

be so high that the sand faces become caked and relatively impervious to the flow of oil through them. Apparently the temperature at which oil-(or oil- and water-) saturated sands cake as a result of heat depends upon the size of the sand grains and the water content of the sands.

### Techniques and Laboratory Analyses for Secondary-Recovery Research

#### Core-and Water-Analysis Laboratories

In the Bureau's secondary-recovery studies, core and water analyses are essential tools. Laboratories for core analysis are maintained at each station and field office engaged in the secondary-recovery work, and facilities are available at the Franklin, Pa., Field Office, at the Bartlesville, Okla., Petroleum Experiment Station, and at the Laramie, Wyo., Petroleum and Oil-Shale Experiment Station for analysis of oil-field brines.

Also a laboratory to be used for routine core and water analyses is nearly completed at Dallas, Tex. This laboratory is relatively small and was designed to take care of the analytical needs relative to both primary- and secondary-recovery studies conducted by the Dallas and Wichita Falls offices. When not being used in connection with field studies, this laboratory will be used for research purposes.

At the Petroleum and Oil-Shale Experiment Station, Laramie, Wyo., studies were continued on oil-well cores, oil-field waters, and clay components of oil-bearing formations to develop information on the Newcastle sandstone in the Brush Creek, Fidler Creek, Skull Creek, and Osage oil fields and on the Frontier formation sandstones in the Grass Creek and Salt Creek oil fields in Wyoming. From these and related researches, knowledge was acquired as to how these formations would react to various flooding or driving agents when these are used to recover some of the oil remaining in the formations after primary production has decreased below economic limits of operation.

#### Development of Special Tools

Completion of the well caliper for use in the selective-plugging study has been delayed because of necessary complexity of the instrument. To permit use of the caliper in the numerous water-injection wells completed with 2-inch tubing cemented in place, it has been necessary to restrict the instrument to a diameter of 1-3/4 inches. It also has been necessary to provide means of retracting the caliper arms so that the instrument may be withdrawn through the 2-inch tubing. Although these design problems have been difficult, the instrument is now complete, and shop tests are in progress. Field tests will be started soon.

#### Electric Logging

Electrical logging work of the Franklin, Pa., field office was directed toward application of known methods to the problems of electrically measuring quantitatively the permeability, porosity, and fluid saturations of oil-bearing formations. Resistivity measurements in wells by means of a multiple-electrode system have the inherent weakness of being average values controlled by the probing length of the electrode. As the probing length is increased, the averages apply to a greater vertical length of rock. The conventional single-point electrode is lacking in enough probing length to obtain the accuracy of resistivity measurements in wells necessary for quantitative evaluation of reservoir characteristics. Preliminary work at Pennsylvania State College under the sponsorship of the Pennsylvania Grade Crude

Oil Association indicated promising results with a shielded mono-electrode that constrains the current, flowing from the center electrode, to a horizontal pattern for some distance from the electrode. Only the current flowing from the center electrode is used in resistivity measurements, and the "sampling" thickness is equal only to the length of the center electrode.

In the laboratory of the Franklin Office, satisfactory electrical measuring circuits were assembled, shielded mono-electrodes having various characteristics were constructed and calibrated, and radial sandstone specimens 4 inches in diameter and 4 inches in length were prepared. The permeability and porosity determinations were made by core-analysis methods, and the formation-resistivity factor was determined for each of the specimens before they were logged electrically in the laboratory. The electrically determined values of porosity and permeability when brines having different resistivities are used to fill the pore spaces check the values determined by core-analysis methods. Future laboratory work will involve two-phase saturation (water and oil) and three-phasesaturation (water, oil, and gas) and will check the possibilities for accurate quantitative determinations by electrical logging methods.

#### PETROLEUM CHEMISTRY AND REFINING

The research program on chemistry and refining has continued to be directed toward the improved and increased utilization of marginal crude oils, especially those with high sulfur contents. The work has been integrated with the Bureau's broad program to furnish fundamental data on the characteristics of the sulfur compounds in petroleum. This broad program is conducted with the financial support of the American Petroleum Institute as API Research Project 48A, and the advice and constructive criticism of members of the Advisory Committee for this project have aided greatly in the progress of the overall program.

The major parts of the Bureau's broad program dealing with sulfur in petroleum were indicated in the 1949 annual report<sup>15/</sup> as follows:

1. Synthesis and purification of pure sulfur compounds.
2. Determination of significant physical and chemical properties of these compounds.
3. Determination of thermodynamic properties of pure sulfur compounds.
4. Development of analytical methods for sulfur compounds.
5. Separation and identification of sulfur compounds in petroleum.
6. Characteristics of distillates from high-sulfur crude oils.
7. Thermal stability of sulfur compounds in distillates and crude oils.
8. Thermal decomposition studies of pure sulfur compounds.

The funds made available for the refining processes studies were utilized in continuing studies on items 5 to 8 of the program. A number of sulfur compounds have been identified in petroleum distillates and other compounds have been shown not to

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<sup>15/</sup> See footnote 2.

be present. Distillates from a rather large number of high-sulfur crude oils were prepared and their characteristics studied. Types of sulfur compounds in these distillates were determined, and it has been shown that these types vary with the crude oil. Extensive studies of the thermal stability of distillates and of the sulfur compounds in them have been made and important results obtained. Pure sulfur compounds were obtained in quantity; thermal decomposition studies of these compounds were initiated and the results analyzed.

Items 5 to 8 in the above outline are discussed in detail in the following paragraphs:

#### Separation and Identification of Sulfur Compounds in Petroleum

From a study of data previously obtained, it was decided to choose the Wasson, Tex., crude oil as the first upon which extensive study would be made in order to identify the individual sulfur compounds present and to determine their percentages in the total crude oil. To this end, special distillation apparatus was constructed to separate the light distillates from the crude oil with a minimum of thermal decomposition. This equipment is made entirely of glass and operates on an isothermal basis, using steam at atmospheric pressure as the heating medium. With this equipment, distillates have been prepared and steps taken to concentrate the sulfur compounds in the 0°-100° C. boiling range by means of adsorption on silica gel and alumina. In the silica-gel experiments, considerable success was obtained where it was found that more than half of the sulfur compounds in the naphtha had been concentrated in a fraction constituting only 1.2 percent of the naphtha. Using alumina as the adsorbent, approximately 38 grams of a sulfur concentrate were finally obtained from 7,200 grams of Wasson distillate. This concentrate is essentially all sulfur compounds and will be further separated by distillation in high-efficiency columns and possibly by additional chemical means to determine the individual compounds present.

Additional light material, boiling below 38° C., removed from the Wasson distillate, was fractionated in a Podbielniak high-temperature column in the hope of concentrating the two sulfur compounds (ethanethiol and 2-thiapropene) thought to be present and expected to be found either at their own boiling points or, more likely, at some azeotropic boiling point. Infrared analyses of fractions thought to contain the compounds indicated that their concentration was too small for certain identification. Upon recombining the fractions and filtering through alumina, fractions were obtained that gave positive evidence of the presence of ethanethiol and 2-thiapropene. Theoretically there are five possible sulfur compounds in this boiling range, but the other three were not found in this distillate and are thought to be absent in petroleum. There is no evidence to date that these three occur in any crude oils. These three are thiophene, thiacyclopropane, and 2-methylthiacyclopropane.

Where separation of the sulfur compounds present in naphthas is impossible or difficult, the sulfur compounds often can be identified by chemical means. The active chemicals are added to the distillates, and the chemical compounds formed by the addition can be identified by their boiling points or their spectra. Fractions from the distillation of the sulfur concentrate obtained from the Wasson distillate were treated to produce 2,4-dinitrophenyl sulfides from the thiols present in the distillates. Infrared analysis was used to show the presence of a number of thiols having boiling points below 70° C.

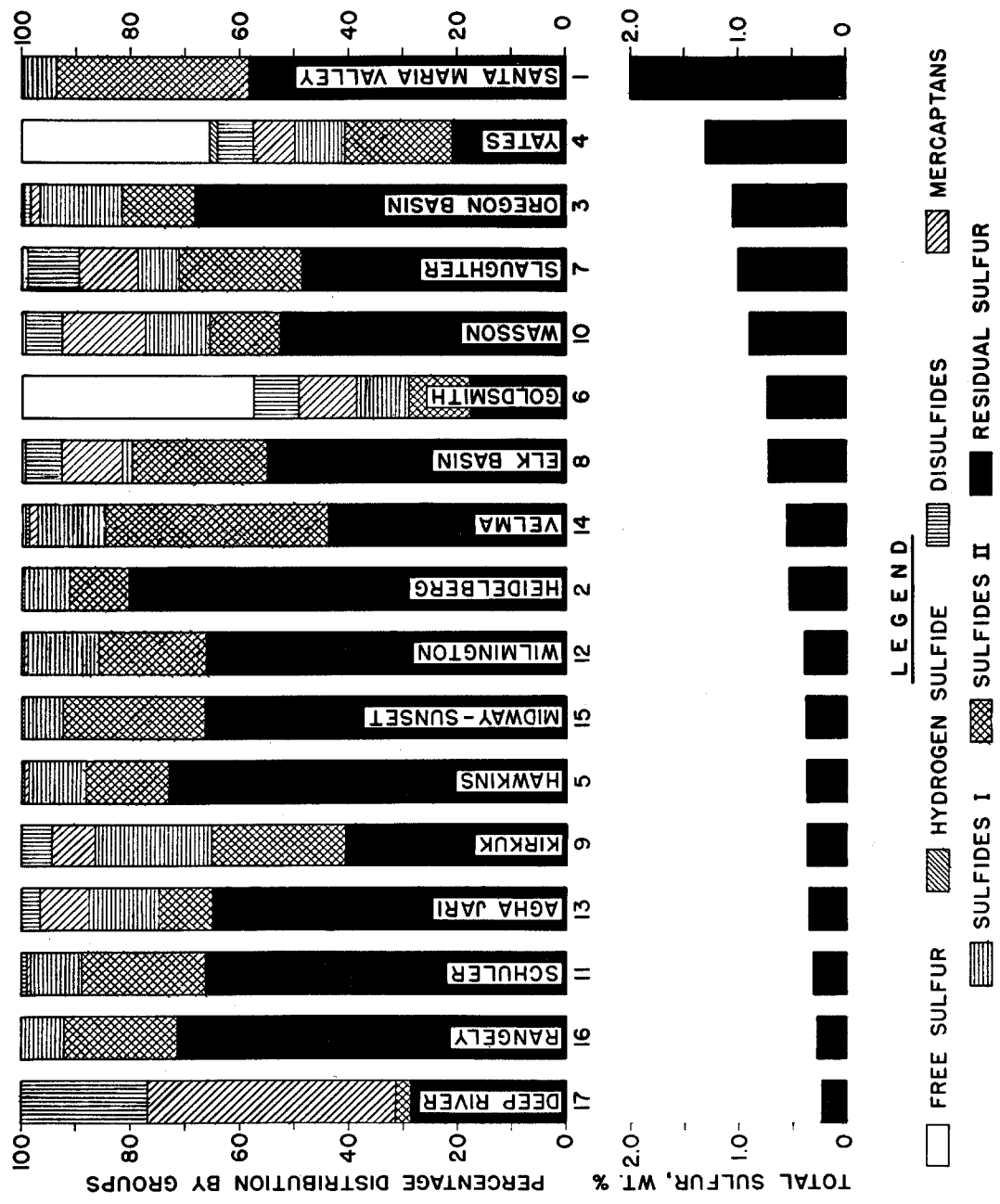


Figure 6. - Group sulfur analyses of naphthas from vacuum distillations.

While investigators in the past have reported the presence of various sulfur compounds in distillates prepared from crude oils, the results being obtained by the Bureau in these studies will give industry the first real comprehensive survey of the sulfur compounds and the types of sulfur compounds present in all types of crude oils. The industry is following this work with a great deal of interest.

#### Characteristics of Distillates from High-Sulfur Crude Oils

During the past year, the Bureau completed the first survey ever made of the types of sulfur compounds present in virgin naphthas from a variety of high-sulfur crude oils. The data,<sup>16/</sup> shown in part in figure 6, indicate a wide variation in the proportions in which the different sulfur types are present. Such data should eventually be helpful in developing proper refining processes for high-sulfur crude oils. This survey presents data showing the distribution of free sulfur, hydrogen sulfide, mercaptans, disulfides, two types of sulfides having different activities, and residual (less-reactive) sulfur compounds for naphthas prepared from 17 typical high-sulfur crude oils of the United States and of the Middle East. These naphthas are straight-run distillates produced in the laboratory by distillation, either at atmospheric pressure or very low pressures (0.5-2.0 mm. of Hg), so that comparative data were obtained showing the effect of heating to the temperatures attained in the ordinary distillation of naphtha. The naphthas cover a boiling range from the initial boiling point up to an end point, at atmospheric pressure, of approximately 482° F (250° C.). Some of the relationships between the types of compounds present, such as sulfides and mercaptans and sulfides and "residual sulfur", were determined. One of the most interesting changes observed was the almost universal decrease in the content of the less-reactive sulfur group, called "residual sulfur", in the naphthas produced at atmospheric pressure compared to those obtained at reduced pressure. In general, this reduction of residual sulfur shows up as sulfide sulfur in the distillate made at atmospheric pressure. Further valid conclusions concerning some of the results shown by the data must await development of better analytical methods than are currently available and also further study of similar data obtained under other conditions.

#### Thermal Stability of Sulfur Compounds in Distillates and Crude Oils

To determine the temperature stability of sulfur compounds occurring naturally in crude petroleum, various crude oils were subjected to prolonged heating at each of several successively higher temperature levels, and the hydrogen sulfide and mercaptans evolved at each temperature level were measured. Hydrogen sulfide and mercaptans probably predominate among the final decomposition products from the thermal cracking of the original sulfur compounds and should therefore be a measure of the extent or ease of decomposition. In the survey of the 17 crude oils mentioned above, two crude oils yielded distillates that contained elemental sulfur. Further experiments proved that, under the low-temperature distillation conditions employed, if free or elemental sulfur is present in a crude oil, it will also occur in the distillate from that oil. Further, at high temperatures evidence indicates that the reaction between elemental sulfur and the hydrocarbons can contribute a large part of the hydrogen sulfide appearing at the temperature levels in the vicinity of 300°-400° F.

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<sup>16/</sup> Hale, J. H., Thompson, D. J., Barker, M. G., Smith, H. M., and Ball, J. S., Distribution and Type of Sulfur Compounds in Straight-Run Naphthas: Presented before Division of Petroleum Chemistry, American Chemical Society, Houston, Tex., Mar. 29, 1950.

One of the oils subjected to the thermal-stability tests was the Goldsmith, Tex., crude oil. This oil apparently contains a considerable proportion - 15 percent or more - of its total sulfur as elemental sulfur. It was anticipated, therefore, that in the stability test a large evolution of  $H_2S$  would be obtained on the temperature plateaus above  $220^\circ F.$ , and this was found. On elevating the bottom temperature to  $440^\circ F.$ , an extraordinary production of  $H_2S$  was encountered, and 43 percent of the total sulfur in the crude oil was accounted for as  $H_2S$  on this plateau. It is thought that the entire elemental sulfur content of the crude oil was converted to  $H_2S$  at this point by reaction with hydrocarbons, although other decomposition reactions probably contributed to the  $H_2S$  evolved.

#### Thermal Decomposition Studies of Pure Sulfur Compounds

Thermal treatment is the most common operation in petroleum refining. Consequently, it is important to know the reactions that sulfur compounds undergo when they are heated. Such knowledge can be used in designing processes so that the sulfur is removed when it is in the form most amenable to treatment. Different types of pure sulfur compounds will be studied at various temperatures and times of exposure to trace the decomposition reactions which they undergo.

In the previous annual report,<sup>17/</sup> apparatus for conducting these thermal decomposition studies was described and its operation discussed. The first compound to be studied was 2-methyl-2-propanethiol (t-butyl mercaptan). Temperatures of  $300^\circ$ ,  $350^\circ$ ,  $400^\circ$ ,  $450^\circ$ , and  $500^\circ C.$ , with residence times of 10 to 120 seconds, resulted in decompositions ranging from 0 to 97 percent. The primary reaction is decomposition of the thiol into hydrogen sulfide and isobutane. Subsequent reactions give free sulfur and isobutane. Thermal decomposition studies on thiacyclopentane at  $500^\circ C.$  were completed. Exposure times were 30, 60, 90, and 120 seconds. Based on the thiacyclopentane recovered, the decompositions ranged from 15 percent at 30 seconds to 75 percent at 120 seconds. The formation of thiophene and/or aromatic sulfides is insignificant at exposure times of 90 seconds and less but becomes appreciable at 120 seconds.

Work was begun on the thermal stability of pure sulfur compounds at reflux temperatures. 2-Methyl-2-propanethiol, the first compound studied, was refluxed for a period of 240 hours. A purity measurement by the freezing point method before and after refluxing indicated no measurable decomposition. There was no evidence of volatile decomposition products in any of the traps or absorbers used in the set-up. The thermal stability at reflux temperatures of 2,3-dithiabutane also was investigated. Purity measurements by the freezing-point method indicated a slight decrease in purity. The compound turned very light yellow and evolved a trace of hydrogen sulfide and/or thiol during the 240-hour refluxing period.

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<sup>17/</sup> See footnote 2.