of the water and silt settle out in a period of 12 to 16 hours. The final settling temperature is 200° F. Attached to the mixing paddle shaft are four scrapers that revolve on the cone-bottom of the settling tank and move the settled sludge to the center of the tank, where it is drained through the bottom outlet valve. The dragging action of the scrapers also frees globules of diluted bitumen from the sand grains on the bottom of the tank, permitting the freed globules to float upward through the water into the layer of diluted bitumen.

One of the most troublesome problems in the preliminary settling operation in the gun-barrel tank is the formation of sludge or cuff in the lower part of the oil (diluted bitumen) and immediately above the wash water. Centrifuge tests of a sample of the sludge from a conventional separation run showed that it contained 8 percent emulsion of oil and water, 14 percent water, and 32 percent sediment. On complete resolution of the emulsion, 26 percent water, 28 percent sediment, and 46 percent oil were obtained. There is good reason to believe, therefore, that the predominating cause of the formation of sludge is the fine silt that is associated with the froth. A satisfactory method of handling the sludge was found to be retreatment in the pulper. (See fig. 2.) It was found that the sludge became resolved in the pulper, permitting the bitumen to be separated in the flotation cells.

Quantity of Diluent Used to Dilute the Oil Froth

The quantity of diluent added directly to thin the bitumen in the separated froth affected the quantity of silt and water that remained in the diluted bitumen. The more diluent added, the greater the gravity differential between the diluted bitumen, water, and mineral matter and, therefore, the greater the differential force affecting settling. Thus, the ash content of the bitumen, the sediment determined by extraction, and the sediment and water determined by centrifuge usually decreased as the quantity of diluent added to the froth was increased. The decrease in foreign matter, however, was negligible when the added diluent was in excess of two parts diluent to one part bitumen.

Recoveries of Bitumen

Based on the results of several runs in which optimum operating conditions were maintained in the laboratory separation plant, 95 percent of the bitumen originally contained in Edna bituminous sandstone was recovered. The recovery percentage is based upon an original average bitumen content of Edna sandstones of 11 percent and represents a recovery of 24.7 gallons per ton of bituminous sandstone.

Under optimum conditions of laboratory pilot-plant operation, a loss of 5 percent (1 percent to the tailings and 4 percent to the slimes) of bitumen originally in the sandstone normally can be expected in treating Edna bituminous sandstones. This loss may be attributed in large measure to the fineness of some bitumen particles, which combine with the iron hydroxide and fine silt in the pulping operation and are not floated in the separation cells with the recovered bitumen.

Summary of Results of Separation Tests

The studies described in this report show that the hot-water method of separation may be applied satisfactorily to separating hydrocarbons from the Edna bituminous sandstones. On the basis of results of 52 separation tests in the laboratory plant, fundamental data on the principles underlying the recovery of bitumen from these bituminous sandstones have been obtained, and a method of processing them has been developed.

Hot-water washing of the Edna bituminous sandstones prior to treatment is necessary to remove water-soluble iron and calcium salts. Unless removed, these salts react with the alkaline reagents in the pulper and form gelatinous iron and calcium hydroxides, which are precipitated in the separation cells, preventing the flotation of fine particles of bitumen and causing excessive quantities of bitumen to be lost to the slimes and sand tailings and the percentage recovery to be reduced.

The results of separation tests demonstrate that neutralization of the acidity of the charge with sodium silicate or sodium carbonate solutions is a fundamental requirement for complete displacement of the bitumen from the sand grains. The addition of a light-gravity fuel-oil diluent facilitated displacement of the bitumen. The removal of the acid iron salts greatly reduces the quantity of alkaline reagents required to neutralize acidity in pulping the bituminous sandstones. The most satisfactory diluent to use in pulping the sandstone and in diluting the oil froth to facilitate settling of the water, sand, and silt is one containing substantial quantities of aromatic compounds.

Careful control of the pH of the treating system also is an important factor in processing the Edna sandstones. Best results, as reflected by complete displacement of the bitumen from the sand grains in the pulper, rapid separation of the oil froth in the flotation cells, and effective settling of the water and silt from the end product were obtained when the alkalinity of the system was maintained at pH 8.

Settling of water and silt from the end product is complicated by the formation of a cuff or sludge consisting of an emulsion of oil, silt, and water that accumulates below the diluted bitumen in the gun-barrel settling tank and interferes with the settling process. The presence of very fine silt in the oil froth has made efforts to prevent the formation of cuff only partly successful. A satisfactory method of overcoming the problem was to remove the cuff from the settling tank and return it to the pulper for retreatment.

Under carefully controlled operating conditions a maximum recovery of 95 percent of the bitumen in the Edna sandstones can be expected.

In a typical run under optimum conditions, about 2.5 pounds of sodium carbonate, 4.4 pounds of sodium silicate, and about 8 gallons of diluent were consumed in pulping a ton of bituminous sandstone. Approximately 0.1 gallon of the diluent was lost to the sand tailings. From 18 to 50 gallons of diluent per ton of bituminous sandstone treated was added to the froth to facilitate desilting and dewatering the bitumen. In many runs the water and silt content of the diluted bitumen after settling as determined by centrifuge was less than 2.0 percent, the sediment by extraction less than 0.6 percent, and the ash content less than 0.6 percent.

The determination of the cost of recovering bitumen from these sandstones would require building a pilot plant, which would involve mining, separation, and preliminary refining. Data from such a plant would furnish the basis for sound estimates of the cost of recovery on a commercial scale.

APPENDIX I

Products from Edna Bitumen

Evaluation of the separated bitumen in terms of commercial products includes both technical and economic considerations. It involves determination of the possible products that reasonably can be produced from the bitumen, which of these products will have the greatest demand, and how cheaply they can be produced.

It is probable that motor fuels, Diesel fuels, and fuel oils will be the products in greatest demand and that the separated bitumen will be of importance primarily as a source of these products; other products, such as asphalt and coke, probably will be of lesser importance.

Products Obtained by Cracking^{15/}

Following the removal of the diluent by distillation, samples of the bitumen were subjected to various degrees of thermal cracking to ascertain

^{15/} The cracking experiments were performed at the Laramie Petroleum and Oil Shale Experiment Station, Bureau of Mines, Petroleum and Natural Gas Branch, by P. L. Cottingham and N. M. Melton, under the supervision of W. I. R. Murphy.

(1) the percentage yield of products that distill within the temperature range of gasoline, kerosine, and gas oil, (2) the percentage yields of products having viscosities and flash points within the range of fuel-oil specifications, (3) the extent to which the viscosity of the bitumen would be reduced by mild cracking in order that it may be transported to a refinery by pipe lines, tank cars, or tank trucks if necessary, and (4) the percentage yield of coke.

Products Obtained by Mild Cracking

Two samples of bitumen were cracked at temperatures and for time intervals that resulted in the yield of appreciable quantities of low-boiling products and a small amount of coke. The results of these tests are shown in table 1.

TABLE 1. - Results of cracking Edna bitumen

	Sample A	Sample B
Cracking temperature, °F.	823	895
Cracking time, seconds	867	151
Cracking pressure, p.s.i.g.	103	100
Liquid recovery, weight, percent ...	93.3	96.2
Coke, weight, percent	3.4	1.8
Gas plus loss, ^a / weight, percent ...	3.3	2.0

^a/ Based on a gas weight of 40 grams per cubic foot at 760 mm. and 60° F.

The liquids from the cracking tests (table 1) were distilled by the Bureau of Mines Hempel method. The complete results of these analyses^{16/} are presented in tables 2 and 3. An approximate summary of the results is given in the following tabulation:

^{16/} The analytical distillations of the cracked bitumen and the fuel-oil evaluation work were done at the Laramie Petroleum and Oil Shale Experiment Station, Bureau of Mines, Petroleum and Natural Gas Branch, by W. J. Wenger, under the supervision of J. S. Ball.

Figure 5. - Curve showing recovery of diluent from sand tailings to which measured quantities of diluent had been added.

Figure 6. - Curve showing yield of distillate from tailings containing different percentages of bitumen and no diluent.

TABLE 2. - Distillation analyses of Edna bitumen cracked
at 823° F. for 867 sec.

GENERAL CHARACTERISTICS

Specific gravity, 0.986	A.P.I. gravity, 12.0
Sulfur, percent, 2.56	Color, black
Saybold Universal viscosity at - OF., - sec., at - OF., - sec.	
Furol viscosity at 100° F., 210 sec., at 130° F., 74 sec.	

DISTILLATION, BUREAU OF MINES HEMPEL METHOD

Distillation at atmospheric pressure, 760 mm. First drop 49° C. (120° F.)

Frac- tion No.	Cut °C.	at °F.	Per- cent	Sum per- cent	Sp. gr. 60/60°F.	°A.P.I. 60° F.	C.I.	S.U. visc., 100°F.	Cloud test, °F.	Aniline point, °C.
1	50	122	-	-	-	-	-	-	-	-
2	75	167	2.2	2.2	0.681	76.3	13	-	-	-
3	100	212	1.3	3.5	.722	64.9	22	-	-	-
4	125	257	2.8	6.3	.751	56.9	27	-	-	-
5	150	302	3.7	10.0	.779	50.1	33	-	-	-
6	175	347	3.6	13.6	.803	44.7	37	-	-	-
7	200	392	3.5	17.1	.825	40.0	41	-	-	-
8	225	437	4.5	21.6	.842	36.5	44	-	-	38.0
9	250	482	5.5	27.1	.863	32.5	49	-	-	39.0
10	275	527	9.9	37.0	.892	27.1	58	-	-	39.2

Distillation continued at 40 mm.

Distillation continued at 40 mm.										Less than
11	200	392	0.2	37.2	) -	-	-	-	5	-
12	225	437	1.7	38.9	) 0.920	22.3	-	54	5	44.0
13	250	482	4.6	43.5	.939	19.2	69	80	5	-
14	275	527	6.6	50.1	.958	16.2	75	165	5	-
15	300	572	8.3	58.4	.985	12.1	84	740	5	-

Residuum	39.6	98.0	1.153
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Carbon residue of residuum 43.2 percent; carbon residue of crude 20.0 percent.

APPROXIMATE SUMMARY

	Percent	Sp. gr.	°A.P.I.	Viscosity
Light gasoline	3.5	0.696	71.8	
Total gasoline and naphtha	17.1	0.772	51.8	
Kerosine distillate	None	-	-	
Gas oil	20.3	.874	30.4	
Nonviscous lubricating distillate	5.1	.917-.943	22.8-18.5	50-100
Medium lubricating distillate	4.8	.943-.960	18.5-15.9	100-200
Viscous lubricating distillate	11.1	.960-1.000	15.9-10.0	Above 200
Residuum	39.6	1.153	-	
Distillation loss	2.0			

TABLE 3. - Distillation analyses of Edna bitumen cracked
at 895° F. for 151 sec.

GENERAL CHARACTERISTICS

Specific gravity, 1.018
 Sulfur, percent, 2.92
 Saybolt Universal viscosity at - °F. - sec., at - °F., - sec.
 Furol viscosity at 100° F., 1770 sec., at 130° F., 340 sec.

A.P.I. gravity, 7.4
 Color, black

DISTILLATION, BUREAU OF MINES HEMPEL METHOD

Distillation at atmospheric pressure, 760 mm. First drop 49° C. (120° F.)

Frac- tion No.	Cut °C.	at °F.	Per- cent	Sum per- cent	Sp. gr. 60/60°F.	°A.P.I. 60° F.	C.I.	S.U. visc., 100°F.	Cloud test, °F.	Aniline point, °C.
1	50	122	-	-	-	-	-	-	-	-
2	75	167	1.0	1.0	0.716	66.1	29	-	-	-
3	100	212	1.6	2.6	.761	54.4	41	-	-	-
4	125	257	-	2.6	-	-	-	-	-	-
5	150	302	1.9	4.5	.789	47.8	37	-	-	-
6	175	347	2.3	6.8	.811	43.0	41	-	-	-
7	200	392	2.1	8.9	.832	38.6	45	-	-	-
8	225	437	3.1	12.0	.848	35.4	47	-	-	37.4
9	250	482	4.5	16.5	.871	31.0	52	-	-	36.8
10	275	527	10.8	27.3	.882	28.9	53	-	-	40.0

Distillation continued at 40 mm.

									Less than	
11	200	392	0.6	27.9	-	-	-	44	5	-
12	225	437	.7	28.6	0.915	23.1	-	54	5	-
13	250	482	3.0	31.6	.939	19.2	69	94	5	48.2
14	275	527	7.6	39.2	.952	17.1	72	230	5	-
15	300	572	8.3	47.5	.978	13.2	81	990	5	-

Residuum 50.4 97.9 1.122 -

Carbon residue of residuum 35.9 percent; carbon residue of crude 19.9 percent.

APPROXIMATE SUMMARY

	Percent	Sp. gr.	°A.P.I.	Viscosity
Light gasoline	2.6	0.744	58.7	
Total gasoline and naphtha	6.8	0.779	50.1	
Kerosine distillate	None	-	-	
Gas oil	21.2	.871	31.0	
Nonviscous lubricating distillate	2.4	.916-.939	23.0-19.2	50-100
Medium lubricating distillate	3.9	.939-.949	19.2-17.6	100-200
Viscous lubricating distillate	13.2	.949-.985	17.6-12.1	Above 200
Residuum	50.4	1.122	-	
Distillation loss	2.1			

Product	Liquid cracked at 895° F. for 151 sec., percent	Liquid cracked at 823° F. for 867 sec., percent
Gasoline	7.0	17
Gas oil	21.0	20
No. 5 fuel oil	19.0	21
Residuum	50.0	40

It will be noted that the yield of gasoline from the sample that was cracked for 867 seconds is more than double the yield obtained from the sample that was cracked for only 151 seconds. The yields of gas oil and fuel oil were altered very little. To meet motor-fuel specifications, the gasoline obtained from the cracked bitumen would require treating to remove most of the sulfur.

Cracking to Coke

A sample of bitumen was cracked until only coke remained, and the percentage yields by weight of liquid, coke, and gas were 70.7, 22.6, and 6.7, respectively. The liquid from the cracking test was distilled by the Bureau of Mines Hempel method. The complete results of the analyses are presented in table 4. The following tabulation is an approximate summary of the results:

	Percent
Gasoline	19.4
Gas oil	26.7
No. 5 and No. 6 fuel oils ..	53.9

As the No. 5 and No. 6 fuel oils are distilled products, they are free of silt.

Sodium carbonate^{17/} only may be used as a pulping reagent when the bitumen is cracked to coke, as all the silt will remain in the coke and, therefore, the silt content of the bitumen is not critical. For a run in which only sodium carbonate was the pulping reagent, the ash content of the diluted bitumen was only about 70 percent higher than when sodium silicate also was used to pulp the bituminous sandstone. If the diluent from the end product of the run were recovered and the bitumen cracked to a coke, the coke would contain less than 8 percent ash, which is less than the ash content of many cokes made from coal.

^{17/} The silt content of the separated bitumen was found to be appreciably less when sodium silicate combined with sodium carbonate was used in pulping, but the cost is considerably less when sodium carbonate only is used to pulp the bituminous sandstone.

Cracking to Obtain No. 6 Fuel Oil

A sample of bitumen was cracked to obtain the maximum yield of a No. 6 fuel oil. The bitumen was cracked at a pressure of 58 pounds per square-inch gage and a temperature of 827° F. for 3,060 seconds. The percentage yields by weight of liquid, coke, and gas were 75.5, 11.5, and 13.0, respectively. After 12.8 percent of the low-boiling material was removed from the liquid, the remainder met the flash point and viscosity specifications for a No. 6 fuel oil. The flash point was higher than 150° F., and the viscosity 235 seconds Saybolt furol at 122° F.

Cracking to Lower Viscosity

The economics of the location of sites may be such that the flotation plant and the refinery to process the recovered bitumen would be miles apart. In that event, it would be desirable to lower the viscosity of the bitumen by cracking in order to transport the bitumen to the refinery by pipe line, tank car, or tank truck.

Four samples of bitumen were cracked for different time intervals to determine the extent to which the viscosity would be lowered. The cracking temperatures, cracking time, pressures, and yields are shown in table 5, and the resulting viscosities are listed in table 6.

TABLE 5. - Results of cracking Edna bitumen to break viscosity

	C	D	E	F
Cracking temperature, °F.	830	845	852	827
Pressure (He. gas), p.s.i.g.	60	58	58	58
Cracking time, seconds	163	287	750	3060
Liquid recovery, weight	97.8	99.6	91.9	75.5
Coke, weight, percent	-	0.1	1.2	11.5
Gas plus loss, weight, percent	2.2	.3	6.9	13.0

TABLE 6. - Viscosities of cracked Edna bitumen

	Original	C	D	E	F
Viscosity, Saybolt Furol, seconds, at:					
100° F.	-	-	-	-	41
122° F.	-	-	1370	200	26
140° F.	-	-	550		
180° F.	-	600			
210° F.	1140	150			
275° F.	130				
Flash point, °F.	505		88	65	too low

Fuel Oil Obtained Without Removing Diluent

A few tests were made to obtain an end product from the separation plant that would meet the specifications of a No. 6 fuel oil without removing the diluent added to the bitumen in the separation process.

To obtain a diluted-bitumen end product having a viscosity within the specification limits of a No. 6 fuel oil, enough diluent was added in the separation process to obtain an end product within the viscosity limits for a No. 6 fuel oil. The viscosity requirements were met when the end product contained approximately equal parts of bitumen and diluent. Within this required viscosity range, however, the oil had a retarding effect upon settling of the silt, and more silt was retained in the oil than is permitted by the sediment specification for No. 6 fuel oil. It was found, however, that by distilling off the water (about 4 percent of the volume of diluted bitumen) and allowing the dehydrated oil to settle, the oil passed the specification tests for a No. 6 fuel oil. Table 7 shows the results of the specification tests on two end products of different viscosities made in the foregoing manner.

TABLE 7. - Comparison of characteristics of diluted bitumen from separation plant with A.S.T.M. specifications for No. 6 fuel oil

	Diluted bitumen, sample 1	Diluted bitumen, sample 2	Specification limits, CS-12-40
Viscosity, seconds	45	107	45-300
Sediment by extraction, percent..	0.28	0.23	Max. 0.5
Water by distillation, percent...	Trace	Trace	Max. 1.0
Flash point, °F.	Higher than 150	Higher than 150	Min. 150, no max.

Although this method involves the least amount of processing to obtain a satisfactory fuel oil, the cost of the diluent is an important factor influencing the economics of the product.

The diluent used in the separation process was a No. 3 fuel oil manufactured from crude oil. A similar diluent was made from Edna bitumen by cracking the bitumen to coke. After removing the "light ends," the coke distillate was added to Edna bitumen, and the mixture met the specifications for No. 6 fuel oil. See table 8.

TABLE 8. - Properties of a fuel oil containing diluent obtained by cracking Edna bitumen to coke

	Fuel oil	Specification limits, CS-12-40
Viscosity, seconds	150	45-300
Sediment by extraction, percent...	0.18	Max. 0.5
Water by distillation, percent....	0.0	Max. 1.0
Flash point, °F.	165	Min. 150, no max.

Asphalt Properties

The asphalt properties^{18/} of unaltered Edna bitumen and two residuums obtained by distillation at reduced pressure and prepared according to the method described by Stanfield^{19/} were determined by standard asphalt tests. The results of the tests on the three asphalts having different degrees of hardness (penetration) are given in table 9. It will be noted that the penetrations at 77° F. for the unaltered bitumen and the two residuums are 80, 37, and 19, respectively.

Of the data shown in the table, only the ash and spot tests require special comment. The ash contents of 0.6, 0.6, and 0.5 percent were determined by the A.S.T.M. Designation D 4-42,^{20/} method 1; commonly used in asphalt testing, and the ash contents of 2.1, 2.0, and 2.0 percent were determined by direct ashing of the samples. The difference between the two ash percentages for each sample shows the presence of finely divided inorganic matter that passed through the asbestos mat in the A.S.T.M. D 4-42, method 1, test. The passage of this fine material through the mat results in an erroneously high bitumen content, as the fine material is not soluble bitumen.

In the spot tests, the Oliensis test was positive and the heptane-xylene equivalent was failing. These tests were determined on Edna bitumen recovered from the sandstone by flotation with the use of a diluent, and, therefore, the bitumen contains the mineral matter not removed in the process. To remove the diluent, the bitumen was subjected to a temperature of about 275° C. In order to determine the influence on the spot tests of the mineral matter and the effect of the high temperature used to remove the diluent, some bitumen was extracted from the sandstone by use of benzene. The benzene extract was then filtered, centrifuged, and refiltered to remove as much silt as possible. The benzene in the extract was removed at a much lower temperature (not more than 155° C.) than that required to distill the diluent from the bitumen that was floated. The ash content of the bitumen after the removal of the benzene by evaporation was 0.1 percent, thus showing that most but not all of the silt was removed. The asphalt properties of this bitumen (benzene extracted) are shown in table 9.

The Oliensis spot test (see table 9) is still positive, but the heptane-xylene equivalent is passing to 35 percent xylene, thus showing that the low temperature used to remove the solvent or the reduced content of silt improved the heptane-xylene equivalent.

- ^{18/} The asphalt was prepared and analyzed at the Laramie Petroleum and Oil Shale Experiment Station, Bureau of Mines, Petroleum and Natural Gas Branch, by Mrs. R. L. Hubbard, under the supervision of K. E. Stanfield.
- ^{19/} Stanfield, K. E., Asphalts from Some Wyoming and Other Asphalt-Bearing Crude Oils: Bureau of Mines Report of Investigations 3568, 1941, 53 pp.
- ^{20/} American Society for Testing Materials, A.S.T.M. Standards. Part II, Nonmetallic Materials: Philadelphia, Pa., 1946, p. 570.

TABLE 9. - Properties of asphalts from Edna bituminous sandstone

	Unaltered bitumen penetration 80	Asphalt residuum A penetration 37	Asphalt residuum B penetration 19
Bitumen charge, gm.	-	1341	1184
Asphalt yield, gm.	-	1284	1082
Asphalt yield, weight-percent	100	95.8	91.4
Maximum pressure during vacuum distillation, mm. mercury	-	3.5	6
Maximum temperature of vapors, °F.	-	414	460
Maximum temperature of liquid, °F.	-	509	550
Liquid temperature of initial cracking (cracking temperature), °F.	-	-	547
Ash, ^{1/} percent	.5	.6	.6
Ash, ^{2/} percent	2.0	2.0	2.1
Bitumen, ^{3/} percent	99.3	99.1	99.2
Bitumen soluble in carbon tetrachloride, percent	99.6	99.8	99.9
Carbon residue, percent	19.2	20.4	20.9
Composition:			
Asphaltenes, percent	21.0	22.1	25.1
Oils, percent	44.1	41.2	36.9
Resins, percent	33.0	34.6	36.4
Fire point, °F.	580	600	630
Flash point, °F.	505	545	570
Loss on heating, percent	.45	.20	.08
Penetration:			
At 32° F., 200 gm. wt., 60 sec., dmm.	14	6.7	less than 1
At 60° F., 100 gm. wt., 5 sec., dmm.	26	13	6.4
At 77° F., 100 gm. wt., 5 sec., dmm.	80	37	19
At 100° F., 100 gm. wt., 5 sec., dmm.	soft	165	89
At 115° F., 50 gm. wt., 5 sec., dmm.	soft	256	152
Penetration at 77° F., of residuum from loss on heating test, dmm.	66	34	18
Softening point, °F.	116	124	137
Specific gravity at 77°/77° F.	1.037	1.042	1.046
Spot tests, Oliensis:			
Initial	Pos.	Pos.	Pos.
After 24 hours	Pos.	Pos.	Pos.
Heptane-xylene equivalent ^{4/}	Failing	Failing	Failing
Sulfur	3.28	3.39	3.51

^{1/} Determined by ASTM Designation D 4-42, method 1, ASTM Standards 1946, pt. II, p. 570-571.

^{2/} Determined by direct ashing of sample.

^{3/} Results obtained are probably high because of discrepancy in ash determination.

^{4/} Solvent used was 100 percent xylene.

TABLE 9. -- Properties of asphalts from Edna bituminous sandstone (Cont'd.)

	Unaltered bitumen penetration 80	Asphalt residuum A penetration 37	Asphalt residuum B penetration 19
Viscosity at 210° F.:			
Furol, seconds	1143	2196	3771
Kinematic, stokes	24.7	47.4	81.5
Absolute, poises	24.4	47.1	81.2
Viscosity at 275° F.:			
Furol, seconds	130	202	301
Kinematic, stokes	2.81	4.36	6.50
Absolute, poises	2.71	4.23	6.33

In table 10 the asphalt properties of Edna bitumen are compared with asphalts of the same (80) penetration made from crude oils from the Kern River field, California; Oregon basin, Wyoming; and Tampico, Mexico. The table shows that, except for the ash and spot tests, the properties of Edna bitumen are similar to those of asphalts from Oregon basin, Wyoming, and intermediate between those of Kern River, California, and Tampico, Mexico.

Because of the silt (inorganic matter) contained in the Edna bitumen, specifications for Edna asphalts generally would meet native asphalt specifications rather than those of asphalts from petroleum.

TABLE 10. - Comparison of 80-penetration asphalts
from different sources

	Edna bitumen, Cali- fornia ^{1/}	Kern River, Cali- fornia ^{2/}	Oregon basin, Wyoming ^{2/}	Tampico, Mexico ^{2/}
Asphalt yield, weight-percent	100.0	53.0	43.6	72.2
Maximum liquid temperature during vacuum distillation, °F.		575	575	500
Average initial cracking temperature of crude oil, °F.	545 3/2.0	600	590	600
Ash, percent	.5	.0	.0	.0
Bitumen, percent	99.3	100.0	100.0	99.9
Bitumen soluble in carbon tetra- chloride, percent	99.6	100.0	100.0	100.0
Carbon residue, percent	19.2	14.5	20.7	22.3
Composition, percent:				
Asphaltenes	21.0	13.0	20.5	30.0
Oils	44.1	46.5	46.0	42.5
Resins	33.0	40.5	33.5	27.5

See footnotes on page 28.

TABLE 10. - Comparison of 80-penetration asphalts
from different sources (Cont'd.)

	Edna bitumen, Cali- fornia ^{1/}	Kern River, Cali- fornia ^{2/}	Oregon basin, Wyoming ^{2/}	Tampico, Mexico ^{2/}
Ductility, 5 cm. per minute:				
At 32°F., cm.	-	0	-	-
At 77°F., cm.	-	100+	100+	-
Fire point, °F.	580	645	660	610
Flash point, °F.	505	550	570	510
Loss on heating, percent	.45	.00	.00	.2
Penetration:				
At 32°F., 200 gm. wt., 60 sec., dmm.	14	10	17	26
At 60°F., 100 gm. wt., 5 sec., dmm.	26	22	26	34
At 77°F., 100 gm. wt., 5 sec., dmm.	80	80	80	80
At 100°F., 100 gm. wt., 5 sec., dmm.	Soft	Soft	Soft	4/240
At 115°F., 50 gm. wt., 5 sec., dmm.	Soft	Soft	Soft	Soft
Penetration at 77°F., of residuum from loss on heating test, dmm.	66	71	70	68
Softening point, °F.	116	111	116	121
Specific gravity at 77°/77°F.	1.087	1.012	1.028	1.038
Spot tests, Oliensis:				
Initial	Pos.	Neg.	Neg.	Neg.
After 24 hours	Pos.	Neg.	Neg.	Neg.
Heptane-xylene equivalent	5/Failing	-	-	-
Sulfur	3.28	1.24	4.83	6.16
Viscosity at 210°F.:				
Furol, sec.	1143	880	1600	3400
Kinematic, stokes	24.7	19.0	34.6	73.4
Absolute, poises	24.4	18.3	33.8	72.6
Viscosity at 275°F.:				
Furol, sec.	130	95	180	350
Kinematic, stokes	2.80	2.05	3.88	7.56
Absolute, poises	2.71	1.93	3.72	7.31

1/ Experimental data for the 80-penetration asphalt from extract of Edna bituminous sandstone, San Luis Obispo County, Calif.

2/ Estimated data for 80-penetration asphalt.

3/ Value obtained by direct ashing of sample, whereas all other ash values were determined by ASTM D 4-42, Method I.

4/ Value obtained by extrapolation.

5/ Testing solution was 100 percent xylene.

APPENDIX II

Determination of Bitumen Content of Sandstones

The bitumen content of the sandstone samples was determined by the method designed by Rall and Taliaferro^{21/} of the Bureau of Mines for the determination of the water and oil content of cores obtained during the drilling of wells. This method has the advantage over the method recommended by the American Society for Testing Materials Method D 4-42,^{22/} in that even if the water content of a sample is more than 2 percent it is not necessary to dehydrate the sample of bituminous sandstone. Also, the large size of the sample (15 to 30 gm.) used in the Rall-Taliaferro apparatus, compared to the small (about 2 grams) sample used in the A.S.T.M. method, makes for greater accuracy.

Colorimetric Determination of Bitumen in Sand Tailings

The quantity of bitumen in the sand tailings is usually so small that a slight error in determining the large water content of tailings or a slight error in weight of the thimble and its contents, owing to absorption of moisture, results in an appreciable error in the determination of the bitumen content. A gravimetric method for determining the bitumen content of sand tailings, therefore, is not satisfactory. Accordingly, a colorimetric method was used, as follows:

About 20 to 30 grams of the tailings were placed in a weighed fiber thimble,^{23/} covered with a weighed wad of cotton, and weighed. The bitumen was extracted in a Rall-Taliaferro distillation apparatus containing about 100 ml. of toluol. Complete extraction requires 2 to 3 hours. When cool, the extract was compared with known color standards for bitumen content.

Empirical Determination of Diluent in Sand Tailings

Construction of Empirical Curves

The small quantity of diluent lost to the sand tailings from the separation process was determined by making use of the phenomenon that in a mixture of liquids not mutually soluble, the boiling point of the mixture is lower than either of the components alone. Thus, by boiling the tailings in water,

^{21/} Rall, Cleo Griffith, and Taliaferro, D. B., A Method for Determining Simultaneously the Oil and Water Saturations of Oil Sands; Bureau of Mines Rept. of Investigations 4004, 1946, 16 pp.

^{22/} See footnote 20.

^{23/} Rall and Taliaferro, in Bureau of Mines Rept. of Investigations 4004 (see footnote reference 21, p. 48), mention an alundum thimble. More reflux will pass through a fiber thimble than through an alundum thimble in the same length of time; consequently, a shorter time is required for an extraction when fiber thimbles are used. If a few sandstone grains should be lost owing to the use of a fiber thimble instead of an alundum thimble, the accuracy of the colorimetric method is not changed, as it does not affect the color reading.

the diluent was distilled with the water at a low temperature without cracking. However, trial tests showed that some of the diluent adhered to the distillation equipment, that a small percentage of diluent adhered to the sand grains even after boiling for a long time, and that the bitumen in the tailings yielded hydrocarbon liquid that was difficult to distinguish from the diluent. Therefore, it was expedient to determine the quantity of diluent in the tailings by the use of two empirical curves, which were prepared by correlating (1) known quantities of diluent added to special sand-tailing samples with the quantities of diluent recovered by distillation with water (fig. 5) and (2) the yields of liquid hydrocarbons distilled with water from different quantities of bitumen contained in tailings (fig. 6).

The points on curve 5 were determined by distilling mixtures of water and special sand-tailing samples containing different known quantities of diluent and measuring the quantities of diluent recovered. The special sand tailings were obtained by separating the bitumen without the aid of a diluent and contained 0.7 percent bitumen.

The first point for the curve was obtained by thoroughly mixing 4 pounds (on a dry-weight basis) of special tailings with 1.4 ml. of diluent and placing the mixture in a 6-liter flask containing 3 liters of water. The flask was connected to a condenser, which was coupled to a 1-liter globe-shaped separatory funnel by means of an adapter tube. Periodically, the level of the condensate in the separatory funnel was lowered by draining off part of the water. Care was taken not to drain off any of the distillate (diluent) floating on top of the water.

After 2 liters of water were distilled over, nearly all the water was drained from the separatory funnel, and the remainder, with the floating diluent, was drained into a small graduate, where the diluent was measured. Using this volume of diluent as the ordinate and the volume (1.4 ml.) of diluent mixed with the sand tailings as the abscissa, the first point for the curve was obtained.

The next run was made with the same weight of special tailings and 2 ml. of diluent; in subsequent runs, 3, 5, 6, and 8 ml. of diluent was used. After each distillation, the water condenser, adapter, and separatory funnel were cleaned with a sulfuric acid and potassium dichromate solution to remove the diluent that adhered to the apparatus.

As stated, the special tailings used to determine the basic data of the curve in figure 5 contained 0.7 percent bitumen. To correct for the yield of distillate from tailings containing more or less than 0.7 percent bitumen, the curve (fig. 6) was prepared from data obtained by distilling tailings containing different percentages of bitumen and no diluent. The apparatus and procedure were the same as those used to obtain the curve in figure 5.

It is significant that the extrapolation (dotted line) of the curve in figure 6 shows that tailings containing about 0.6 percent bitumen (and no diluent) yield enough light hydrocarbon liquid during a distillation to wet the distillation equipment. Thus, if the yield of light hydrocarbons should

exceed that necessary to wet the distillation equipment, they would flow from the condenser and be collected as a distillate.

Method of Using the Empirical Curves

Using 4.5 pounds of wet sand tailings from a separation test in which No. 3 fuel oil had been used as a diluent and 3 liters of water, the yield of distillate was 2.5 ml. (Four and one-half pounds of wet tailings is the approximate equivalent of 4 pounds of dry tailings. If a 4.5-pound charge of wet tailings does not contain 4 pounds of dry tailings, a correction is made for the difference.) Referring to figure 5, this yield shows that the tailings contained 3.5 ml. of diluent originally. From the bitumen content determination, the water percentage of the tailings was found to be 13; therefore, the 4.5 pounds of tailings contained 4.5 less 13 percent of 4.5, or 3.9 pounds of dry sand. The curve (figure 5) is based on a charge of 4 pounds of dry sand. As only 3.9 pounds of dry sand was used in the determination, the quantity of distillate remaining in the sand is $\frac{3.9}{4} \times 3.5$, or 3.4 ml.

According to the colorimetric method of analysis, the bitumen content was 1 percent. Figure 6 shows the yield of distillate to be 0.5 ml. when 1.0 percent bitumen and no diluent were present in 4 pounds of dry sand; therefore, $\frac{3.9}{4} \times 0.5 = 0.49$ ml. Therefore, $3.4 - 0.49 = 2.9$ ml. remaining in the sand.

By converting 2.9 ml. to gallons and correcting 3.9 pounds of dried sand for original bitumen and water (2 percent water for this example) content of the bituminous sandstone, the result shows that 0.34 gallon of diluent was lost per ton of bituminous sandstone treated.