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DEPARTMENT OF THE INTERIOR
FRANKLIN K. LANE, Secretary

UNITED STATES GEOLOGICAL SURVEY
GEORGE OTIS SMITH, Director

Professional Paper 117

THE SUNSET-MIDWAY OIL FIELD CALIFORNIA

PART II. GEOCHEMICAL RELATIONS OF THE OIL, GAS, AND WATER

BY

G. SHERBURNE ROGERS

WASHINGTON
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PREFATORY NOTE.

The report on the Sunset-Midway field is published in two parts. Part I (Professional Paper 116), by R. W. Pack, describes the general geology of the Sunset-Midway region and the development and underground conditions in the productive field and discusses also the origin and migration of the oil. Part II (Professional Paper 117), by G. S. Rogers, contains analyses of the oil, gas, and oil-field waters and a discussion of their composition in relation to their geologic occurrence; some figures on the geothermal gradient; and a brief discussion of the invasion of oil sands by water.

The reader is referred to Part I for all general information regarding the field and for detailed acknowledgments to those who cooperated in the field work. In addition, however, the author of Part II desires to express his especial appreciation of the generosity of Dr. E. A. Starke, who freely discussed the problems of the chemistry of oil-field waters and who contributed some of the analyses used in this report.

THE SUNSET-MIDWAY OIL FIELD, CALIFORNIA.

PART II. GEOCHEMICAL RELATIONS OF THE OIL, GAS, AND WATER.

By G. SHERBURNE ROGERS.

CHEMICAL AND PHYSICAL PROPERTIES OF THE OIL AND GAS.

INTRODUCTION.

California petroleum differs in many important respects from the varieties produced in other parts of the United States, and a considerable amount of chemical study has been devoted to it. The most refined and detailed studies have been made of oils from the coastal fields of California, but a large number of analyses or tests of the oil and gas from the Sunset-Midway field have also been made from time to time by different chemists. Although many of these analyses have already been published, it has appeared advisable to collect the best of them and reprint them here in order that the properties of the hydrocarbons may be studied in relation to their geologic occurrence. Despite the fact that the ordinary analysis of an oil is designed primarily for the use of the refiner and represents but poorly the geochemical character of the oil, it nevertheless gains in interest and significance when considered in relation to geologic conditions.

In the following pages a number of selected analyses or tests of the oil and gas from this field are given, with such descriptions of the analytical methods used as are necessary to an understanding of the results. These are followed by a discussion of the character of the oil and gas in relation to their geologic occurrence, and of the probable changes that they have undergone in the course of their migration.

CHEMICAL AND PHYSICAL PROPERTIES OF THE OIL.

METHODS OF ANALYSIS.

Petroleum consists of an extremely complex mixture of many bodies or compounds composed chiefly of carbon and hydrogen. Some of these hydrocarbon compounds may also contain smaller quantities of oxygen, nitrogen, or sulphur, which have an important bearing on the properties of the oil.

The simple hydrocarbon compounds may be separated according to the proportion of their hydrogen to their carbon atoms into several well-recognized series, each of whose members thus has a general type formula. The so-called paraffin series, for example, comprises hydrocarbons having the following specific formulas: CH_4, C_2H_6, C_3H_8, $C_{20}H_{42}$, etc. All these compounds contain two more than twice as many hydrogen atoms as carbon atoms, and the general formula for the series is therefore C_nH_{2n+2}. Similarly the naphthene or polymethylene series (C_nH_{2n}), the acetylene series (C_nH_{2n-2}), the terpene series (C_nH_{2n-4}), and the benzene series, or aromatic hydrocarbons (C_nH_{2n-6}) may be distinguished and certain members of still other series have been identified in some oils. The members of each hydrocarbon series, though having the same type formula, differ from one another in specific composition and in physical properties, such as boiling point, specific gravity, and index of refraction. Thus the first four members of the paraffin series, CH_4 to C_4H_{10}, are gases at ordinary temperatures; the next group, comprising more than a dozen, are liquids; and the most complex members of the series are solids. In addition, the same specific formula may represent two distinct compounds or isomers, differing slightly in physical properties. Finally there are the oxygen, nitrogen, and sulphur derivatives of the hydrocarbon compounds.

Any given crude oil may be a mixture of scores of hydrocarbon compounds of several different series and of their oxygen, nitrogen, and sulphur derivatives. As all these compounds differ slightly from one another in their boiling points and in their behavior toward chemical reagents, it is possible, by extremely careful work, to separate many of them out. The preliminary separation is accomplished by taking advantage of the difference in boiling points; for example, the liquid that distills from an oil between 160° and 162° C. will probably consist largely of one hydrocarbon, and after repeated distillation and purification by reagents the compound may be obtained in a practically pure condition. This method, however, can be applied only to the compounds that boil below a certain temperature. When the heat is raised above this point the heavy fractions remaining in the flask begin to "crack" or to break down. The exact chemical constitution of very heavy tar or asphalt can therefore only be inferred. Furthermore, as an analysis of the oil by these methods is an extremely long and tedious process, requiring many months, it will readily be seen that its application to a large number of samples is impracticable.

A much shorter method of determining in a general way the composition of an oil is the ultimate or elemental analysis—that is, the determination of the proportions of carbon and hydrogen and usually of the nitrogen, oxygen, and sulphur. If the oil consisted of a single hydrocarbon such an analysis would identify it precisely, but as all crude oils are mixtures the ultimate analysis simply indicates the general type or average of the hydrocarbons present. Such an analysis has no direct value for commercial purposes, but it sums up conveniently the broader differences between oils from different regions.

The third and by far the most common type of analysis is based on the fractional distillation of the oil. Certain arbitrary temperature points are selected, and the volume of liquid distilling over between each successive pair of these points is recorded. These figures correspond roughly with the proportions of gasoline, lamp oil, etc., that the crude oil will yield in refining and are therefore a rough index of the market value of the oil. An analysis of this type also constitutes a kind of epitome of the analysis by detailed fractionation; in other words, the gasoline fraction consists of several hydrocarbons belonging to one or more series, the kerosene fraction consists chiefly of several different hydrocarbons, and so on. If the oil has been first carefully studied and its general constitution determined, some idea of the character of the hydrocarbons in each fraction can therefore be gained. On the other hand, such analyses, which are stated chiefly in arbitrary or conventional terms, are open to many criticisms. Slight differences in the character of the retort used or in details of technique may cause a very appreciable difference in results, and unless the methods used by the chemist are known the analyses have little comparative value.[1] Although made primarily for commercial purposes they indicate only approximately the refining value of the oil, partly because they test only small quantities and partly because they do not show definitely the stability of the hydrocarbons, which depends chiefly on the series to which they belong and which has become especially important since the introduction of the various cracking processes. Nevertheless, such analyses, especially if made in the same laboratory, furnish a valuable and convenient means of comparing at least the relative character of different varieties of petroleum.

CONSTITUTION OF CALIFORNIA PETROLEUM.

Although the presence of petroleum in California was known more than 50 years ago, few attempts were made to study the oil chemically until production on a commercial scale was begun in Los Angeles County, in the early nineties. The marked differences in gravity, flash point, color, etc., between California petroleum and the Appalachian oil exploited at that time were early recognized, however, and when chemical study was made possible by commercial production steps were taken to ascertain the chemical basis for those differences. It was found, in brief, that whereas Pennsylvania petroleum is made up chiefly of hydrocarbons of the paraffin series, the California petroleum is practically lacking in paraffins and is composed of hydrocarbons belonging to series lower in hydrogen, principally the naphthenes, terpenes, and aromatic compounds.

As far back as 1894 S. F. Peckham published a general description of California oil and called attention especially to the nitrogen bases that it contains. In 1896 Frederick Salathé gave the preliminary results of his

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[1] Rittman, W. F., and Dean, E. W., The analytical distillation of petroleum: Bur. Mines Bull. 125, p. 8, 1916.

studies, stating that he had identified members of the paraffin, terpene, and aromatic series, as well as nitrogen bases of the pyridine and chinoline series. In 1897 C. F. Mabery began a detailed study of California petroleum, which was not completed until 1904. Clifford Richardson, in 1906, published the results of his studies and reviewed the previous work. Ultimate analyses, determinations of nitrogen and sulphur content, etc., have been contributed also by O'Neill, Prutzman, Allen and Jacobs, and others, but Mabery's work remains the most complete and valuable study of the chemical constitution of California oil. The most important discussions of the character and chemical constitution of California oil are the following:

Allen, I. C., and Jacobs, W. A., Physical and chemical properties of the petroleums of the San Joaquin Valley, Calif.: Bur. Mines Bull. 19, 1911. Gives result of fractional distillations of many samples and ultimate analyses of five composite samples.

Allen, I. C., Jacobs, W. A., Crossfield, A. S., and Matthews, R. R., Physical and chemical properties of the petroleums of California: Bur. Mines Tech. Paper 74, 1914. Deals with fractional distillation and determination of commercial values of several hundred samples of oil from various California fields.

Lengfeld, F., and O'Neill, E., A study of California petroleum: Am. Chem. Jour., vol. 15, p. 19, 1893. Preliminary note on the general character of California oils.

Mabery, C. F., Preliminary paper on the composition of California petroleum: Am. Chem. Jour., vol. 19, p. 796, 1898. Describes detailed fractionation of oil from Ventura County.

Mabery, C. F., and Hudson, E. J., On the composition of California petroleum: Am. Acad. Arts and Sci. Proc., vol. 36, p. 255, 1900. Describes the separation and identification of many hydrocarbons in samples of oil from Coalinga. This paper is also published in the Am. Chem. Jour., vol. 25, p. 253, 1901.

Mabery, C. F., and Hudson, E. J., Nitrogen compounds in California petroleum: Soc. Chem. Industry Jour., vol. 19, p. 504, 1900. Discusses the character of nitrogen compounds in California oil and describes the separation and identification of a series of basic compounds, probably hydrochinolines.

Mabery, C. F., Hydrocarbons in Santa Barbara crude oil: Am. Acad. Arts and Sci. Proc., vol. 40, p. 340, 1904. Describes the separation and identification of seven hydrocarbons in sample of oil from the Summerland field.

Mabery, C. F., The composition of American petroleum: Am. Chem. Soc. Jour., vol. 28, p. 415, 1906. Sums up the composition of California petroleum and compares it to the oil from other fields.

O'Neill, Edmond, Petroleum in California: Am. Chem. Soc. Jour., vol. 25, p. 699, 1903. Gives a brief description of California oil, including fractional-distillation tests, determination of sulphur and nitrogen content, and ultimate analyses.

Peckham, S. F., Notes on the origin of bitumens: Am. Philos. Soc. Proc., vol. 10, p. 445, 1868. Describes California oil, contrasts it with Pennsylvania oil, and discusses the chemical basis for the differences between the two.

Peckham, S. F., On the nitrogen content of California bitumen: Am. Jour. Sci., 3d ser., vol. 48, pp. 250, 389, 1894. Discusses the general character of California petroleum with special reference to the nitrogen and sulphur compounds.

Prutzman, Paul, Production and use of petroleum in California: California State Min. Bur. Bull. 32, p. 220, 1904. Discusses the chemical character of California oil, gives a few ultimate analyses, and many fractional-distillation tests.

Prutzman, Paul, Petroleum in southern California: California State Min. Bur. Bull. 63, 1913. Contains a great many commercial analyses of southern California oils.

Richardson, Clifford, Petroleum from the Olinda field, Cal.: Soc. Chem. Industry Jour., vol. 19, p. 123. A short note on the fractionation of Olinda oil.

Richardson, Clifford, Petroleums of North America: Franklin Inst. Jour., vol. 162, pp. 57, 81, 1906. Gives the results of many tests of the chemical character of California petroleum and reviews most of the earlier work. Compares the character of California oil with that of the petroleum from other fields.

Salathé, Frederick, Résumé of original researches, analyses, and refining methods of petroleum, mainly from the southern counties of California: California State Mineralogist Thirteenth Ann. Rept., pp. 656-661, 1896. A short preliminary discussion of the chemical character of California oil, with special reference to the nitrogen compounds.

Mabery studied samples of oil from a number of the southern California oil fields and also a sample from the Coalinga field. The southern California oils examined comprise varieties which closely resemble those produced in the Sunset-Midway field and which are probably very similar chemically. The Coalinga sample presumably represents Cretaceous oil, which differs from the ordinary Tertiary oil of California in being somewhat lighter in gravity and in containing some paraffin. A list of the hydrocarbons identified by Mabery in these oils, compiled from his articles already cited, is presented in the accompanying table. In interpreting these data it must be remembered that the hydrocarbons identified do not by any means include all the compounds present in the oil but only the simple hydrocarbons having boiling points below the temperature at which cracking begins. The nitrogen and oxygen compounds were eliminated by treatment with reagents and were not considered.

TABLE 1.—*Hydrocarbons in California petroleum.*

[C. F. Mabery and E. J. Hudson, analysts.]

Sample.	Fraction boiling at—	Hydrocarbon.	Formula.	Boiling point.	Specific gravity.	Index of refraction.	Series.
	°C.			°C.			
Well of Coalinga Oil Co., Oil City district, Coalinga field. Specific gravity 0.8423, or 36° B.	68–70	Mixture of hexane and hexamethylene.	C_6H_{14} and C_6H_{12}.				Paraffin (C_nH_{2n+2}) and naphthene (C_nH_{2n}).
	79–81	35.5 per cent benzol	C_6H_6				Benzene (C_nH_{2n-6}).
	96–98	Heptamethylene	C_7H_{14}	96–98	0.7413		Naphthene (C_nH_{2n}).
	109–110	54 per cent toluol	C_7H_8				Benzene (C_nH_{2n-6}).
	118–120	Octonaphthene	C_8H_{16}	118–120	.7532		Naphthene (C_nH_{2n}).
	134–135	Nononaphthene	C_9H_{18}	134–135	.7591		Do.
	137–140	60 per cent meta-xylol.	C_8H_{10}				Benzene (C_nH_{2n-6}).
	150			150	.8117		Naphthene (C_nH_{2n}).
	160–161	Dekanaphthene	$C_{10}H_{20}$	160–161	.7841		Do.
	169–170				.7749		Benzene (C_nH_{2n-6}).
	181–191	Undekanaphthene	$C_{11}H_{22}$	195	.8044		Naphthene (C_nH_{2n}).
	208–210	Dodekanaphthene	$C_{12}H_{24}$	216			Do.
Well of Puente Oil Co., Puente Hills field, Los Angeles County. Specific gravity 0.892, or 26.9° B.	96–98	Heptamethylene	C_7H_{14}	96–98	.7440		Do.
	118–120	Octonaphthene	C_8H_{16}	118–120	.7540		Do.
	160–162	Dekanaphthene	$C_{10}H_{20}$	160–162	.7745		Do.
	168–172	Chiefly a benzol homologue.					Benzene (C_nH_{2n-6}).
	190–200	Undekanaphthene	$C_{11}H_{22}$	195	.8046		Naphthene (C_nH_{2n}).
Owens No. 2 well of Union Oil Co., Bardsdale district, Ventura County. Specific gravity 0.8923, or 26.8° B.	96–100	Heptamethylene	C_7H_{14}	96–100	.7420		Do.
	116–120	Octonaphthene	C_8H_{16}	116–120	.7566		Do.
	160–162	Dekanaphthene	$C_{10}H_{20}$	160–162	.7905		Do.
	190–194	Undekanaphthene	$C_{11}H_{22}$	190–194	.8046		Do.
Well at Scotts Hill, Sespe district, Ventura County. Specific gravity 0.8782, or 29.4° B.	66–70	Hexamethylene and hexane.	C_6H_{12} and C_6H_{14}.				Naphthene (C_nH_{2n}) and paraffin (C_nH_{2n+2}).
	96–98	Heptamethylene	C_7H_{14}	96–98	.7436		Naphthene (C_nH_{2n}).
	118–120	Octonaphthene	C_8H_{16}	118–120	.7569		Do.
	158–160	Dekanaphthene	$C_{10}H_{20}$	158–160	.7751		Do.
	194–196	Undekanaphthene	$C_{11}H_{22}$	195	.8022		Do.
	230–232	Tridekanaphthene	$C_{13}H_{26}$	230–232	.8134	1.4745	Do.
	244–246	Tetradekanaphthene	$C_{14}H_{28}$	244–246	.8154	1.4423	Do.
	260–262	Pentadekanaphthene	$C_{15}H_{30}$	260–262	.8171		Do.
Well at Summerland, Santa Barbara County. Depth of well 245 feet. Specific gravity of oil 0.9845, or 12.2° B.	[a]150–155	Hydrocarbon	$C_{13}H_{24}$	[a]150–155	.8621	1.4681	C_nH_{2n-2}.
	[a]175–180	do	$C_{10}H_{30}$	[a]175–180	.8808	1.470	Do.
	[a]190–195	do	$C_{17}H_{30}$	[a]190–195	.8919	1.4778	Terpene (C_nH_{2n-4}).
	[a]210–215	do	$C_{18}H_{32}$	[a]210–215	.8996	1.484	Do.
	[a]250–255	do	$C_{24}H_{44}$	[a]250–255	.9299		Do.
	[a]310–315	do	$C_{27}H_{46}$	[a]310–315	.9451	1.5146	C_nH_{2n-8}.
	[a]340–345	do	$C_{29}H_{50}$	[a]340–345	.9778		Do.

[a] At 60 millimeters mercury pressure.

The table shows that the paraffin hydrocarbons, which are the main constituents of the Appalachian and Mid-Continent oils, are practically lacking in the California petroleum. The only paraffin compound identified was hexane, which forms a portion of the fractions boiling between 66° and 70° C. It is probable, however, that hexane and still lighter paraffins form a larger proportion of the small fractions boiling below 66°. The fractions boiling above 70° seem to consist entirely of members of the naphthene or polymethylene series and of the benzene series or aromatic hydrocarbons, both of which are important constituents of the Russian petroleum. The very heavy Summerland oil, however, contains no naphthenes except perhaps in its lightest fractions; the portions examined consist of members of unsaturated series still lower in hydrogen. The presence of members of the series C_nH_{2n-8} is noteworthy, for these very heavy and unstable hydrocarbons have been found only in certain foreign petroleums.

The broader differences between California petroleum and that from the Appalachian fields are well summarized in the following table, which shows the ultimate composition of a series of oils ranging in gravity between 12° and 42° B. The first five analyses represent composite samples of oil from the main fields of San Joaquin Valley and indicate that the composition of the average oil from those fields varies but slightly. The next four analyses represent samples from several of the southern California fields. In a broad sense all these analyses indicate that California oil is fairly uniform in composition, and no sample differs markedly from the average of the nine. Analysis 10, which represents oil from the famous Lucas gusher of the Spindletop field, Tex., shows somewhat more hydrogen and a higher percentage of sulphur, though in general similar to the average of the California samples. Analyses 11 to 13 represent the lighter and higher-grade oils of the Mid-Continent and Appalachian fields. They differ from the California oils in their higher hydrogen content, which is due to the fact that their hydrocarbons belong chiefly to the paraffin series. The eastern oils are also lower in nitrogen and sulphur than the California petroleum. It is noteworthy, however, that despite the progressive increase in hydrogen, the percentage of carbon is practically constant. With increase in hydrogen there is supposed to be a tendency toward decrease in heating value, but variation in this property is apparently very small. The relation of these eastern oils to the Californian oil is shown graphically in figure 1, which is based on the decrease in gravity that accompanies increase in hydrogen.

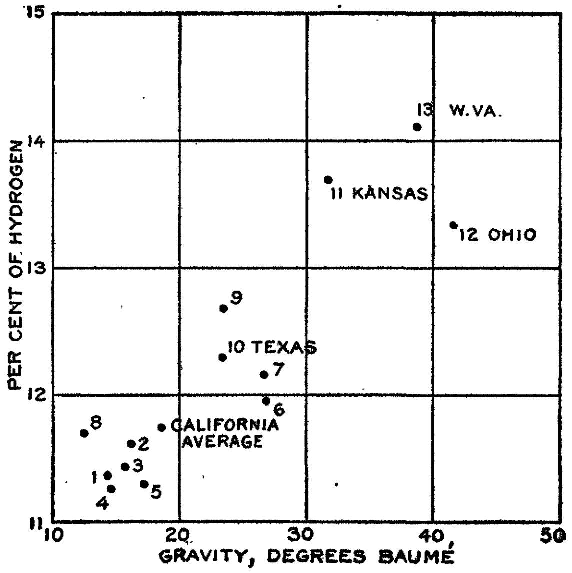

FIGURE 1.—Diagram showing relation of gravity to percentage of hydrogen in California and other varieties of petroleum.

TABLE 2.—*Ultimate analyses of petroleum from California and other fields.*

Field.	Specific gravity.	Gravity (°B.).	Carbon.	Hydrogen.	Nitrogen.	Sulphur.	Oxygen.	Heating value, per gram.
California fields:								*Calories.*
1. Sunset, Kern County (composite sample)	0.9705	14.3	85.64	11.37	0.84	1.06	[a]1.09	10,233
2. Midway, Kern County (composite sample)	.9580	16.1	86.58	11.61	.74	.82	[a].25	10,314
3. McKittrick, Kern County (composite sample)	.9600	15.8	86.51	11.41	.58	.74	[a].76	10,186
4. Kern River, Kern County (composite sample)	.9670	14.8	86.36	11.27	.74	.89	[a].74	10,312
5. Coalinga, Fresno County (composite sample)	.9505	17.3	86.37	11.30	1.14	.60	[a].59	10,400
6. Puente Hills, Los Angeles County	.8920	26.9	84.96	11.96	1.20	.80	......	......
7. Bardsdale, Ventura County	.8923	26.8	84.17	12.15	1.25	1.50	......	......
8. Summerland, Santa Barbara County	.9845	12.2	86.32	11.70	1.25	.84	......	......
9. Ventura County (composite sample)	.9120	23.5	84.00	12.70	1.70	.40	1.20	......
Average	.9430	18.5	85.66	11.72	1.05	.85	......	10,289
Other fields:								
10. Spindletop, Tex	.9130	23.3	85.03	12.30	[b].92	1.75	......	10,874
11. Cherryvale, Kans	.8650	31.8	85.43	13.07	......	.27	......	......
12. Findlay, Hancock County, Ohio	.8149	41.8	84.35	13.36	.13	.68	......	......
13. Burning Springs, W. Va	.8302	38.6	84.30	14.10	......	......	[c]1.60	10,223

[a] Undetermined; probably chiefly oxygen. [b] Includes oxygen. [c] Probably includes nitrogen and sulphur.

1–5. Allen, I. C., and Jacobs, W. S., Physical and chemical properties of the petroleums of the San Joaquin Valley, Calif.: Bur. Mines Bull. 19, p. 28, 1911.

6–7. Mabery, C. F., and Hudson, E. J., On the composition of California petroleum: Am. Acad. Arts and Sci. Proc., vol. 36, p. 255, 1900.

8. Mabery, C. F., Hydrocarbons in Santa Barbara crude oil: Am. Acad. Arts and Sci. Proc., vol. 40, p. 340, 1904.

9. Salathé, Fred, State Mineralogist California Thirteenth Rept., p. 656, 1896.

10. Richardson, Clifford, The petroleums of North America: Franklin Inst. Jour., vol. 162, p. 113, 1906. Calorific value determined on another sample of oil from same well: Redwood, Boverton, Petroleum and its products, vol. 1, p. 208, 1906.

11. Bartow, Edward, and McCollum, E. V., Kansas petroleum: Kansas Acad. Sci. Trans., vol. 19, p. 58, 1903.

12. Mabery, C. F., On the composition of the Ohio and Canadian sulphur petroleums: Am. Chem. Jour., vol. 17, p. 727, 1895.

13. Ste. Claire-Deville, H., Sur les propriétés physiques et le pouvoir calorifique des pétroles et des huile minérales: Compt. Rend., vol. 66, p. 442, 1868; vol. 68, pp. 349, 485, 686, 1869.

The nature of the oxygen, sulphur, and nitrogen compounds in California oils has never been fully studied, though their presence was recognized by the earliest investigators. Probably the commonest oxygen compounds are the phenols and the naphthenic acids. The latter are formed by the oxidation of the naphthene hydrocarbons and have the general formula $C_nH_{2n-2}O_2$. They have been recognized by W. E. Perdew in waters associated with the oil in the Sunset-Midway and Coalinga fields. They are probably potent agents in the emulsification of the oil that is so troublesome in some localities in the California fields; and they are important also because their presence in water may be regarded as an indication that the water has been closely associated with oil.

California petroleum contains in general a fairly high proportion of sulphur, though the nature of its compounds has apparently never been investigated. Salathé[1] states that the sulphur is contained chiefly in the heaviest fractions and that most of it is transferred to the middle fractions during distillation in the form of sulphur addition products. The sulphur in California oils is easily removed in refining and is not an especially deleterious constituent as it is in some of the eastern oils. The sulphur content of oils from the Sunset-Midway field appears to be closely related to their gravity, the heaviest oils containing the most sulphur. (See p. 13 and fig. 3.)

California petroleum is especially noteworthy for its high nitrogen content; Mabery[2] states that some specimens examined by him contain 20 or 25 per cent of nitrogen compounds. These compounds are not difficult to remove in refining but, being valueless in themselves, reduce the value of the crude oil accordingly. The nitrogen bases have been investigated to some extent by Peckham, Salathé, and Mabery. Salathé states that he isolated pyridin and chinoline, but Mabery regards the nitrogen compounds as probably hydrochinolines and states that they have a high specific gravity and a pungent odor resembling that of nicotine. The following series of nitrogen bases have been identified by Mabery:[3]

	Boiling point (°C.).
$C_{12}H_{17}N$	130–140
$C_{13}H_{18}N$	197–199
$C_{14}H_{19}N$	215–217
$C_{15}H_{19}N$	223–225
$C_{16}H_{19}N$	243–245
$C_{17}H_{21}N$	270–275

Although the details of the particular hydrocarbons identified in an oil are perhaps of little interest except to specialists, the broad conclusions for which such work forms the basis are of interest both to the oil operator and to the geologist. The most striking physical properties of California oil are its high gravity and its high viscosity; its most important characteristics from the refiner's standpoint are the comparatively small proportions of distillate obtained below 250° C. and the instability of the crude oil when subjected to higher temperatures. These characteristics are explained by the fact that the oil is composed so largely of naphthene hydrocarbons and of series still poorer in hydrogen. The early attempts to refine California oil by methods which had proved successful in Pennsylvania were failures, and for a long time the oil was used chiefly as fuel. Owing to the comparatively small proportions of light paraffins or of light hydrocarbons of other series it contains, the gasoline yield was very low, and owing to the high proportions of naphthenes and of aromatic hydrocarbons the kerosene was rather unstable and burned with a smoky yellow flame. Finally, the unstable character of all the heavier hydrocarbons rendered them liable to decompose when distilled in the presence of air at high temperatures. These difficulties, which were thus directly due to the peculiar chemical character of the oil itself, were later in large measure overcome by controlling the temperature and pressure under which the distillation is conducted and by the increased use of reagents in purifying the distillates obtained. It is interesting to note, however, that even now the gasoline produced from California oil averages about 5° Baumé heavier than gasoline of similar volatility and

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[1] Salathé, Frederick, op. cit., p. 658.

[2] Mabery, C. F., The composition of American petroleum: Am. Chem. Soc. Jour., vol. 28, p. 415, 1906.

[3] Mabery, C. F., On the nitrogen bases in California petroleum: Soc. Chem. Industry Jour., vol. 19, p. 505, 1900.

working efficiency derived from Appalachian oils. More recently it has been found that the conditions under which decomposition of the heavier hydrocarbons takes place may be controlled by regulating the temperature and pressure so that gasoline or light distillate is obtained as a decomposition product. Several processes for "cracking" or decomposing the heavier hydrocarbon molecules into lighter and more valuable ones have been commercially introduced and offer promise of greatly increasing the yield of motor fuel from California oil.

The chemical composition of the oil is a matter of interest to the geologist also, for it furnishes important evidence as to the origin and history of the oil. For example, the nitrogen present in such noteworthy proportions in California oil is regarded as very strong evidence of the derivation of the oil from organic remains, which is completely in accord with the geologic evidence on the origin of the oil. (See Prof. Paper 116.) The fact that California petroleum consists chiefly of naphthenes, terpenes, aromatic hydrocarbons, and other series poor in hydrogen indicates its relationship with the oils of southern Texas and Louisiana, of Mexico, of Russia, etc., rather than with the light paraffin oils of the Appalachian and Mid-Continent fields. This relationship is corroborated by the geologic evidence, for the California and similar oils are chiefly of Tertiary age, whereas the Appalachian and Mid-Continent oils are of Paleozoic age. David White[1] has recently suggested that the ultimate criterion is not strictly the age but rather the degree of regional metamorphism to which the containing rocks have been subjected. He has shown that the light paraffin oils occur only in regions in which the coal has reached the bituminous stage of alteration, whereas the heavy asphaltic oils are found where the coal is still in the stage of lignite. His compilations indicate a remarkably close sympathy, regionally considered, between the composition and character of the organic detrital residues or coal and the gravity of the oil. Another factor that probably has an influence on the character of oil is the composition of the organic remains from which it was derived, but concerning this little is yet known.

Although considerable progress has been made in correlating broadly the chemical composition of an oil with its geologic history, there is yet little definite information as to the reasons for the variation in the character of the oil from different parts of a single district. White's work throws light on the fundamental differences between California and Pennsylvania petroleum, but it does not explain why oil from the eastern part of the Sunset-Midway field has an average gravity of about 30° Baumé, whereas that from the western part is 10° or more heavier. As the constitution of these oils has never been studied, the true chemical basis for this difference is unknown, but light is shed on the subject by the many commercial analyses available, and the question will be considered in more detail in the following pages.

COMMERCIAL ANALYSES.

METHODS OF TESTING.

The commercial analyses and fractional distillations whose results are given in the large tables below (pp. 17–21) were made according to standardized methods by the Bureau of Mines, and a brief description of these methods is therefore given.[2]

Sampling.—The samples were collected at the wells by members of the Bureau of Mines. They were put in 1-gallon tin cans that were soldered tight and shipped at once to the laboratories where the analyses were made. The samples were taken, where possible, by allowing the oil to run from the outflow of the well directly into the sample can; where this method was impracticable a dipper was used.

Specific gravity.—The specific gravity was determined by means of the Westphal balance.

Flash point.—As most of the crude oils examined contained at least a trace of water, they showed a marked tendency to froth when heated and gave considerable difficulty with the closed Pensky-Martens flash tester, many of them frothing over at temperatures much below the flash point of the oil. For this reason, and to obtain comparative tests, it was considered advisable to determine the flash points of all the crude samples in an open Pensky-Martens cup carefully screened from air currents. On account of the frothing of the samples the temperature had to be increased slowly; a rise of 2° to 3° C. a minute was found to give

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[1] White, David, Some relations in origin between coal and petroleum: Washington Acad. Sci. Jour., vol. 5, pp. 189, 212, 1915.

[2] Abstracted from Bureau of Mines Tech. Paper 74, pp. 6–10, 1914.

good results. The gas test flame, of the size and form recommended for the Abel tester, was exposed for 1 second 1 centimeter above the surface of the oil at each rise of 1° C., beginning at 10° below the flash point as determined by a preliminary test.

Burning point.—After the flash point had been determined, the heating was continued without interruption, exactly as before, until the "flash" became permanent—that is, until the oil ignited and continued to burn quietly.

Viscosity.—The viscosity was determined in an Engler viscosimeter at 20° C.

Calorific value.—The calorific value was determined in a Berthelot combustion bomb of the Dinsmore-Atwater model. The British thermal units per pound were calculated by multiplying the calories per gram by 1.8.

Sulphur.—Sulphur was determined by carefully washing out with distilled water the contents of the bomb after the combustion, the sulphuric acid being precipitated with barium chloride in the usual manner and the percentage of sulphur calculated.

Water.—Water was most accurately and most conveniently determined during the course of an ordinary fractionation; it distilled over in those fractions having a boiling point between 100° and 150° C. under atmospheric pressure and could be removed readily from the receivers with a micropipette and weighed.

Fractionation.—The fractionation, or separation of each oil into its crude commercial components, was made in an electrically heated still and was conducted as follows: 200 grams of the sample of oil was weighed into a ½-liter flask. The flask was then connected to a Liebig condenser placed vertically, and the distillates were collected in weighed receiving tubes placed in a Bruehl receiver.

The oil was distilled under atmospheric pressure at increasing temperatures up to 325° C., the receivers being changed at each increment of 25°. The temperature was then allowed to drop to 125° C., to keep the oil from boiling over when the vacuum was used, and the distillation was again continued under a vacuum of 10 to 20 millimeters mercury pressure till the temperature within the flask reached 325° C. These cuts at each increment of 25° C. are termed collectively the "fractional distillation."

Refining.—The oils—motor fuels, lamp oils, and lubricants—were refined as follows: 250 grams of the oil was put in a 1-liter separatory funnel and shaken vigorously—that is, 120 to 150 shakes a minute for 15 minutes—in a shaking machine, four times with 10 cubic centimeters of concentrated sulphuric acid (or until the oil was not appreciably colored by this acid treatment), once with a 10 per cent solution of sodium carbonate to remove the free acids, and three or four times with water to remove the last traces of soda, etc. The oil was then dried with Glauber's salt and distilled. This refining acid treatment yielded a water-white, practically odorless product of excellent quality.

Because of their high viscosity, it is advisable to dilute the heavier fractions (those distilled under a vacuum at temperatures above 250° C.) with 1 part of chemically pure benzene before subjecting them to the acid treatment.

RESULTS OF TESTS.

The accompanying sets of tables show in detail the results of the examination of 64 samples of oil; the samples being grouped according to the geologic zone in which the oil occurs. Each table consists of two parts; the first part gives particulars regarding the source of the sample, the results of various commercial tests, and the percentage of refined products; the second part gives simply the results of the fractional distillation.

The analyses are taken, with certain modifications, from the tables published in Bureau of Mines Bulletin 19 and Technical Paper 74. Many of the lease names under which the samples were listed in those publications have since been changed, and the accompanying tables give the present names. In determining the geologic zone and the depth from which the oil came some uncertainty may be introduced by the fact that the well has been deepened or reperforated since the sample was taken, but the zone and the depth shown are believed to be correct for the sample actually analyzed, though they may not indicate the source of the oil produced by the well at the present time.

TABLE 3-A.—*Physical and chemical properties of oils from zone A.*

Serial No.	Lease.	Well No.	Location.	Portion of geologic zone.	Approximate depth of zone.	Date of sampling.	Specific gravity at 15° C.	Gravity on Baumé scale at 60° F.	Heating value.		Flash point (open cup).	Burning point (open cup).	Viscosity at 20° C. (Engler scale).	Sulphur.	Refined commercial products.			Refining losses.	Asphaltum (commercial).	Laboratory No of analysis.
									Calories per gram.	British thermal units per pound.					Motor fuel.	Lamp oils.	Lubricants.			
					Feet.			° *B.*			° *C.*	° *C.*		*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	
1	Chanslor-Canfield Midway Oil	1	Sec. 8, T. 32 S., R. 23 E	....	1,000	July 14, 1909	0.9625	15.5	10,297	18,535	96	110	256.8	1.32	......	13.0	41.4	6.7	37.9	472
2	Midland Oilfields	2	Sec. 16, T. 32 S., R. 23 E	....	1,000	....do	.9550	16.6	10,368	18,662	78	95	89.1	.75	......	14.7	43.3	7.0	34.5	471
3	North American Oil Consolidated	1	....do	Upper?	......	Oct. 21, 1907	.9880	11.7	9,939	17,890	122	138	7,903.3	1.14	......	4.2	38.5	5.6	49.7	102
4	Fairbanks	2	Sec. 22, T. 32 S., R. 23 E	....	800	July 14, 1909	.9695	14.4	10,311	18,560	106	123	474.2	.71	......	12.6	40.7	6.5	39.6	469
5	Indian & Colonial	2	....do	....	1,000	....do	.9700	14.3	10,041	18,074	115	140	821.5	.76	......	4.8	38.5	5.6	47.6	467
6	Elkhorn	1	Sec. 25, T. 32 S., R. 23 E	....	1,100	July 13, 1909	.9570	16.3	10,369	18,664	66	96	182.3	.87	1.5	16.0	38.6	6.6	36.7	456
7	Paraffine	1	....do	....	1,100	Oct. 21, 1907	.9645	15.2	10,322	18,580	99	116	341.1	.87	......	8.0	39.6	6.0	45.9	108
8	Princeton	1	....do	....	1,200	July 13, 1909	.9540	16.8	10,389	18,700	62	93	109.6	.84	.3	14.7	40.9	6.8	36.6	458
9	Section Twenty-five	2	....do	Lower	1,350	....do	.9665	14.8	10,299	18,538	95	115	444.4	.69	......	11.9	43.6	6.9	36.6	459
10	W. T. & M.	1	....do	Upper?	1,050	Oct. 21, 1907	.9260	21.2	10,455	18,819	20	35	12.1	.65	1.4	27.9	31.9	6.7	30.5	104
11	Mascot	2	Sec. 26, T. 32 S., R. 23 E	Lower?	650	....do	.9560	16.4	10,345	18,621	81	102	211.7	.88	......	13.7	41.2	6.7	37.9	105
12	....do	6	....do	Lower	1,250	July 14, 1909	.9685	14.6	10,321	18,578	95	115	511.0	.82	......	9.7	43.0	6.6	40.3	460
13	....do	8	....do	All	600	....do	.9630	15.4	10,377	18,679	85	103	210.3	.61	......	17.3	41.7	7.0	33.3	462
14	North American Oil Consolidated	5	....do	....	950	Oct. 19, 1910	.9654	15.0	10,317	18,571	91	127	220.4	.84	......	7.2	34.5	13.2	44.2	610
15	General Petroleum	1	....do	....	1,000	Oct. 16, 1910	.9690	14.5	10,340	18,612	114	142	440.1	.86	......	.0	38.1	13.9	47.5	579
16	Union	2	Sec. 33, T. 12 N., R. 24 W	Upper	550	July 13, 1909	.9660	14.9	10,321	18,578	60	88	313.7	1.11	......	11.3	39.9	6.3	42.0	453
17	Boston Pacific	2	Sec. 34, T. 12 N., R. 24 W	....	......	Oct. 22, 1907	.9770	13.3	10,269	18,484	107	134	1,488.2	1.14	......	7.5	40.0	6.0	45.4	110
18	Tannehill	8	....do	....	500	July 13, 1909	.9660	14.9	10,324	18,583	60	81	316.0	.76	......	12.6	36.9	6.0	43.9	452
19	Union (J. B. and B.)	3	Sec. 35, T. 12 N., R. 24 W	Lower	600	Oct. 21, 1907	.9705	14.3	10,271	18,488	101	126	....	1.07	......	5.1	40.6	5.9	48.1	111
20	Case M. and P.	2	Sec. 1, T. 11 N., R. 24 W	....	......	July 13, 1909	.9940	10.8	10,129	18,232	120	144	....	1.20	......	6.0	38.9	5.8	48.4	446
21	Adeline Consolidated	5	Sec. 2, T. 11 N., R. 24 W	....	600	Oct. 22, 1907	.9775	13.2	10,202	18,364	124	154	....	1.30	......	2.6	39.2	5.5	52.3	118
22	Ida May	2	....do	....	......	....do	.9665	14.8	10,326	18,587	98	126	....	1.05	......	5.1	40.2	5.9	48.4	116
23	Standard (Monarch)	4	....do	....	550	....do	.9660	14.9	10,265	18,477	111	134	....	1.11	......	5.4	41.4	6.1	47.8	113
	Average, 23 samples from zone A	......	....	....	......	....	.9660	14.9	10,286	19,690	93	114	796.9	.92	.1	10.0	39.6	6.6	42.3	......

TABLE 3-B.—*Fractional distillation of oils from zone A.*

Serial No.	Lease.	Well No.	Water.	Summary of distillation (unrefined products).				Distillation in detail.																		Distilling loss.
								At atmospheric pressure.									In vacuum.									
				Motor fuel (up to 175° C.).	Lamp oils (175°-300° C.).	Lubricants (300° at atmospheric pressure to 325° C. in vacuum).	Asphaltum (residue).	Pressure of mercury.	Up to 150° C.	150°-175° C.	175°-200° C.	200°-225° C.	225°-250° C.	250°-275° C.	275°-300° C.	300°-325° C.	Pressure of mercury.	150°-175° C.	175°-200° C.	200°-225° C.	225°-250° C.	250°-275° C.	275°-300° C.	300°-325° C.	Residue (asphaltum).	
			P. ct.	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*Mm.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*Mm.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*
1	Chanslor-Canfield Midway Oil	1	0.4	......	14.0	47.1	37.9	739	......	......	0.3	0.2	0.6	3.1	9.8	8.5	18	1.5	4.0	5.2	6.0	6.0	6.2	9.7	37.9	0.6
2	Midland Oilfields	2	Tr.	......	15.8	49.2	34.5	743	......	......	.7	1.0	2.5	4.5	7.1	9.4	18	.6	3.3	5.5	6.6	7.0	7.2	9.6	34.5	.5
3	North American Oil Consolidated	1	1.5	......	4.5	43.8	49.7	739	......	......	......	......	2.6	.4	1.5	8.1	18	......	2.9	4.2	6.2	7.4	5.0	10.0	49.7	.5
4	Fairbanks	2	Tr.	......	13.6	46.2	39.6	748	......	......	.1	.1	.7	4.2	8.5	9.3	18	......	3.0	4.4	6.3	6.3	7.0	9.9	39.6	.6
5	Indian & Colonial	2	2.8	......	5.2	43.7	47.6	746	......	......	......	......	1.1	.4	3.7	10.4	20	......	1.0	6.5	4.7	6.0	6.2	8.9	47.6	.7
6	Elkhorn	1	.1	1.6	17.2	43.9	36.7	741	0.8	0.8	1.0	1.1	2.1	5.9	7.1	7.1	18	.3	2.1	4.6	5.3	5.8	6.9	11.8	36.7	.5
7	Paraffine	1	Tr.	......	8.6	45.0	45.9	751	......	......	......	.1	.3	1.6	6.6	10.2	20	......	1.1	3.7	7.4	8.0	5.3	9.3	45.9	.5
8	Princeton	1	Tr.	.3	15.9	46.5	36.6	738	......	.3	.3	.7	2.2	5.0	7.7	8.7	18	.4	1.8	5.1	7.4	6.9	7.2	9.0	36.6	.7
9	Section Twenty-five	2	Tr.	......	12.8	49.6	36.6	741	......	......	......	......	1.7	4.0	7.1	10.4	18	.4	2.5	4.4	7.0	7.0	6.7	11.2	36.6	1.0
10	W. T. & M.	1	......	1.5	30.1	36.3	30.5	747	.2	1.3	3.2	6.5	7.4	4.5	8.5	5.0	14	.4	2.4	4.1	6.5	5.6	4.4	7.9	30.5	1.6
11	Mascot	2	......	......	14.8	46.8	37.9	736	......	......	.2	.4	2.4	5.7	6.1	10.2	13	.3	2.2	6.4	6.6	6.4	5.7	9.0	37.9	.5
12	.....do	6	Tr.	......	10.4	48.9	40.3	750	......	......	......	......	.8	4.8	4.8	9.8	18	1.1	3.8	6.7	6.5	6.0	6.6	8.4	40.3	.4
13	.....do	8	Tr.	......	18.6	47.4	33.3	756	......	......	......	1.0	3.5	6.4	7.7	9.3	18	.3	1.4	4.8	6.4	6.6	7.1	11.5	33.3	.7
14	North American Oil Consolidated	5	.4	......	7.7	47.2	44.2	745	......	......	......	......	.8	1.1	5.8	7.8	21	.4	3.6	4.9	6.1	6.0	7.4	11.0	44.2	.5
15	General Petroleum	1	.1	......	......	52.0	47.5	744	......	......	......	......	......	......	......	13.0	13	......	......	5.3	6.2	7.9	7.8	11.8	47.5	.4
16	Union	2	Tr.	......	12.2	45.3	42.0	742	......	......	1.1	1.5	2.7	3.0	3.9	7.8	18	......	3.2	4.2	5.3	7.0	7.8	10.0	42.0	.5
17	Boston Pacific	2	Tr.	......	8.1	45.4	45.4	739	......	......	.6	.3	.7	1.7	4.8	7.8	14	.7	1.6	7.0	5.8	6.5	7.7	8.3	45.4	1.1
18	Tannehill	8	Tr.	......	13.6	41.9	43.9	740	......	......	.8	.5	2.5	3.3	6.5	6.2	18	......	1.1	5.8	4.9	6.3	7.0	10.6	43.9	.6
19	Union (J. B. and B.)	3	Tr.	......	5.5	46.1	48.1	744	......	......	......	.1	.5	2.3	2.6	8.0	15	......	1.1	4.1	8.4	6.3	8.0	10.2	48.1	.3
20	Case M. and P	2	Tr.	......	6.5	44.2	48.4	735	......	......	......	......	.7	1.5	4.3	6.8	18	......	3.3	4.2	6.1	5.7	7.5	10.6	48.4	.9
21	Adeline Consolidated	5	Tr.	......	2.8	44.5	52.3	734	......	......	......	.3	.2	.5	1.8	5.9	18	.2	3.1	4.7	5.0	8.1	8.0	9.5	52.3	.4
22	Ida May	2	Tr.	......	5.5	45.7	48.4	743	......	......	......	......	.3	1.0	4.2	5.6	18	.5	.5	4.5	7.9	8.0	9.0	9.7	48.4	.4
23	Standard (Monarch)	4	Tr.	......	5.8	47.1	46.8	740	......	......	.2	.2	.5	1.3	3.6	10.0	17	......	1.2	3.1	7.5	6.3	7.8	11.2	46.8	.3
	Average, 23 samples from zone A	....	......	1.6	10.8	45.8	42.3	742	.04	.1	.3	.6	1.6	2.8	5.3	8.4	17	.3	2.1	4.9	6.3	6.6	6.9	9.9	42.3	.6

TABLE 4-A.—*Physical and chemical properties of oils from zone B.*

Serial No.	Lease.	Well No.	Location.	Portion of geologic zone.	Approximate depth of zone.	Date of sampling.	Specific gravity at 15° C.	Gravity on Baumé scale at 60° F.	Heating value.		Flash point (open cup).	Burning point (open cup).	Viscosity at 20° C. (Engler scale).	Sulphur.	Refined commercial products.			Refining losses.	Asphaltum (commercial).	Laboratory No. of analysis.
									Calories per gram.	British thermal units per pound.					Motor fuel.	Lamp oils.	Lubricants.			
					Feet.			°*B*.			° *C*.	° *C*.		*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	
24	General Petroleum	3	Sec. 14, T. 31 S., R. 22 E	Lower	1,000	Oct. 18, 1910	0.9740	13.74	10,152	18,274	120	156	884.6	1.06	0	0	34.3	13.8	46.8	591
25	do	1	Sec. 15, T. 31 S., R. 22 E	(*a*)	900	do	.9750	13.59	10,269	18,484	126	152	943.7	.97	0	0	32.8	12.9	52.8	584
26	Pinal Dome	1	Sec. 23, T. 31 S., R. 22 E		700	do	.9535	16.83	10,354	18,637	71	104	61.8	.72	0	6.7	35.7	13.6	43.6	588
27	El Camino	10	Sec. 26, T. 31 S., R. 22 E		1,400	do	.9940	10.85	9,569	17,224	135	187		1.57	0	0	23.2	11.0	59.8	587
28	American Oilfields	79	Sec. 36, T. 31 S., R. 22 E		750	do	.9220	21.84	10,481	18,866	17	42	7.1	.60	0	22.5	32.1	12.5	32.0	598
29	Honolulu	1	Sec. 31, T. 31 S., R. 23 E		1,850	do	.9160	22.84	10,554	18,997	34	56	7.5	.53	0	19.8	33.7	13.0	32.8	586
30	do	2	do		2,300	do	.9410	18.78	10,483	18,869	60	88	27.7	.67	0	12.7	35.3	13.7	37.9	590
31	United	2	Sec. 6, T. 32 S., R. 23 E	Lower	950	do	.9125	23.42	10,524	18,943	10	35	5.0	.58	0	25.1	30.3	12.3	31.9	594
32	do	5	do	do	1,200	do	.9440	18.31	10,444	18,799	55	76	34.4	.69	0	11.0	33.0	12.5	42.9	595
33	Babcock Petroleum	7	Sec. 23, T. 32 S., R. 23 E		1,250	Oct. 19, 1910	.9384	19.19	10,434	18,781	42	71	18.5	.65	.6	22.6	29.9	12.0	33.8	611
34	Griffith Crude	1	do	Upper	1,600	July 14, 1909	.9500	17.37	10,403	18,725	72	93	47.5	.84	0	20.2	38.5	6.9	33.9	466
35	Standard	1	Sec. 24, T. 32 S., R. 23 E	do	1,400	do	.9295	20.62	10,437	18,787	15	30	12.0	.59	2.7	24.5	36.4	7.1	28.3	464
36	do	5	do		1,750	do	.9180	22.51	10,467	18,841	15	24	7.5	.75	1.5	28.5	34.3	7.0	27.6	465
37	do	1	Sec. 20, T. 32 S., R. 24 E		3,000	Oct. 17, 1910	.9105	23.76	10,530	18,954	10	38	5.2	.54	.2	26.4	29.3	12.0	31.3	583
37a	do	9	do			May 11, 1918	.916	22.8						.51						00229
38	do	3	Sec. 30, T. 32 S., R. 24 E	Lower	2,150	do	.9275	20.94	10,453	18,815	29	54	13.6	.82	0	21.0	26.5	11.4	40.3	580
39	do	8	do	Upper	1,700	do	.9480	17.68	10,436	18,785	72	103	49.7	.61	0	9.3	34.1	12.9	42.9	582
40	American Oilfields	4	Sec. 32, T. 32 S., R. 24 E		1,350	July 13, 1909	.9550	16.60	10,357	18,643	49	65	109.7	.97	.7	16.7	36.4	6.4	39.0	454
41	Pacific Midway	1	Sec. 32, T. 12 N., R. 23 W		1,600	Oct. 16, 1910	.9349	19.75	10,406	18,731	24	58	17.8	.74	0	17.2	28.8	11.0	42.6	567
42	Lakeview (Union)	1	Sec. 25, T. 12 N., R. 24 W	Lower	1,950	Oct. 17, 1910	.9285	20.78	10,420	18,756	33	58	17.9	.85	0	17.5	28.8	11.6	41.4	577
43	Kern Trading Oil	1	Sec. 1, T. 11 N., R. 24 W	All	1,150	do	.9553	16.55	10,332	18,598	55	97	103.9	.94	0	10.3	27.5	11.0	49.3	571
44	do	25	do	Upper [a]	1,200	do	.9398	18.97	10,412	18,742	24	56	24.0	.68	.6	15.5	27.0	10.9	45.1	569
45	do	27	do		1,150	do	.9430	18.46	10,380	18,684	29	67	36.3	.89	.8	14.5	26.8	11.0	45.2	570
46	Standard	1	do	Upper [a]	1,000	do	.9613	15.64	10,319	18,574	66	105	173.7	.92	0	9.9	27.8	11.2	50.1	574
47	do	4	do		1,000	do	.9515	17.14	10,332	18,598	38	77	63.0	1.02	0	12.7	26.3	10.6	49.0	573
48	do	8	do	Upper [a]	1,100	do	.9453	18.10	10,372	18,670	28	70	41.6	.88	.5	13.9	27.6	11.3	45.5	572
49	do	12	do	do	1,100	July 13, 1909	.9451	18.13	10,375	18,675	31	70	42.6	.79	0	14.5	26.6	10.8	47.2	449
50	Ruby	8	Sec. 2, T. 11 N., R. 24 W		1,000	Oct. 17, 1910	.9644	15.17	10,281	18,506	75	115	261.9	.88	0	8.9	27.4	10.8	51.8	575
51	do	10	do		1,050	do	.9700	14.33	10,273	18,491	84	129	543.5	1.10	0	7.7	26.5	11.1	53.2	576
52	Good Roads	5	Sec. 12, T. 11 N., R. 24 W		1,050	July 13, 1909	1.0050	10.00			85	108			0	6.4	24.9	3.9	30.4	445
53	New Center	4	do		950	Oct. 22, 1907	.9760	13.44	10,247	18,445	109	122		1.18	0	6.8	37.2	5.6	49.8	120
54	Maricopa National	1	Sec. 6, T. 11. N., R. 23 W	Upper [a]	1,350	Oct. 16, 1910	.9211	21.99	10,444	18,799	9	40	7.5	.62	1.2	20.8	28.4	10.9	38.2	568
	Average, 32 samples from zone B						.9458	18.13	10,030	18,060	52	82	127.5	.78	0.2	14.6	30.5	10.7	41.8	

[a] May include oil from zone A.

TABLE 4-B.—*Fractional distillation of oils from zone B.*

Serial No.	Lease.	Well No.	Water.	Summary of distillation (unrefined products).				Distillation in detail.																		Distilling loss.
								At atmospheric pressure.									In vacuum.									
				Motor fuel (up to 175° C.).	Lamp oils (175°-300° C.).	Lubricants (300° at atmospheric pressure to 350° C. in vacuum).	Asphaltum (residue).	Pressure of mercury.	Up to 150° C.	150°-175° C.	175°-200° C.	200°-225° C.	225°-250° C.	250°-275° C.	275°-300° C.	300°-325° C.	Pressure of mercury.	150°-175° C.	175°-200° C.	200°-225° C.	225°-250° C.	250°-275° C.	275°-300° C.	300°-325° C.	Residue (asphaltum).	
			P. ct.	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*mm.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*mm.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*
24	General Petroleum	3	4.3	0	0	48.1	46.8	745	......	......	......	......	......	......	......	1.6	10	......	6.4	6.2	7.1	7.9	7.7	11.2	46.8	0.8
25	do	1	.3	0	0.6	45.7	52.8	744	......	......	......	......	......	0.3	0.3	5.5	13	......	2.9	4.9	6.5	7.9	7.7	10.3	52.8	.6
26	Pinal Dome	1	.1	0	7.2	48.8	43.6	743	......	......	......	......	......	.6	6.6	11.4	12	......	......	5.4	6.6	7.3	8.0	10.1	43.6	.3
27	El Camino	10	4.1	0	0	34.2	59.8	744	......	......	......	......	......	......	......	1.2	10	......	......	4.1	5.6	6.5	5.5	11.3	59.8	1.9
28	American Oilfields	79	Tr.	0	23.7	43.4	32.0	748	......	......	0.2	2.5	8.1	6.4	6.5	8.6	9	......	3.3	4.9	5.6	5.8	5.5	9.7	32.0	.9
29	Honolulu	1	Tr.	0	20.9	45.6	32.8	746	......	......	......	.3	6.0	7.1	7.5	9.8	9	......	2.7	4.9	6.0	6.4	6.5	9.3	32.8	.7
30	do	2	.1	0	13.5	48.2	37.9	746	......	......	......	......	......	3.3	10.2	9.8	9	......	2.1	5.4	6.2	6.9	7.2	10.6	37.9	.3
31	United	2	Tr.	0	26.4	41.3	31.9	745	......	......	0.3	5.2	6.9	6.6	7.4	8.0	9	......	2.7	4.2	5.3	5.9	6.3	8.9	31.9	.4
32	do	5	Tr.	0	11.7	44.8	42.9	748	......	......	......	......	2.1	3.9	5.7	7.3	20	......	4.6	4.9	5.2	6.3	7.0	9.5	42.9	.6
33	Babcock Petroleum	7	Tr.	0.7	23.6	40.8	33.8	741	0.1	0.6	2.6	4.6	5.4	5.5	5.5	7.7	19	......	2.9	4.1	5.1	5.0	5.1	10.9	33.8	1.1
34	Griffith Crude	1	......	0	21.8	43.8	33.9	740	......	......	.5	1.2	5.4	7.3	7.4	8.3	18	0.6	2.4	5.7	5.9	4.9	6.5	9.5	33.9	.5
35	Standard	1	......	2.9	26.4	41.4	28.3	750	.7	2.2	6.3	4.9	3.9	5.2	6.1	6.1	18	.4	1.4	5.4	7.2	4.1	5.0	11.8	28.3	1.0
36	do	5	......	1.6	30.7	39.0	27.6	754	.3	1.3	5.0	5.7	9.8	5.3	4.9	10.5	18	......	1.0	3.3	4.3	5.9	5.5	8.5	27.6	1.1
37	do	1	Tr.	.2	27.7	40.0	31.3	748	......	.2	1.0	5.9	7.3	6.9	6.6	7.0	10	.6	2.9	3.0	4.8	6.1	6.6	9.0	31.3	.8
37a	do	9	......	15.8	29.2	23.0	32.0	743	10.6	5.2	4.6	6.4	6.6	5.5	6.1	......	40	2.0	1.0	4.0	4.5	4.5	7.0	......	32.0	......
38	do	3	Tr.	0	22.0	36.9	40.3	745	......	......	.9	4.3	6.1	5.3	5.4	6.6	23	......	1.0	3.0	4.5	5.1	6.4	10.3	40.3	.8
39	do	8	.2	0	9.9	46.4	42.9	750	......	......	......	......	.1	1.5	8.3	10.6	14	......	1.1	4.1	5.9	9.0	6.3	9.4	42.9	.6
40	American Oilfields	4	.2	.7	18.1	41.4	39.0	748	......	.7	1.4	2.7	4.9	4.4	4.7	6.9	18	.2	1.9	6.6	5.3	4.6	6.3	9.6	39.0	.6
41	Pacific Midway	1	0	0	18.0	39.0	42.6	741	......	......	1.4	3.9	4.4	4.1	4.2	6.3	21	1.2	3.3	4.3	4.4	4.9	6.0	8.6	42.6	.4
42	Lakeview (Union)	1	.1	0	18.4	39.5	41.4	751	......	......	.3	.8	6.0	5.8	5.5	7.5	13	......	2.2	3.9	4.5	5.3	6.3	9.8	41.4	.6
43	Kern Trading & Oil	1	Tr.	0	10.9	37.9	49.3	748	......	......	......	.9	2.9	3.6	3.5	5.2	23	1.1	2.7	3.8	4.8	4.5	5.8	10.0	49.3	1.9
44	do	25	.2	.6	16.3	37.1	45.1	749	.2	.4	1.4	3.4	3.9	3.6	4.0	5.5	20	.8	2.8	3.7	4.3	4.6	5.9	9.5	45.1	.7
45	do	27	.4	.8	15.3	37.0	45.2	736	.2	.6	1.1	2.6	3.6	3.6	4.4	5.6	21	.3	2.2	3.5	4.7	5.9	5.5	9.3	45.2	1.3
46	Standard	1	.1	0	10.5	38.4	50.1	750	......	......	......	......	3.0	3.3	4.2	5.7	20	......	3.3	3.7	4.2	4.6	6.5	10.4	50.1	.9
47	do	4	.4	0	13.4	36.2	49.0	750	......	......	1.3	1.9	2.7	3.1	4.4	5.5	21	......	3.5	3.3	3.9	4.5	6.0	9.5	49.0	1.0
48	do	8	.1	.5	14.6	38.2	45.5	737	......	.5	1.5	2.6	3.4	3.5	3.6	5.4	21	......	3.4	3.6	4.2	4.8	6.2	10.6	45.5	1.1
49	do	12	Tr.	0	15.2	36.7	47.2	726	......	......	.8	2.9	3.5	3.8	4.2	5.3	21	.7	2.7	3.8	4.5	4.2	5.8	9.7	47.2	.9
50	Ruby	8	.4	0	9.4	37.7	51.8	734	......	......	......	......	2.2	2.7	4.5	6.2	21	......	3.0	3.2	4.7	5.2	5.8	9.6	51.8	.7
51	do	10	.6	0	8.1	37.2	53.2	748	......	......	......	......	2.1	2.0	4.0	5.4	21	......	1.8	4.0	4.2	3.9	6.8	11.1	53.2	9
52	Good Roads	5	33.0	0	6.9	28.3	30.4	754	......	......	4.6	.1	.2	.6	1.4	2.6	18	......	2.9	3.2	3.6	4.6	4.7	6.7	30.4	1.4
53	New Center	4	Tr.	0	7.3	42.3	49.8	745	......	......	......	.3	.5	1.8	4.7	7.0	18	......	.3	1.4	8.1	6.9	7.2	11.4	49.8	.6
54	Maricopa National	1	0	1.3	21.7	38.3	38.2	733	.1	1.2	3.1	4.3	4.5	4.6	5.2	6.7	20	1.1	3.4	3.9	4.4	4.9	5.7	8.2	38.2	.5
	Average, 32 samples from zone B	....	......	.8	15.6	40.0	41.5	744	.4	.4	1.2	2.1	3.6	3.8	4.9	6.4	17	.3	2.3	4.1	5.2	5.6	6.2	9.5	41.5	.8

TABLE 5-A.—*Physical and chemical properties of oil from zone C.*

Serial No.	Lease.	Well No.	Location.	Portion of geologic zone.	Approximate depth of zone.	Date of sampling.	Specific gravity at 15° C.	Gravity on Baumé scale at 60° F.	Heating value.		Flash point (open cup).	Burning point (open cup).	Viscosity at 20° C. (Engler scale).	Sulphur.	Refined commercial products.			Refining loss.	Asphaltum (commercial).	Laboratory No. of analysis.
									Calories per gram.	British thermal units per pound.					Motor fuel.	Lamp oils.	Lubricants.			
					Feet.			*° B.*			*° C.*	*° C.*		*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	
55	Midland Oilfields	1	Sec. 12, T. 31 S., R. 22 E	....	1,750	Oct. 18, 1910	0.9550	16.60	10,411	18,740	93	122	93.9	0.74	0	0	41.7	14.5	43.2	589
56	Rock	2	Sec. 23, T. 31 S., R. 22 E	Upper	2,000	Oct. 19, 1910	.9295	20.62	10,468	18,842	40	63	12.4	.61	0	17.8	33.4	13.3	34.7	602
57	Chanslor-Canfield Midway Oil	1	Sec. 25, T. 31 S., R. 22 E	....	2,450	Oct. 18, 1910	.9300	20.54	10,504	18,907	64	93	20.2	.62	0	13.3	35.3	14.1	36.8	593
58	Consolidated Mutual	1	Sec. 30, T. 31 S., R. 23 E	....	2,750	....do	....	....	10,554	18,997	20	35	5.2	.49	0	23.3	30.5	11.7	34.0	592
59	Standard	1	Sec. 31, T. 31 S., R. 23 E	....	2,000	....do	.8975	25.99	10,513	18,923	10	11	3.0	.53	1.5	26.9	27.1	11.0	33.2	599
60	California Midway	1	Sec. 32, T. 31 S., R. 23 E	....	2,900	Oct. 19, 1910	.9050	24.70	10,564	19,015	15	39	4.5	.51	0	25.2	31.0	12.7	30.2	601
61	California Counties	1	Sec. 4, T. 32 S., R. 23 E	....	2,900	....do	.8915	27.04	10,561	19,010	0	24	2.8	.46	.7	27.5	30.5	11.8	28.3	600
62	Standard	1	Sec. 14, T. 32 S., R. 23 E	Upper	2,650	....do	.9294	20.63	10,464	18,835	25	76	10.4	.63	6.1	16.0	25.8	10.0	31.1	607
63	....do	2	....do	...do	2,900	....do	.9091	24.00	10,438	18,788	18	50	5.1	.55	3.6	24.5	26.7	10.9	30.9	606
64	Standard (Derby)	7	Sec. 16, T. 32 S., R. 24 E	....	....	May 11, 1918	....	....	....	....	....	....	....	.53	....	....	....	....	....	00228
	Average, 9 samples from zone C	....	....	....	....	....	.9163	22.51	10,497	18,895	32	57	17.5	.63	1.3	19.4	31.3	12.2	33.6	......

TABLE 5-B.—*Fractional distillation of oils from zone C.*

Serial No.	Lease.	Well No.	Water.	Summary of distillation (unrefined products).				Distillation in detail.																			Distilling loss.
								At atmospheric pressure.									In vacuum.										
				Motor fuel (up to 175° C.).	Lamp oils (175°-300° C.).	Lubricants (300° at atmospheric pressure to 325° in vacuum.	Asphaltum (residue).	Pressure of mercury.	Up to 150° C.	150°-175° C.	175°-200° C.	200°-225° C.	225°-250° C.	250°-275° C.	275°-300° C.	300°-325° C.	Pressure of mercury.	150°-175° C.	175°-200° C.	200°-225° C.	225°-250° C.	250°-275° C.	275°-300° C.	300°-325° C.	Residue (asphaltum).		
			P. ct.	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*mm.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*mm.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*
55	Midland Oilfields	1	0.1	0	0.4	55.8	43.2	746	......	......	......	......	......	......	0.4	11.6	12	......	3.7	6.3	7.8	7.9	7.6	10.9	43.2	0.5
56	Rock	2	Tr.	0	18.8	45.7	34.7	742	......	......	......	0.2	2.9	7.1	8.6	9.3	10	......	1.7	5.2	6.5	6.0	6.8	10.2	34.7	.8
57	Chanslor Canfield Midway Oil	1	.1	0	14.1	48.6	36.8	742	......	......	......	......	.3	4.3	9.5	10.2	9	......	......	7.4	6.6	6.9	7.2	10.3	36.8	.4
58	Consolidated Mutual	1	Tr.	0	24.4	41.1	34.0	753	......	......	2.3	5.8	6.5	4.4	5.4	6.4	20	1.3	4.0	4.4	5.0	5.4	6.4	8.2	34.0	.5
59	Standard	1	Tr.	1.5	28.2	36.8	33.2	742	......	1.5	5.5	6.2	6.2	4.9	5.4	6.2	20	......	3.4	4.3	4.7	5.2	5.7	7.3	33.2	.3
60	California Midway	1	Tr.	0	26.5	42.4	30.2	746	......	......	.4	4.9	6.2	6.9	8.1	8.5	9	......	2.0	4.3	5.5	6.2	6.4	9.5	30.2	.9
61	California Counties	1	Tr.	.7	28.8	41.0	28.3	746	......	.7	4.0	6.4	5.9	6.1	6.4	8.4	9	......	3.6	4.0	6.1	4.9	5.7	8.3	28.3	1.2
62	Standard	1	9.5	6.1	16.9	34.9	31.1	745	5.6	.5	.3	1.0	3.5	6.8	5.3	7.2	21	......	2.4	3.2	4.6	4.7	5.2	7.6	31.1	1.5
63	....do	2	1.1	3.6	25.7	36.4	30.9	753	2.5	1.1	3.9	5.6	4.6	6.3	5.3	7.2	21	......	2.3	3.5	4.6	4.9	5.3	8.6	30.9	2.3
64	Standard (Derby)	7	......	25.1	21.0	25.5	28.4	742	19.6	5.5	4.9	5.2	5.8	5.1	......	......	40	4.0	2.0	5.0	4.5	4.5	5.5	......	28.4	......
	Average, 10 samples from zone C.	....	1.1	3.7	20.5	40.8	33.1	746	2.8	.9	2.1	3.5	4.2	5.2	5.4	7.5	17.1	.5	2.5	4.8	5.6	5.7	6.2	8.1	33.1	.8

In the tables headed "Fractional distillation" are given the volume of the fractions distilled in each 25° interval up to 325° C. at atmospheric pressure and thence in vacuum up to 325° C., making in all 15 "cuts." The part remaining in the flask undistilled is termed asphaltum or residue. A summary of the results is given at the beginning of the table by grouping the fractions under their commercial names—motor fuel, lamp oils, lubricants, and asphaltum. In the tables published by the Bureau of Mines the term "naphthas" was used for the fraction distilling below 150° C., "lamp oils," for the fraction between 150° and 300° C., and "lubricants" for the fractions between 300° C. at atmospheric pressure and 325° C. in vacuum. Owing to modifications in commercial practice since those tables were published it is thought advisable to include the fractions up to 175° C. under the term "motor fuel" and those between 175° and 300° C. under the term "lamp oils," the terms "lubricants" and "asphaltum" being used as before. Similarly, in the columns headed "refined products" in the first table of each group an amount equal to the volume of the fraction boiling between 150° and 175° C. minus the refining loss has been added to the figure under "motor fuel" and subtracted from that under "lamp oils." In most of the samples no distillate was obtained below 175°, so that the figures are unaltered, and in the remainder the value of this fraction is very small. It should be recognized that these commercial groups have no very distinct limits and are always subject to modification—for example, the fraction boiling between 300° and 325° C. (atmospheric pressure) is sometimes sold as unrefined stove oil and is sometimes refined and used for medicinal purposes or as a very light lubricant.

GRAVITY AS AN INDEX OF THE PROPERTIES OF OIL.

Aside from the detailed determinations given in the foregoing tables, which should be useful simply as matters of reference, it is interesting to study the relation between the gravity of an oil and its commercial characteristics. California oil from a given field is usually purchased by the pipe-line companies at prices determined by its gravity, the lowest price being paid for the heavy oil and the highest for the light oil. Gravity is doubtless the most convenient general index of the refining quality of oils from a given district, but the tables indicate that two oils of the same gravity may differ considerably in regard to many minor characteristics. Analyses 35 and 57, representing oils of about 0.93 gravity (20.5° Baumé), and analyses 30 and 44, representing oils of about 0.94 gravity (18.8° Baumé), illustrate this fact. Furthermore, not only may two oils of the same gravity yield different volumes of distillate at a given temperature, but these distillates themselves generally differ somewhat in gravity.[1] These differences are too great to be due to analytical error and indicate slight differences in the chemical character of the oil. Additional evidence of this fact is afforded by the close relation between the gravity of the oils and their sulphur content, as shown in figure 3 (p. 30).

It is commonly supposed that the heavy oil produced in the western part of the Sunset-Midway field is or might be derived from the lighter oil by the loss of the lighter fractions through simple evaporation, but the foregoing evidence that variation in gravity is related to variation in chemical character casts doubt on this assumption. Mabery's work furnishes additional evidence, for the sample of heavy Summerland oil consists largely of terpenes and series even poorer in hydrogen and could not have been derived by simple evaporation from the lighter oils composed chiefly of naphthenes and aromatic hydrocarbons. It therefore seems probable that although variation in gravity may be brought about by evaporative losses it is in nature generally due more to difference in chemical composition. In other words, variation in gravity is more likely to be caused by chemical influences than by purely physical conditions.

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[1] The gravity of the several fractions is not shown in the foregoing tables but was determined by Allen in his examination of similar oils from the Coalinga field. See Allen, I. C., Chemical and physical properties of the petroleums of the Coalinga district: U. S. Geol. Survey Bull. 398, p. 264, 1910.

PROPERTIES OF THE OIL IN RELATION TO ITS GEOLOGIC OCCURRENCE.

FACTORS INFLUENCING THE PROPERTIES OF OIL.

Although the chemical and physical properties of oil have been extensively investigated by chemists and the occurrence of oil in the rocks has been studied by geologists, the two lines of work have unfortunately never been correlated. The geochemistry of petroleum, or its chemical relation to the reactive minerals and solutions in the rocks, has received but scant attention. The factors influencing the properties of oil can therefore only be inferred from field observations of variation in gravity and interpreted in the light of the few physical and chemical data bearing on the subject.

The three producing oil zones in the Sunset-Midway field are characterized by oils that differ appreciably in average gravity, the highest zone, A, carrying the heaviest oil, and the lowest zone, C, carrying the lightest. Although individual samples may depart widely from the average for the zone, and although the normal downward succession from heavy oil to light is in places reversed, the deeper zone in most localities carries oil perceptibly lighter than the upper zone. Abundant evidence of this is presented in the paragraphs headed "Character of the oil" in Part I of this report, and additional data are contained in the analytical tables (pp. 17–21), in which the samples are grouped according to the zone from which they were taken. The averages given in these tables indicate that the average gravity of the oil in zone A is 0.966 (14.9° Baumé), that in zone B 0.946 (18.1° Baumé), and that in zone C 0.916 (22.5° Baumé). If more samples of the light oil from zones B and C in the deeper eastern part of the field were included the difference in average gravity would be considerably greater.

If the three producing zones represented distinct formations, the difference in the gravity of their oils might be due to variation in the composition of the organic matter from which the oils were derived or to difference in the degree of dynamic metamorphism to which the oils had later been subjected. The producing zones, however, are simply groups of sandy beds in the later Tertiary deposits, and the oil they carry is believed to have been all derived from organic remains in the formation underlying them. As these broader factors have played no part, the differentiation of the oil must have been effected by local conditions or forces either during its migration into the several zones or after it had come to rest in them. Most of the variation probably represents the algebraic sum of the effects of several factors, the most important of which are the following:

1. Physical or structural conditions, such as depth beneath the surface, distance from the outcrop of the producing sands, position on the structure, faulting or fissuring in the surrounding rocks, and grain of the containing reservoir.
2. The action of chemical reagents, such as sulphur and oxygen, carried for the most part by mineralized waters.

The influence of the physical or structural conditions mentioned is very marked, and they are probably to be regarded as the chief immediate causes of variation in the gravity of the oil, not only as between the different zones but also within any one zone. The influence of most of these conditions has usually been ascribed to their action in facilitating or preventing loss of volatile constituents by evaporation. In the writer's opinion, however, the explanation for much of their influence is to be found in the second factor, the chemical action of mineralized water, which thus seems both directly and indirectly to be a potent cause of variation in the gravity of the oil. In the following pages the influence of physical and structural conditions will be analyzed and the chemical action of water, the importance of which perhaps has not hitherto been realized, will be pointed out.

INFLUENCE OF PHYSICAL OR STRUCTURAL CONDITIONS.

The fact that the oil in the three producing zones differs appreciably in average gravity is due partly to the fact that in each of these zones it is exposed to slightly different conditions. As stated elsewhere in this report, the three zones have fairly definite vertical and areal limits. (See Part I, Pl. III.) Thus zone A is recognized only within a mile or so of the outcrop and extends down the dip only to a depth beneath the surface of about 1,500 feet. Zone C, on the other hand, is recognized only in the deeper territory several miles from the outcrop, as beneath Midway Valley and the Buena Vista

Hills. The territory in which zone B is productive overlaps that of the other two zones; zone B is recognized in the deep Buena Vista Hills territory and also in the northern part of the field at shallow depths and close to the outcrop. This zone thus has wider areal limits than the other two zones and also a greater range in depth, and its oil is therefore characterized by wider variation. Where it lies at shallow depth and close to the outcrop its oil is heavy and seems entirely similar to the normal oil of zone A, but in the Buena Vista Hills, where zones B and C are both deep and far from the outcrop, their oils differ very slightly.

The chief factors causing variation in the gravity of oil within a given zone also seem to be related to distance from the outcrop and depth beneath the surface. Thus in zones A and B, which both approach close to the outcrop in different localities, a gradual increase in gravity with increase in proximity to the outcrop is commonly apparent. This increase is of course generally most apparent within a mile or so of the outcrop and culminates at the outcrop itself, where the oil is a heavy tar or asphalt. At some localities, however, the decrease in gravity down the dip from the outcrop is apparent for several miles. For example, on Twenty-five Hill, near the outcrop, zone A yields oil having a gravity of about 0.983 (12.5° Baumé), and about 2 miles away zone A yields oil of about 0.966 (15° Baumé); zone B in this locality yields oil of about 0.933 gravity (20° Baumé) and about 2 miles farther down the dip to the northeast yields oil as light as 0.897 (26° Baumé). A similar decrease in gravity is well shown by analyses 43 to 51 and 54 in Table 4–A, the gravity decreasing rather regularly down the dip away from the outcrop for a distance of nearly a mile and a half. This decrease is shown graphically in figure 2.

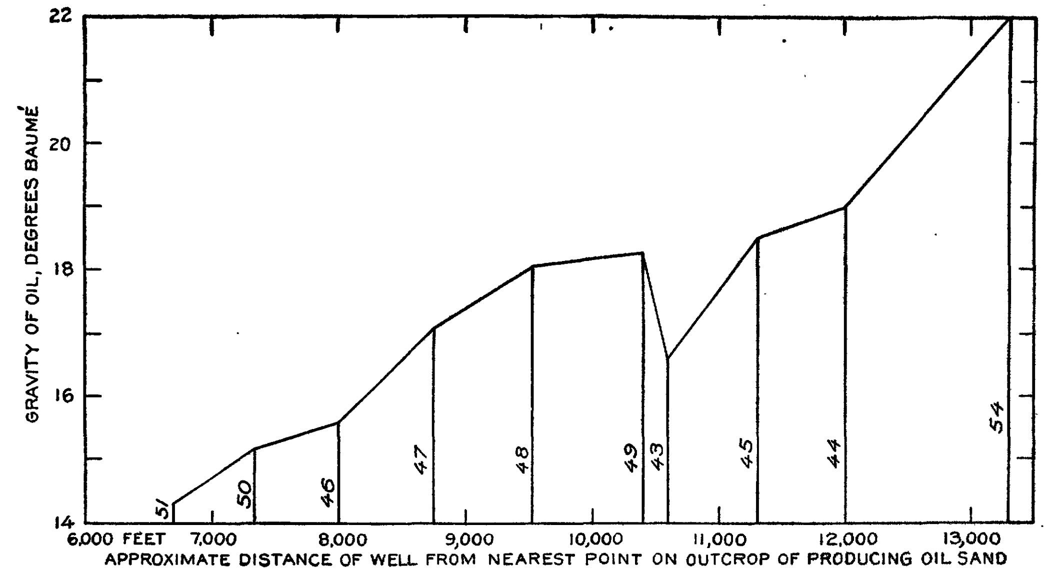

FIGURE 2.—Diagram showing decrease in gravity with increase in distance from the outcrop as illustrated by 10 samples of oil from zone B. Numbers refer to analyses in Table 4–A.

The decrease in gravity with increase in depth is naturally most apparent at relatively shallow depths. The most conspicuous examples are the so-called tar sands, which in the western part of the field normally occur several hundred feet nearer the surface than the productive sands and carry very heavy and viscous oil or tar. On Twenty-five Hill there is a fairly regular gradation in gravity from the tar sands through the uppermost producing heavy-oil sands of zone A to the lighter-oil sands at the base of zone A. In the territory where the sands lie deeper decrease in gravity with increase in depth is generally less marked, though on Maricopa Flat the uppermost sand yields oil as heavy as 0.946 (18° Baumé) and the lowest sands produce oil of 0.892 gravity (27° Baumé). Although variation in depth or distance from the outcrop thus appears to be rather generally accompanied by variation in gravity, it must not be supposed that the gradation is everywhere as regular as in the localities described. In some places variation in the factors mentioned has no very marked effect on the gravity, and on the other hand there are many irregularities in gravity that seem to be entirely unrelated to these factors.

The general increase in gravity with increasing proximity to the surface has usually been ascribed to the escape and loss of the lighter hydrocarbons. The gas and the more volatile constituents of the oil are supposed to have worked their way to the surface and escaped, leaving the heavier fractions behind as a kind of residuum. Although this process has probably been effective to some extent, it is inadequate, in the writer's opinion, to explain the facts. The gas pressure in the shallow zone near the outcrop is of course much lower than in the deeper territory to the east, but it is by no means negligible. Practically every well drilled in the shallow territory has shown some gas; a few have produced considerable volumes of gas, and many have yielded a small but constant supply for years. If the gas itself is not wholly lost, it is illogical to argue that a large proportion of the lighter liquid hydrocarbons, which are less mobile than gas, have escaped. Moreover, underground evaporation could have little effect on the gravity of the oil several miles from the outcrop or 2,000 feet beneath the surface, yet the decrease in gravity may in places extend as far as this. Furthermore, as already noted, it is probable that the heavy oil has a different chemical constitution from the light oil and could not represent a residuum derived from it through simple evaporation. Most of the variation in gravity, therefore, seems to be a function of chemical rather than physical change. The most potent chemical reagent with which oil is likely to come into contact is mineralized water, especially surface water; and the fact that the chances of contact are greatest near the outcrop or near the surface seems to offer the best explanation of the increase in the gravity of the oil in those directions.

The influence of the other structural or physical conditions noted above is less marked and less common. Fracturing or faulting of the containing rocks, however, is of importance in the extreme northern part of the field, where zone B consists chiefly of tar sands and zone C yields abnormally heavy oil. The increase in gravity is probably due in part to the escape of the more volatile hydrocarbons, and in part to oxidation and to contact with sulphate waters. How large a part the action of mineralized water has played in this locality is doubtful, as the producing beds do not contain much water at present. Circulation of water across the strata must have been at first facilitated by the fissuring, although as the oil grew heavier and sealed the fissures the circulation would naturally become more nearly normal again.

The relation between the gravity of oil and its structural position is apparent in some localities, the lighter oil occurring near the crest of the fold. Thus, as pointed out by Mr. Pack (Part I, p. 154), zone C, in the Calidon-Record area, carries oil averaging about 0.892 (27° Baumé) near the crest of the United anticline, whereas down the dip to the west the average gravity of its oil is about 0.921 (22° Baumé). In the Buena Vista Hills, southeast of this locality, a similar but much smaller variation may be observed in the gravity of the zone B oil. Whether this segregation of the lighter oil near the crest of the fold is entirely due to gravitational adjustment is not clear. It is possible that an edge-water condition, or the presence of water in increasing quantity down the flanks of the folds, has to some extent influenced the gravity of the oil.

Within certain limits the grain of the reservoir rock appears to influence the gravity of the oil, shale or very fine grained sand usually carrying a somewhat lighter oil than the medium or coarse grained sands near by. Thus the "shale oil" produced by a few wells near Taft and by others south of Maricopa is a few degrees lighter than that obtained from neighboring sandy beds. This association of lighter oil with shale has been observed in many fields throughout the world, and in many areas it is more marked than in the Sunset-Midway field. The shale probably acts as a kind of filter, allowing only the lighter and less viscous portion of the oil to migrate into it. Day's work[1] on the fractionation of oil by diffusion through fuller's earth has shown that under certain conditions a true chemical separation is effected in this way, the heavy unsaturated compounds being largely removed.

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[1] Day, D. T., Gilpin, J. E., and Cram, M. P., The fractionation of crude petroleum by capillary diffusion: U. S. Geol. Survey Bull. 365, 1908.

EFFECTS OF CONTACT WITH WATER.

GENERAL NATURE OF EFFECTS.

Although the chemical action of mineralized water on oil has apparently never been scientifically studied, there is a common belief among practical oil men that contact with water increases the gravity of oil. This belief is partly founded on the observation, to which frequent reference has been made in Part I of this report, that wells in which water is troublesome usually yield slightly heavier oil than those in which the water has been shut out. This difference is of course due partly to the facts that oil containing a small proportion of water is heavier than clean oil and that in the process of eliminating the water in order to test the true gravity some of the volatile constituents of the oil doubtless escape. The belief that contact with water "injures the gravity" of oil can not, however, be wholly explained in this manner, for it is corroborated by many field observations.

In the Sunset-Midway field the most obvious example of the association of very heavy oil with water is afforded by the tar sands, which generally occur several hundred feet above the producing sands of zones A or B. The tar sands are regarded as marking the farthest limit of migration of the oil from the diatomaceous shale below. They are sands partly impregnated with a heavy viscous oil or tar having a gravity of 0.993 (11° Baumé) or heavier. The tar sands generally carry sulphur water, and it is now recognized that they should in general be treated as water sands and cased off. A study of the well logs indicates that most of the tar sands become wholly water-bearing farther down the dip.

Detailed study of underground conditions reveals the fact that certain beds in the producing zones themselves also become water-bearing down the dip. This edge-water condition has been fully described by Mr. Pack in Part I of this report (Professional Paper 116) and is illustrated in his Plates XVI, XVII, XXVII, XXVIII, XXIX, and XXXI. There is good reason to believe that the gravity of the oil in such sands increases as the water is approached, though as most wells produce a mixture of oil from several sands it is difficult to obtain data as to the gravity of the oil in a single sand unless it is so heavy as to be actually tar. In some wells, however, which have penetrated an edge-water sand near the lower boundary of the oil body, the petroleum encountered is definitely reported to be tar. This condition is suggested also in Plates XVI, XVII, and XXVII of Part I. The writer has noted a similar condition in several localities in the Coalinga field, and it is probable that if more data could be obtained this marked increase in gravity near the water line might be found to be fairly widespread.

A somewhat different illustration of the effect of water upon oil is afforded by sands which though apparently not actually containing water are in close proximity to water sands. For example, in much of the area northwest of Fellows zone C is closely underlain by a water sand and the lowest beds in the producing zone carry oil several degrees heavier than that in the upper beds. Similarly, in the eastern part of sec. 32, T. 12 N., R. 23 W., an oil sand lying close above the big water sand carries oil of 0.972 gravity (14° Baumé), though the neighboring sands both above and below generally yield oil of 0.927 to 0.892 gravity (21° to 27° Baumé). It is reasonable to suppose that where the variation in gravity is so marked as this the oil and water sands are connected at some point and that the two fluids either are now in contact or have been at some time in the past.

It has already been pointed out that increase in gravity with increase in proximity to the outcrop or surface, though perhaps due partly to the escape of the volatile fractions, may be more reasonably explained on the ground that oil near the surface or outcrop is most likely to come into contact with descending surface waters. So far as the field evidence indicates, therefore, contact with water is probably the most important single cause of increase in the gravity of the oil.

INTERACTIONS BETWEEN WATER AND HYDROCARBONS.

The belief that mineralized water may exercise a chemical effect upon oil is corroborated by the reverse evidence—that is, the effect of the reaction upon the composition of the water itself. It has been shown elsewhere by the writer[1] that the waters associated with the oil in the San Joaquin Valley oil fields are

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[1] Rogers, G. S., Chemical relations of the oil-field waters in San Joaquin Valley, Calif.: U. S. Geol. Survey Bull. 653, 1917.

almost or quite lacking in sulphate, notwithstanding the fact that the shallower waters of the region are characterized by a large concentration of sulphate. An equally striking feature of many of the waters associated with the oil is the presence of alkali carbonate, which is lacking in the shallow waters on the west side of the valley. Between the sulphate and carbonate zones is a zone characterized by waters carrying hydrogen sulphide. Outside the oil fields sulphate and carbonate maintain the same mutual proportions to great depths and hydrogen sulphide waters are rare; the conclusion is therefore irresistible that a change in the composition of the oil-field waters has been caused directly or indirectly by constituents of the oil or gas. As sulphate is abundant in the shallower waters everywhere on the west side of the San Joaquin Valley, whereas sulphide is found only near the hydrocarbons, it is reasonable to suppose that the sulphide has been derived under special conditions through reduction of the sulphate.

The observation that waters associated with oil contain no sulphate is by no means new, for it was pointed out in 1874 by Eichler [1] that the waters associated with oil in the Caucasian oil fields contain no sulphate, and this observation has been amply confirmed by later workers there and in other fields. Höfer [2] mentions this widespread peculiarity of oil-field waters and presents a compilation of 27 analyses of sulphate-free water from various fields in Europe, Asia, and North America. It is generally supposed that the absence of sulphate is due to the reducing action of hydrocarbons, the sulphate being reduced to sulphide, which passes off as hydrogen sulphide, and an equivalent portion of the oil or gas being oxidized to carbon dioxide or carbonate. Höfer writes the reaction substantially as follows:

$$CaSO_4 + CH_4 = CaO + H_2S + CO_2 + H_2O$$

or

$$CaSO_4 + CH_4 = CaS + CO_2 + 2H_2O = CaCO_3 + H_2S + H_2O$$

These reactions, however, are hypothetic and have never been definitely substantiated in the laboratory. It has long been known that sulphate solutions are decomposed under some conditions in the presence of organic matter with the formation of hydrogen sulphide, but it was shown by Meyer,[3] and more definitely by Plauchud,[4] that this decomposition is due not to the mere presence of dead organic matter but to the vital processes of microorganisms. Numerous observers have since studied these creatures, whose functions are diverse and whose importance from the standpoint of the geochemist appears to be considerable.[5] Thus Van Delden,[6] in experimenting with a species of bacteria that inhabits the estuaries on the coast of Holland, finds that they liberate in 27 days 843 milligrams of hydrogen sulphide per liter, which represents the reduction of 1,984 milligrams of sulphur trioxide. Hydrogen sulphide has been repeatedly observed in sea water at places where organic matter is abundant and where the circulation is slight, and has been quantitatively determined by several observers. Lebedinzeff [7] finds that water from a depth of 8,290 feet in the Black Sea contains 6,550 parts per million of hydrogen sulphide, and Zelinsky [8] has identified in the bottom muds of the Black Sea several species of anaerobic bacteria that are very active in the formation of hydrogen sulphide. It is therefore well established that sulphate may be reduced by bacteria in the presence of organic matter, but the bearing of this process upon the reduction of sulphate in the oil-field waters is doubtful. There is no evidence to show that even anaerobic bacteria can continue to exist in the muds after the muds have been covered with a thousand feet or more of sediments and elevated into land, yet there is reason to sup-

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[1] Eichler, W., Einige vorläufige Mittheilungen über das Erdol von Baku: Soc. imp. nat. Moscou Bull., vol. 48, No. 4, 1874.

[2] Engler, C., and Höfer, H., Das Erdol, Band 2, p. 28, 1909.

[3] Meyer, Lothar, Chemische Untersuchung der Thermen zu Landeck in der Grafschaft Glatz: Jour. prakt. Chemie, Band 91, pp. 5-6, 1864.

[4] Plauchud, E., Recherches sur la formation des eaux sulfureuses naturelles: Compt. Rend., vol. 84, p. 235, 1877; Sur la réduction des sulfates par les sulfuraires, et sur la formation des sulfures métalliques naturels: Idem, vol. 95, p. 1363, 1882. See also Étard, A., and Olivier, L., De la réduction des sulfates par les êtres vivants: Idem, vol. 95, p. 846, 1882.

[5] Winogradsky, Sergius, Ueber Schwefelbacterien: Bot. Zeitung, Nos. 31-37, 1887.

[6] Van Delden, A., Beitrag zur Kenntnis der Sulfatreduktion durch Bakterien: Centralbl. Bakteriologie, Band 11, Abt. 2, pp. 92-93, 113-119, 1903.

[7] Lebedinzeff, A., Vorläufige Mitteilung über den chemischen Untersuchungen des Schwarzen und Asowischen Meeres in Sommer 1891: Soc. nat. Odessa Trav., vol. 16, fasc. 2, p. 149, 1891; abstract in Roy. Geog. Soc. Proc., new ser., vol. 14, p. 461, 1892.

[8] Zelinsky, N. [Sulphydric fermentation in the Black Sea]: Russ. Chem. Soc. Jour., vol. 25, pp. 298-303, 1894; abstract in Chem. Soc. Jour. vol. 66, pt. 2, p. 200, 1894. Andrussow, N., Physical exploration in the Black Sea: Roy Geog. Soc. Jour., vol. 1, p. 49, 1893.

pose that in some localities surface waters are percolating down to the oil zone and are being altered at the present time.

The belief that hydrocarbons can reduce sulphate in the absence of bacteria and at moderate temperatures has been tacitly accepted for many years, and few attempts have been made to prove it in the laboratory. The experiments of the earlier workers are discredited by the fact that no precautions were taken to exclude bacteria, and certain later attempts proved unsuccessful, but recently Kharitschoff[1] has described some simple experiments that seem to have been at least partly successful. He studied mixtures of equal volumes of 10 per cent sodium sulphate solution and kerosene or benzene under different conditions of temperature and pressure. In three samples heated in the open for 420 hours at 96° C. some sulphide was formed, presumably through reduction of sulphate. A solution of magnesium sulphate mixed with kerosene and heated for 420 hours apparently underwent somewhat more reduction than the solution of sodium sulphate. Kharitschoff concludes from these experiments that the reduction of sulphate can be accomplished by hydrocarbons, but that high pressure and temperature during a long period of time are necesssary to insure complete reduction.

Although the exact manner in which the alteration of the waters is brought about is not definitely known, the usual view, that it is due to reaction with the hydrocarbons, certainly explains the chief phenomena—the disappearance of the sulphate and the formation of sulphide and of carbonate. It should be recognized, however, that the reaction as written above, involving methane, is improbable. Methane, being itself a decomposition product, is the most inert member of the paraffin series, which are the most stable of all hydrocarbons. Certain series, poorer in hydrogen, which are abundant constituents of California oil, are much less stable and probably react more readily with sulphates. In fact, it is quite possible that certain constituents of the oil other than simple hydrocarbons are most active in the reduction of the sulphate solutions. In any event the equation showing the reaction as written can be considered only a condensed representation of the type of change that takes place, the stages in the decomposition of the hydrocarbons on the one hand and of the sulphate on the other being as yet unknown.

Economically the most important result of the reduction of sulphate in the oil-field waters is the formation of hydrogen sulphide. As this gas is found in many of the waters above the oil measures and as these waters still contain some sulphate, it is probable that they are undergoing alteration at the present time. Few waters, however, carry more than 100 parts per million of hydrogen sulphide, and none of the Sunset-Midway waters yet analyzed contain more than a fraction of this amount. As the complete reduction of 100 parts of sulphate would yield 35 parts of hydrogen sulphide, and as all the upper waters carry several hundred or several thousand parts of sulphate, it is evident that either the sulphate in these waters is not all reduced or else the hydrogen sulphide is being removed from solution nearly as fast as it is being formed. Some of it may unite with iron to form iron sulphide, which is precipitated, and some of it may mix with the hydrocarbon gas, but the total quantity accounted for in this way is not great.

Hydrogen sulphide readily oxidizes to sulphur, probably in accordance with the equation $2H_2S+O_2=2H_2O+2S$. Under more strongly oxidizing conditions or in the presence of certain bacteria the sulphur becomes thiosulphuric, sulphurous, and finally sulphuric acid. The complete reversion of hydrogen sulphide to sulphuric acid or sulphate is probably not widespread in buried strata, but the change to free sulphur, which takes place even under very feebly oxidizing conditions, must be taken into account. It is probable that considerable amounts of hydrogen sulphide are oxidized to sulphur and are removed by precipitation from the waters above the oil measures.[2] As the strata above the oil measures have not been examined for sulphur this hypothesis can not be definitely proved, but commercial deposits of sulphur have been found near the south end of Sunset field, in sec. 21, T. 11 N., R. 23 W., in pockets and fissures in the

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[1] Kharitschoff, K. V., The waters in petroleum wells: Petroleum Rev., vol. 29, p. 368, 1913.

[2] The precipitation of sulphur by the oxidation of hydrogen sulphide is discussed in detail by Walter F. Hunt (Origin of the sulphur deposits of Sicily: Econ. Geology, vol. 10, pp. 543-579, 1915).

McKittrick group, which includes the oil measures in the producing field near by. Most of the sulphur is amorphous, but some of it occurs as clear yellow crystals as much as a quarter of an inch in diameter. A steady flow of hydrogen sulphide is emitted from a pipe which has been driven a short distance into the ground near one of the prospect pits. A very interesting feature of this sulphur, to which the writer's attention was first directed by Dr. E. A. Starke, of the Standard Oil Co., is its intimate mixture with hydrocarbon material, which seems to constitute 20 per cent or more of the amorphous substance. No oil or tar seeps are found in the immediate neighborhood of the sulphur deposits, but deposits of brea occur less than a mile away. Small deposits of disseminated sulphur are found elsewhere along the western edge of the Sunset-Midway field, and it seems probable that these accumulations have been derived from sulphate by the reducing action of hydrocarbons.

CHEMICAL ACTION OF SULPHUR AND OXYGEN ON PETROLEUM.

It has been shown above that hydrogen sulphide, presumably formed through the reduction of sulphate by hydrocarbons, exists in the waters directly above the oil measures, and that much of this gas is probably oxidized to sulphur. The chemical action on the oil of this sulphur and also of oxygen, another active agent carried in solution by most descending surface water, will now be considered.

If paraffin or paraffin-bearing oil is digested with sulphur at moderate temperature it becomes black and heavy and finally passes to a substance resembling solid asphalt. Similarly, if a light asphaltic oil is treated with sulphur it also becomes darker and more viscous, finally becoming asphalt. Under laboratory conditions the reaction is accompanied by the evolution of hydrogen sulphide, and in fact an old laboratory method of generating hydrogen sulphide consists in heating paraffin and sulphur in a retort. The sulphur atom, by extracting 2 atoms of hydrogen from the oil, causes a condensation or polymerization of the hydrocarbon molecule, and this change is reflected in the increase of the gravity of the oil itself as it approaches solid asphalt. A simple example of change through the action of sulphur, from the polymethylene series of the general formula C_nH_{2n} to the heavier aromatic series of the general formula C_nH_{2n-6}, may be written as follows:[1]

Hexamethylene+sulphur = benzene+hydrogen sulphide

$$C_6H_{12} + 3S = C_6H_6 + 3H_2S$$

Although this condensation of the hydrocarbon molecule caused by the formation of H_2S is the change of greatest geologic interest, under most conditions some of the sulphur enters into combination with certain oil constituents to form simple sulphur compounds or complex sulphur derivatives. As already stated, California petroleum contains a relatively large percentage of sulphur compounds, though their exact nature is unknown.

Sulphur is readily soluble in petroleum, and certain Texas oils contain both hydrogen sulphide and free sulphur in solution, in addition to the compounds of sulphur. Apparently the solution of sulphur in the heavier hydrocarbons of petroleum is immediate, even at ordinary temperature, though its solubility in oil naturally varies according to the series of hydrocarbons involved. In Peckham's opinion the reaction between sulphur and the hydrocarbons, whereby the latter are rendered heavier and more asphaltic, also proceeds at ordinary temperature.[2] Finally, according to Endemann,[3] heavy hydrocarbons react with pyrite just as free sulphur, half of the sulphur in the pyrite molecule (FeS_2) being given off as H_2S and the rest remaining as a lower sulphide of iron.

Oxygen also exercises a pronounced effect on petroleum, the general character of which is commonly known. When oil is exposed to the air for a long time it becomes dark, heavy, and viscous, and finally passes to asphalt. This change is due chiefly to the evaporation of the more volatile constituents but partly to oxidation. Thus, if hot air is passed through oil for several hours the oil becomes black and asphaltic.[4] The action of oxygen is similar to

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[1] Köhler, H., Die Chemie und Technologie der natürlichen und künstlichen Asphalte, p. 112, Braunschweig, 1904.

[2] Peckham, S. F. and H. E., On the sulphur content of bitumens: Soc. Chem. Industry Jour., vol. 16, pp. 996-997, 1897.

[3] Endemann, H., discussion of paper by S. F. and H. E. Peckham, The analysis of asphaltum: Soc. Chem. Industry Jour., vol. 16, p. 426, 1897.

[4] Jenney, W. P., On the formation of solid oxidized hydrocarbons resembling natural asphalts by the action of air on refined petroleum: Am. Chemist, vol. 5, p. 359, 1875.

that of sulphur; some of the oxygen may be taken into combination with the oil to form complex acids or phenols, and part of it abstracts hydrogen from the hydrocarbon molecule to form water. This reaction is involved in the Byerly process for preparing asphalt by slowly distilling petroleum while passing air through it.[1] Oxygen, like sulphur, may also cause direct polymerization. Hausmann and Pilat[2] note that a naphthene may be transformed into an aromatic hydrocarbon by the action of oxygen at 140° C., and suggest that a similar change may be accomplished underground by some such agent as manganese dioxide.

Oxygen is usually not determined in the analysis of oil, and comparatively little is known of the structure of the oxygen compounds. However, naphthenic acids, which are the oxygen derivatives of the naphthenes, having the general formula $C_nH_{2n-2}O_2$, are known to exist in California oils. According to Ostrejko,[3] if Russian oil, similar to the Californian, is exposed to the air, especially in sunlight, these acids form at ordinary temperature, with resulting turbidity and darkening of the oil. Hydroxyl derivatives of the nature of phenols have been found in California and other oils,[4] and formic and oxalic acids are reported in petroleum from the Grosny district, Russia, the quantity increasing with the gravity of the oil.[5]

The ease with which petroleum takes up oxygen naturally varies according to the pro-

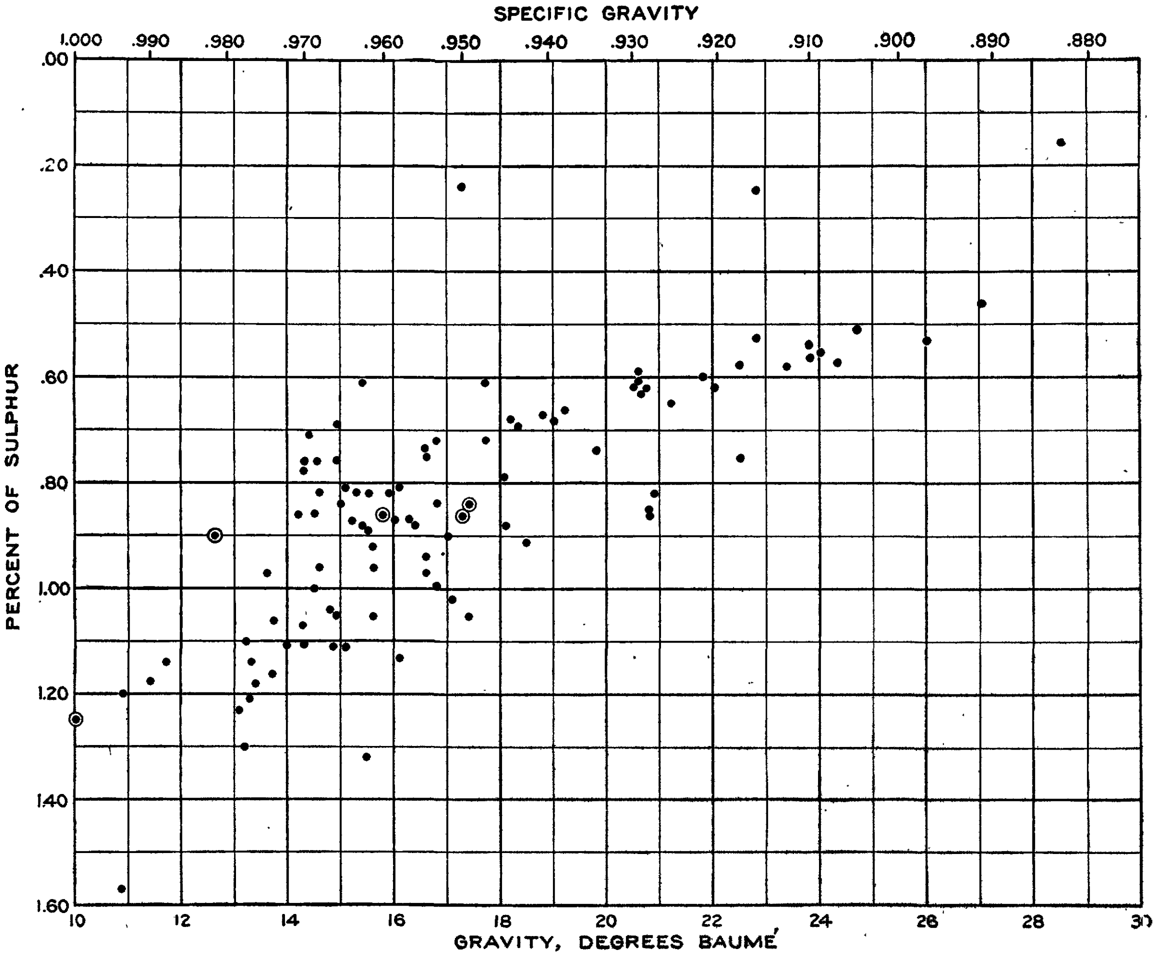

FIGURE 3.—Diagram showing relation of gravity to percentage of sulphur in 100 samples of oil from the Sunset-Midway field. Analyses represented by small solid circles made by Bureau of Mines; the others by different chemists.

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[1] Mabery, C. F., and Byerly, J. H., The artificial production of asphalt from petroleum: Am. Chem. Jour., vol. 18, p. 141, 1896.

[2] Hausmann, J., and Pilat, S., Studien über die Oxydation der Petrolkohlenwasserstoffe: Congrès internat. pétrole Compt. rend. Sess. 3, p. 378, 1907.

[3] Ostrejko, R. A., Influence of sunlight and air on petroleum products (abstract): Soc. Chem. Industry Jour., vol. 26, pp. 345, 645, 1896.

[4] Mabery, C. F., The composition of American petroleum: Am. Chem. Soc. Jour., vol. 28, p. 426, 1906.

[5] Schidkoff, N., Acid content of Grosny petroleum and derivatives (abstract): Soc. Chem. Industry Jour., vol. 18, p. 360, 1899.

vailing series of the hydrocarbons in it. For example, the terpenes, which have the general formula C_nH_{2n-4} and which are noteworthy constituents of some California petroleum, have a well-known tendency to oxidize and to polymerize and doubtless contribute to the viscosity and resinification of the heavy oils.

RELATION OF SULPHUR CONTENT TO GRAVITY.

So far as the chemistry of the process is concerned there is no question as to the ability of sulphur and oxygen to render petroleum heavier and more asphaltic; and if the action of these agents in nature has really been widespread it is reasonable to expect that variation in gravity would be accompanied by variation in the sulphur and oxygen content of the oil, as shown by analysis. It is evident, however, that there can be no exact relation, for the particular part of the sulphur or oxygen that contributes chiefly to increasing the gravity of the oil is the part given off and lost as H_2S or H_2O; and the size of this part in relation to that remaining in the oil as sulphur or oxygen is apparently indeterminate. In other words, only the traces of the reactive substances can be found by analysis; the portions of those substances that have actually been effective have been lost. Furthermore, inasmuch as oxygen is not determined in the industrial analysis of petroleum, the data are not available for studying variation in gravity in relation to oxygen content, and as all the gravity variation can not be ascribed to sulphur alone the relation between sulphur and gravity can not be uniformly exact.

In view of these considerations, the relation between sulphur and gravity, shown in the accompanying diagram (fig. 3), seems reasonably close. This diagram shows the relations in a hundred samples, which include all those analyzed by the Bureau of Mines and the few represented by published analyses made by other chemists. It appears in general that oil lighter than 22° Baumé contains less than 0.6 per cent sulphur, and that oil heavier than 14° Baumé contains more than 1 per cent. The heavy tar found above the productive oil sands in the western part of the field probably contains in general more than 1.5 per cent of sulphur. There are a few samples, however, in which the relation between sulphur and gravity departs more or less widely from the average. It is not unreasonable to suppose that these departures represent variation in the unknown factor, that is, the oxygen content. Heavy oils abnormally low in sulphur may owe their high gravity to excessive oxidation, and light oils that seem abnormally high in sulphur may be free from oxygen and affected only by reaction with sulphur. The great majority, which fall within a fairly narrow zone, have probably been affected by both oxygen and sulphur.

CHANGE IN PROPERTIES DURING MIGRATION.

Although the gravity of oil is affected by several structural or physical conditions, it is evident that a most important factor, geologically as well as chemically, is contact with oxygenated or mineralized water. This explains not only the high gravity of the oil in direct contact with water or even in close proximity to water, but also to a large extent the marked increase in gravity with increase in proximity to the outcrop or the surface. As oil in the course of its migration is practically certain to encounter water, it follows that the gravity of the oil, within certain limits, increases roughly with increase in the distance which the oil has migrated.

As described in Part I of this report, the oil in the Sunset-Midway field is believed to have originated in diatomaceous shale of Miocene age and to have migrated up into the Miocene or Pliocene formations which rest unconformably on the shale. The basal sandy beds of these formations probably constituted the main avenue of migration, the oil working through these beds until it reached the surface. At the outcrop, through evaporation and oxidation and in some degree through the action of sulphate waters, the oil became changed to tar or asphalt and sealed the avenue of escape. Further movement in this direction being cut off, the oil that followed presumably migrated from the general sandy zone into the individual sands that extend out from it in angular unconformity. These sands constitute the reservoirs from which the bulk of the oil is now obtained.

From what has already been shown it is evident that oil which migrates, being more likely to encounter reactive substances (and perhaps fresh supplies of them), is likely to become altered in the course of its migration. It is evident, however, that the action of oxygen, sulphur, or other agents on the oil will be more or less localized, because ordinarily the quantity of these substances available is small compared with that of the petroleum. The oil that is the first to traverse a given course comes into contact with reacting substances at their highest potential and therefore becomes changed more radically than the oil that follows it. If these reacting substances should become exhausted then oil might pass them unaffected. On the other hand, oil that moves with extreme slowness and remains a very long time in contact with reactive agents may undergo changes just as marked as those in oil which had previously moved through the channel at a more rapid rate. In general, however, that portion of the oil which migrated first or farthest will be the most altered.

When the oil migrated up from the diatomaceous shale into the basal sandy zone of the overlying beds it must have come into contact with the water then occupying those beds and displaced the water. As the beds were for the most part laid down beneath the sea it is probable that the water contained in them was mostly sea water, though near the outcrop or the surface meteoric or surface water had doubtless driven out the original sea water to some extent. Some of the later Tertiary beds, however, were laid down in lakes, and these beds were doubtless saturated with brackish or fresh water. Ordinary sea water contains 2,700 parts per million of sulphate, and the fresh or brackish surface waters of the west side of San Joaquin Valley carry from 50 to 7,000 parts, averaging perhaps 2,500 parts. (See analyses, Tables 18 and 19, pp. 81–82.) On the other hand, oxygen is much more soluble in fresh water than in salt water.[1] Such fresh or brackish meteoric water as the oil may have encountered in its upward migration certainly carried more oxygen than the sea water entrapped in the sediments; it may have carried much more or much less sulphate, but on the average it probably carried about the same amount. The 2,700 parts of sulphate contained in the sea water which the oil first encountered was undoubtedly sufficient to effect alteration, especially as the oil in its slow upward migration continually encountered fresh supplies.

The time required for the reduction of a given quantity of sulphate by a given quantity of oil is unknown but is probably fairly long—that is, all the sulphate in the water encountered by the first oil to move was probably not reduced, and most of it remained to react with the oil that followed. The first oil, however, was doubtless the most altered; and when this oil in its upward course reached the zone of surface waters and became subjected also to the action of oxygen its alteration must have become still more pronounced. This more radical alteration culminated at the outcrop itself, where evaporation and atmospheric oxidation became added factors and caused the oil to become so viscous that movement in that direction was largely stopped. The oil that followed migrated into the sands that branch off from the main sandy beds, zone A probably being filled first because the water to be displaced in that zone was under lower pressure. As the oil migrated farther and farther out in zone A it became more and more altered, until the first oil to enter the beds had become so tarry and viscous that movement ceased. Zones B and C were filled with oil which probably had a shorter distance to migrate than that entering zone A and which was accordingly less altered. Further differentiation was doubtless brought about later by descending surface waters, which naturally affected most strongly the oil in zone A and in those portions of all three zones lying nearest the outcrop. How much of the alteration of the oil has come about since it reached its present position is a matter of conjecture; but if, as the writer supposes, much of it was effected during migration it is evident that none of the oil could have migrated very far.

CHEMICAL CHARACTER OF THE GAS.

COMPOSITION OF NATURAL GAS.

Natural gas is much more simple in chemical composition than oil, and its possible constituents are relatively few in number. Most gas is a mixture of two or more light hydrocarbons with small proportions of the inert gases nitrogen and carbon dioxide. It has long been known that the predominating hydrocarbons in all natural gas are the light mem-

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[1] Clarke, F. W., The data of geochemistry, 3d ed.: U. S. Geol. Survey Bull. 616, p. 141, 1916.

bers of the paraffin series—chiefly methane and ethane—but until recently it was supposed that members of the olefin series, such as ethylene, are also present. Burrell and Oberfell[1] have shown, however, that the olefins do not occur in natural gas and ascribe the fact that they are often reported to the erroneous analytical methods in common use. Hydrogen and carbon monoxide are also frequently reported, but the same investigators state that they do not exist in natural gas. Oxygen is present in many samples but in most it is probably due to an admixture of air during sampling. In general, therefore, the constituents of natural gas are the lighter paraffins, carbon dioxide, and nitrogen.

The several lighter paraffins occurring in natural gas are not separated and identified by the ordinary or eudiometric method of analysis. The total paraffins are determined, and it is assumed that they consist entirely of methane and ethane, the proportions of which are calculated from theoretical equations. As a matter of fact, however, it is known that the next higher paraffins, propane and butane, are present in many gases and small quantities of pentane and hexane vapor in some. As all these hydrocarbons are of different heating value, illuminating power, specific gravity, and other properties, it is evident that the ordinary analysis of a gas affords only a rough basis for estimating its commercial value.

In general, the commercial value of natural gas depends chiefly on its heating power and on its content of gasoline vapor. Its heating power is determined by the relative proportions of the several hydrocarbons and of the carbon dioxide and nitrogen. The heating value of methane at 0° C. and 760 millimeters pressure is 1,065 British thermal units, of ethane 1,861 British thermal units, of propane 2,654 British thermal units, and of butane 3,447 British thermal units; that of carbon dioxide and nitrogen is nil. Most natural gas consists chiefly of methane and therefore has a heating value somewhere near 1,100 British thermal units; the presence of ethane, propane, and butane increases the heating value and the presence of carbon dioxide and nitrogen lowers it. As the heating value reported by the chemist is commonly calculated from the proportions of methane and ethane, which are simply assumed quantities, the figure reported may not agree very closely with the actual heating value. The illuminating power of natural gas, which is controlled by the same factors as the heating value, is generally so small that it is of little commercial importance.

The value of gas for gasoline extraction depends on its content of the gases propane and butane and the vapor of the liquids pentane, hexane, and heptane. By compression or refrigeration, or by solution in mineral oil, much of the propane and butane and practically all of the heavier hydrocarbons can be condensed to the liquid form, and after blending with heavier refinery naphtha may be used as motor fuel. As the relative proportions of these higher hydrocarbons are not determined in ordinary gas analysis, it is impossible by inspection of the analysis to estimate the value of the gas for gasoline extraction. The specific gravity of the gas is a rough index of its value for this purpose, though not sufficiently accurate or reliable to serve as a definite criterion. Determination of the proportion of the gas absorbed by claroline or other oil furnishes a better laboratory test, but the only entirely satisfactory method of determining the percentage of gasoline that may be extracted is an actual test with a small portable plant.[2]

ANALYSES.

The accompanying tables show the composition of 27 samples of gas from the Sunset-Midway field as determined by the ordinary analytical methods. Many of the analyses, including most of those of Table 6, represent casing-head gas, which is directly associated with the oil; others represent "dry" gas, occurring several hundred feet above the highest oil-producing zone, and still others represent the gas occurring in an oil zone but at a point where the zone carries only gas. Methane is the predominating constituent in all the samples; ethane is generally present, and in sample 19 it amounts to 37.5 per cent. As the figures for methane and ethane are simply calculated from the determination of

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[1] Burrell, G. A., and Oberfell, G. G., Composition of the natural gas used in twenty-five cities: Bur. Mines Tech. Paper 109, p. 11, 1915.

[2] Burrell, G. A., and Jones, G. W., Methods of testing natural gas for gasoline content: Bur. Mines Tech. Paper 87, 1916. Burrell, G. A., Seibert, F. M., and Oberfell, G. G., The condensation of gasoline from natural gas: Bur. Mines Bull. 88, 1916.

total paraffins, they have no very exact value separately and seem to bear only a slight relation to the geologic horizon at which the gas occurs. Ethane, however, is usually fairly high in the casing-head gas, as in samples 5, 6, 7, and 19, and is generally low or absent in the gas occurring far above the oil, as in samples 8, 15, 25, and 27, though some samples of such gas contain a considerable percentage of ethane. Ethane is of course fairly high in the gases that are valuable for the condensation of gasoline, such as sample 19, and these gases are also characterized by higher specific gravity. Nearly all the samples contain a small percentage of nitrogen, some though not all of which probably represents admixed air.

The most striking feature of the Sunset-Midway gas is its rather high proportion of carbon dioxide. In seven samples from the western part of the field the carbon dioxide averages 18 per cent, and in 20 gases from the eastern part it averages 5.5 per cent. Accordingly the heating value of the 7 gases averages about 900 British thermal units, whereas that of the 20 averages 1,070 British thermal units, or about the same as that of methane. Natural gas from the Appalachian fields contains but little carbon dioxide or nitrogen and accordingly has a higher heating value; the gas used in the city of Cleveland, Ohio, for example, has a heating value of about 1,200 British thermal units.

TABLE 6.—*Analyses of natural gas from the western part of the Sunset-Midway field.*

	1	2	3	4	5	6	7
Carbon dioxide (CO_2)	19. 7	10. 5	20. 0	9. 8	22. 8	24. 2	20. 0
Oxygen (O_2)	. 0	....	. 0	. 0	....	. 0	. 0
Methane (CH_4)	73. 8	87. 7	74. 7	89. 1	65. 9	65. 2	62. 5
Ethane (C_2H_6)	5. 7	. 0	4. 4	. 0	10. 7	9. 4	16. 4
Nitrogen (N_2)	. 8	1. 8	. 9	1. 1	....	1. 2	1. 1
	100. 0	100. 0	100. 0	100. 0	99. 4	100. 0	100. 0
Specific gravity (air=1)	0. 78	....	0. 77	0. 65	....	0. 84	0. 83
Heating value[a]	892	934	904	949	766	869	971

[a] Gross heating value at 0° C. and 760 millimeters pressure, calculated in British thermal units per cubic foot.

1. Chanslor-Canfield Midway Oil Co. well 6, sec. 31, T. 31 S., R. 23 E. Gas associated with oil of 22° B. gravity chiefly in zone C. Sampled by G. S. Rogers, July, 1914; analyzed by G. A. Burrell, Bureau of Mines.
2. Hawaiian Oil Co. well 1, sec. 31, T. 31 S., R. 23 E. Sampled by I. C. Allen, July, 1909; analyzed by G. A. Burrell, Bureau of Mines.
3. Hale-McLeod Oil Co. well 5, sec. 8, T. 32 S., R. 23 E. Gas associated with oil of 17° B. gravity in zone A. Sampled by G. S. Rogers, July, 1914; analyzed by G. A. Burrell, Bureau of Mines.
4. Indian & Colonial Oil Co. well 23, sec. 22, T. 32 S., R. 23 E. Gas associated with oil of 14° B. gravity in zone A. Sampled by G. S. Rogers, July, 1914; analyzed by G. A. Burrell, Bureau of Mines.
5. Kern Trading & Oil Co. wells in sec. 31, T. 12 N., R. 23 W. Gas associated with oil of average gravity of 21° B. in zone B. Sampled and analyzed by W. E. Perdew; authority, Kern Trading & Oil Co.
6. Topaz Oil Co. well 3, sec. 18, T. 11 N., R. 23 W. Gas associated with "shale oil" of 17° B. gravity in zone B, Sampled by G. S. Rogers, July, 1914; analyzed by G. A. Burrell, Bureau of Mines.
7. Spreckels Oil Co. well 5, sec. 32, T. 12 N., R. 23 W. Gas from bed 80 feet above producing oil sand (in zone B). Sampled by G. S. Rogers, July, 1914; analyzed by G. A. Burrell, Bureau of Mines.

TABLE 7.—*Analyses of natural gas from wells of the Standard Oil Co. in the northern part of the Buena Vista Hills, Midway field (T. 31 S., R. 24 E.).*[a]

	8	9	10	11	12	13	14	15
Carbon dioxide (CO_2)	0.3	0.7	3.2	4.1	3.7	3.6	11.7	3.4
Oxygen (O_2)	.1	.3	.3	.3	.2	.8	.1	.1
Methane (CH_4)	96.3	94.3	92.8	86.7	95.1	90.9	82.8	90.5
Ethane (C_2H_6)	......	......	......	6.3	......	1.4	2.4	......
Illuminants (chiefly C_2H_4)	......	.1	.4	.5	.2	.6	1.6	.1
Other hydrocarbons	......	......	......	......	......	......	......	2.3
Nitrogen (N_2)	3.3	4.6	3.3	2.1	.8	2.7	1.4	3.6
	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Specific gravity (air=1)	0.56	0.57	0.63	0.63	0.57	0.59	0.68	0.60
Heating value [b]	1,084	1,030	1,070	1,110	1,092	1,087	1,080	1,014

[a] California State Min. Bur. Bull. 69, pp. 250-251, 1914.

[b] Gross heating value at 0° C. and 760 millimeters pressure, calculated in British thermal units per cubic foot.

8. Well 1, sec. 22. Gas chiefly from bed about 100 feet above top of oil zone B.
9. Well 2, sec. 22. Gas from horizon of oil zone B.
10. Well 2, sec. 26. Gas from horizon of oil zone B.
11. Well 3, sec. 26. Gas from horizon of oil zone B.
12. Well 4, sec. 26. Gas chiefly from horizon of oil zone B but probably in part from horizon of oil zone C.
13. Well 5, sec. 26. Gas chiefly from bed 250 feet above top of oil zone B but probably in part associated with the oil in zone B.
14. Well 7, sec. 36. Gas probably associated with oil in zones B and C.
15. Well 9, sec. 36. Gas from bed about 200 feet above top of oil zone B.

TABLE 8.—*Analyses of natural gas from the southern part of the Buena Vista Hills, Midway field (T. 32 S., R. 24 E.).*

	16	17	18	19	20	21	22	23	24	25	26	27
Carbon dioxide (CO_2)	4.2	7.0	7.6	16.5	8.1	6.9	5.6	1.6	3.0	7.7	7.5	3.2
Carbon monoxide (CO)	.9	......	......	......	1.6	1.1	.5	.3	.7	......	......	......
Oxygen (O_2)	.6	.3	.0	.0	.2	.5	1.7	.9	.2	.7	.1	.3
Methane (CH_4)	86.2	87.6	76.5	42.2	76.4	76.4	85.6	86.1	94.6	87.5	90.0	92.0
Ethane (C_2H_6)	7.6	......	15.2	37.5	12.5	14.1	5.7	9.7	.6	......	1.2	......
Illuminants (chiefly C_2H_4)	.5	.2	......	......	1.2	1.0	.9	1.4	.9	......	.2	.8
Other hydrocarbons	......	......	......	......	......	......	......	......	......	......	......	3.2
Hydrogen (H_2)	......	1.2	......	......	......	......	......	......	......	......	......	.2
Nitrogen (N_2)	.0	3.7	.7	3.8	.0	.0	......	.0	.0	3.6	1.0	.3
	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	99.5	100.0	100.0
Specific gravity (air=1)	0.66	0.65	0.71	0.96	0.72	0.70	0.69	0.74	0.64	......	0.61	0.61
Heating value (British thermal units per cubic foot)	1,073	[a]966	[a]1,097	[a]1,147	1,076	1,100	1,037	1,126	1,040	[a]992	[a]1,056	[a]1,123

[a] Gross heating value at 0° C. and 760 millimeters pressure.

16. Honolulu Oil Co. well 7, sec. 4. Gas about 300 feet above top of oil zone B.
17. Honolulu Oil Co. well 1, sec. 6. "Dry" gas about 200 feet above top of oil zone B. California State Min. Bur. Bull. 69, p. 250, 1914.
18. Honolulu Oil Co. well 5, sec. 6. "Dry" gas about 200 feet above top of oil zone B. Sampled by G. S. Rogers, July, 1914; analyzed by G. A. Burrell, Bureau of Mines.
19. Honolulu Oil Co. well 7, sec. 6. "Wet" gas associated with oil of 31° B. gravity, chiefly in oil zone C. Sampled by G. S. Rogers, July, 1914; analyzed by G. A. Burrell, Bureau of Mines.
20. Honolulu Oil Co. well 5, sec. 8. Gas about 250 feet above top of oil zone B.
21. Honolulu Oil Co. well 6, sec. 8. Gas about 400 feet above top of oil zone B.
22. Honolulu Oil Co. well 7, sec. 8. Gas about 300 feet above top of oil zone B.
23. Honolulu Oil Co. well 3, sec. 10. Gas about 250 feet above top of oil zone B.
24. Honolulu Oil Co. well 4, sec. 10. Gas chiefly from horizon of oil zone C.
25. Honolulu Oil Co. well 1, sec. 14. Gas about 1,000 feet above top of oil zone B. Analyst, W. E. Perdew.
26. Standard Oil Co. well 2, sec. 16. Probably associated with oil in zone B. California State Min. Bur. Bull. 69, p. 251, 1914.
27. Honolulu Oil Co. well 1, sec. 24. Dry gas 1,500 feet or more above horizon of oil zone B. California State Min. Bur. Bull. 69, p. 250, 1914.

CHARACTER OF THE GAS IN RELATION TO ITS GEOLOGIC OCCURRENCE.

The only constituent of the Sunset-Midway gas which appears to vary in relation to its geologic occurrence is the carbon dioxide. The relative proportions of methane and ethane have little significance; the oxygen and nitrogen, though invariably low, are generally due in part to admixture of air; and the carbon monoxide, hydrogen, and ethylene reported in some samples, whether actually present or not, are stated to occur in amounts so small that they are of little importance. Carbon dioxide, however, which occurs in unusually large proportions, appears to vary markedly in different parts of the field. In the western portion of the field or near the outcrop, where the productive sands lie at shallow depths, it is invariably high, whereas in the Buena Vista Hills territory, where the sands lie deeper, it is much lower. In the writer's opinion most of the carbon dioxide has been formed by reaction between the oil and mineralized waters, and this marked increase near the outcrop is due to the fact that the reactions have been more vigorous there, as already described.

According to the conventional reaction between sulphate and hydrocarbons, as written on page 27, the sulphate is reduced to sulphide and an equivalent portion of the hydrocarbon is oxidized to carbon dioxide or carbonate. This theory is corroborated by the fact that the deeper oil-field waters in a broad zone near the outcrop carry large amounts of carbonate, while those farther east have evidently undergone a chemical change in which carbonate, derived from some outside source, has played a part. Furthermore, there is almost invariably sufficient carbonic acid to form bicarbonate exclusively in the waters near the oil zones, and in addition many of these waters contain a dissolved excess of carbon dioxide. Free carbon dioxide is present also in many of the waters close above the oil measures, but it has not been observed in the shallow surface waters, many of which are deficient in carbon dioxide and consequently contain some normal carbonate.

If the reduction of sulphate is to be ascribed to the action of hydrocarbons, the formation of carbonate is a necessary concomitant, and the presence of these unusual amounts of carbonate in the deeper oil-field waters is explained by this reaction. The conventional reaction, it is true, explains only the carbonate and not the excess of carbon dioxide, but the course of the reaction is unknown and it is quite possible that the hydrocarbons actually involved yield both of these end products. It is also possible that oxygenated waters coming into contact with the oil may cause direct oxidation of the hydrocarbons to carbon dioxide. Whatever the exact chemical change may be, it is clear that the largest amounts of carbonate in the waters, and of carbon dioxide in both waters and gas, occur near the outcrop, where waters can most easily come into contact with the oil and where the reaction would naturally be most vigorous.

Although the average carbon dioxide content of 20 gases from the Buena Vista Hills is only 5.5 per cent, 2 samples contain more than 10 per cent. These are not gases from beds above the oil measures and therefore nearest the surface, as perhaps might be expected, but are gases associated with the oil. If this condition is really widespread it suggests that the reaction between water and the hydrocarbons is initiated and perhaps carried on by reactive substances in the oil itself, and that the simple light paraffins of which the gas is composed, being stable and inert, are incapable of reacting with the water.

TEMPERATURE GRADIENT.

GENERAL PHASES.

It is well known that the temperature of the earth increases with depth beneath the surface at a more or less regular rate. It was formerly assumed that the normal increase is 1° F. for every 60 or 70 feet. As data have been accumulated, however, it has been found that so many local factors affect the rate of increase that it varies widely in different localities, and no normal rate can yet be established. Geologic factors such as the structure and lithology of the rocks, the proximity of recent igneous intrusions, and the presence of minerals that are subject to chemical alteration evidently affect the gradient, as well as less obvious factors such as the character of the topography and the proximity of large bodies of water.

Many more or less accurate measurements of the geothermal gradient have been made in different parts of the world, and Prestwich,[1] Höfer,[2] Koenigsberger and Mühlberg,[3] Tanasescu,[4] and others have compared them and have attempted to define some of the factors that cause variation. It is interesting to note that Koenigsberger and Mülhberg, after studying and correcting the measurements, conclude that the geothermal gradient is abnormally high[5] in oil fields and that temperature measurements may therefore be used in prospecting for oil. Their conclusions have not been generally accepted, owing to the facts that the data are very incomplete and that although the average of the known oil-field gradients is somewhat higher than that of gradients in other regions, there is a wide variation between gradients in different oil fields. Accordingly, the writer, in the hope of gaining an approximate idea of the gradient in the Sunset-Midway field, measured the temperature of the fluid produced by 130 oil and water wells. Measurements of this type are affected by many incidental factors and have little absolute value, but they are of considerable interest as showing a wide but fairly regular variation within the limits of a single field. To some extent they support the contention that oil-field gradients are unusually high; and in connection with the corroborative evidence already presented they help to explain this condition. The figures are therefore given in the following pages, with a brief discussion of the factors that have probably caused the wide variation between individual measurements, and also the general steepness of the average as compared with that in other regions.

TEMPERATURE MEASUREMENTS.

In the following tables are given the temperature of the fluid produced by 130 wells. The measurements were made with an ordinary standardized mercury thermometer. The temperature of the fluid was taken where the lead line discharged into the sump or tank; at most of the wells selected this point was within 20 feet of the mouth of the well, and at only one well was it more than 40 feet away. At the same time the method of operation of the well was noted and also the character of the oil—whether it was rich or poor in gas and whether or not accompanied by sand or by water.

The depth of the oil or water sand given in the tables is the mean depth of the producing zone. In some wells the producing zone is only 20 feet or so thick, but in others it is 200 feet thick, and there is usually no way of telling which part of the zone contributes the greatest part of the product. In the few wells which draw their product from several distinct sands scattered through a vertical range of several hundred feet the mean depth given is marked with a ± sign.

The mean annual air temperature of the district is 65° F.[6] Authorities differ as to whether the mean annual ground temperature at the surface is the same or greater or less than the mean annual air temperature, but the simplest assumption is that it is the same. Accordingly, the rate of increase with depth was computed by simply dividing the mean depth in feet of the producing zone by the temperature in degrees Fahrenheit of the fluid minus 65.

Inasmuch as the gradient appears to vary with distance from the outcrop of the producing sands the measurements are grouped in the following tables in order to bring out this variation. Thus Table 9 shows the gradient in the western part of the field, or within 2 miles of the outcrop; Table 10, the gradient in the central part, more than 2 miles and less than 4 miles from the outcrop; and Table 11, the gradient in the eastern part of the field, more than 4 miles from the outcrop. It should be reiterated that these determinations of the gradient, which are based simply on the temperature of the fluid at the mouth of the well, are subject to considerable error and have little absolute value. They should be considered in connection with the discussion of the factors influencing the accuracy of the observations given on pages 38–40.

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[1] Prestwich, J., On underground temperatures: Roy. Soc. London Proc., vol. 41, pp. 1–116, 1886; On underground temperatures: Collected papers on some controverted questions in geology, pp. 166–279, published separately, London, 1895.

[2] Höfer, Hans, The temperature in oil regions (translation by C. W. Washburne): Econ. Geology, vol. 7, p. 536, 1912. Also Engler-Höfer, Das Erdol, Band 2, p. 225, 1909.

[3] Koenigsberger, Joh., Normale und anormale Werte der geothermischen Tiefenstufe: Centralbl. Mineralogie Jahrbuch, 1905, pp. 673–679. Koenigsberger, Joh., and Mühlberg, Max, On the measurements of the increase of temperature in bore holes: Inst. Min. Eng. (England) Trans., vol. 39, pp. 617–644, 1910; Über Messungen der geothermischen Tiefenstufe: Neues Jahrb., Beilage Band 31, pp. 107–157, 1911.

[4] Tanasescu, I., Études préliminaires sur le régime thermique: Inst. Geol. Romanei Annarul, vol. 5, fasc. 1a, p. 111, 1912.

[5] Although the geothermal gradient should strictly be stated in units of temperature per unit of depth, it is customary to use the reciprocal statement, units of depth per unit of temperature—for example, feet per degree. A high or steep gradient is represented by a small number of feet per degree, such as 25, whereas a low gradient is represented by a large number, such as 100.

[6] Climatological data for the United States, vol. 3, No. 13, U. S. Dept. Agr. Weather Bureau, 1917.

TABLE 9.—*Geothermal gradient in the western part of the Sunset-Midway field*

[Based on temperature of oil produced by wells within 2 miles of the outcrop of the lowest producing oil sand.]

No.	Well.				Mean depth of oil sand.	Temperature of oil.	Depth per degree of increase in temperature.	Remarks.
	Location.			How operated.				
	Sec.	T.	R.					
					Feet.	° *F.*	*Feet.*	
1	15	31 S.	22 E.	Pumped	1,000±	95	33.3	Makes much sand.
2	15	31 S.	22 E.	do	750	85	37.5	
3	15	31 S.	22 E.	do	900	93	32.3	
4	15	31 S.	22 E.	do	900	88	39.3	Makes considerable sand.
5	15	31 S.	22 E.	do	880	89	36.8	Do.
6	14	31 S.	22 E.	do	1,475	93	52.8	Makes much sand. Oil very heavy.
7	14	31 S.	22 E.	do	1,200	95	40.0	Makes considerable sand.
8	23	31 S.	22 E.	do	1,500	89	62.6	
9	23	31 S.	22 E	do	1,630	94	56.3	Do.
10	23	31 S.	22 E.	do	1,450	92	53.7	
11	23	31 S.	22 E.	do	1,600	88	69.6	Makes some sand.
12	23	31 S.	22 E.	do	1,700	90	68.0	
13	23	31 S.	22 E.	do	1,800	93	64.4	Makes much sand.
14	23	31 S	22 E	do	1,840	91	70.8	
15	35	31 S.	22 E.	do	1,250	97	39.1	Makes no sand.
16	36	31 S.	22 E.	do	1,300	97	40.7	Makes very little sand.
17	35	31 S.	22 E.	do	1,080	98	32.7	Makes much sand.
18	36	31 S.	22 E.	do	1,050	94	36.2	Makes very little sand. Oil partly emulsion.
19	36	31 S.	22 E.	do	1,860	95	62.0	Makes little sand.
20	36	31 S.	22 E.	do	1,750±	90	70.1	Temperature measured in tank; probably too low.
21	30	31 S.	23 E.	do	2,860	88	124.5	Makes little sand. Oil gassy.
22	31	31 S.	23 E.	do	1,940	102	52.2	Makes considerable sand.
23	31	31 S.	23 E.	do	1,900	89	79.2	Makes little sand.
24	1	32 S.	22 E.	do	510	98	15.5	Makes considerable sand.
25	1	32 S.	22 E.	do	650	84	34.2	Do.
26	1	32 S.	22 E.	do	760	90	30.5	Makes much sand.
27	1	32 S.	22 E.	do	960	88	41.7	Makes some sand.
28	1	32 S.	22 E.	do	910	86	43.3	Makes considerable sand.
29	6	32 S.	23 E.	do	890	88	38.7	Do.
30	6	32 S.	23 E.	do	2,100	90	84.0	Makes much sand.
31	6	32 S.	23 E.	do	1,870	98	56.7	
32	5	32 S.	23 E.	do	2,200	94	75.9	Makes no sand
33	5	32 S	23 E	do	2,210	95	73.7	Makes some sand
34	8	32 S	23 E	do	990	88	43.0	Makes considerable sand.
35	17	32 S.	23 E.	do	840	98	25.5	Makes much sand.
36	21	32 S.	23 E.	do	1,050	84	55.2	Makes considerable sand.
37	23	32 S.	32 E.	do	950	101	26.4	Makes much sand.
38	26	32 S.	23 E.	do	850	93	30.4	Do.
39	26	32 S.	23 E.	do	1,000	91	38.5	Do.
40	26	32 S.	23 E.	do	900	84	47.4	Makes much sand. Oil gassy.
41	23	32 S.	23 E.	do	1,200	89	50.0	Makes considerable gas. Very little sand.
42	23	32 S.	23 E.	do	1,250	89	52.0	Makes some gas. Very little sand.
43	23	32 S.	23 E.	do	1,230±	84	64.8	Makes no sand.
44	24	32 S.	23 E.	do	1,800	92	66.6	Makes very little gas. No sand.
45	26	32 S.	23 E.	do	1,070	93	38.3	Makes considerable sand.
46	26	32 S.	23 E.	do	975	90	39.0	Do.
47	26	32 S.	23 E.	do	1,080	90	43.2	Do.
48	26	32 S.	23 E.	do	1,250	96	40.3	Fluid 75 per cent water.
49	26	32 S.	23 E.	do	1,150	90	46.0	Makes some sand. Considerable gas.
50	35	32 S.	23 E.	do	860±	95	28.7	Makes considerable sand. Oil very heavy.
51	26	32 S.	23 E.	do	1,080	94	37.3	Makes much sand.
52	26	32 S.	23 E.	do	1,060	97	33.1	Do.
53	26	32 S.	23 E.	do	1,100	93	39.3	Makes some sand. Oil gassy.
54	25	32 S.	23 E.	do	1,220	86	58.0	Oil gassy.
55	25	32 S.	23 E.	do	1,350	92	50.0	Makes some sand.
56	25	32 S.	23 E.	do	1,400	91	53.8	
57	25	32 S.	23 E.	do	1,380	97	43.2	Do.
58	25	32 S.	23 E.	do	1,350	92	50.0	Fluid 25 per cent water. Some sand.
59	25	32 S.	23 E.	do	1,350	97	42.2	Fluid 75 per cent water. Little sand.
60	25	32 S.	23 E.	do	1,450	101	40.3	Fluid 75 per cent water. Some sand.
61	25	32 S.	23 E.	do	1,450	93	51.8	Makes some sand.
62	2	11 N.	24 W.	do	520	85	26.0	Makes considerable sand.

TABLE 9.—*Geothermal gradient in the western part of the Sunset-Midway field*—Continued.

No.	Well.				Mean depth of oil sand.	Temperature of oil.	Depth per degree of increase in temperature.	Remarks.
	Location.			How operated.				
	Sec.	T.	R.					
					Feet.	° *F.*	*Feet.*	
63	2	11 N.	24 W.	Compressed air.....	800	87	36. 3	Makes much sand and water.
64	2	11 N.	24 W.	Pumped............	1, 200	90	48. 0	Makes much sand.
65	2	11 N.	24 W.	.....do.............	1, 130	90	45. 2	Do.
66	1	11 N.	24 W.	.....do.............	1, 025	87	46. 6	
67	36	12 N.	24 W.	.....do.............	1, 100	86	52. 4	
68	2	11 N.	24 W.	.....do.............	770	84	40. 5	
69	1	11 N.	24 W.	.....do.............	700	85	35. 0	
70	1	11 N.	24 W.	.....do.............	1, 180	91	45. 4	Oil gassy.
71	1	11 N.	24 W.	.....do.............	1, 170	88	50. 9	Do.
72	12	11 N.	24 W.	.....do.............	1, 170	91	45. 0	Makes much sand.
73	12	11 N.	24 W.	....	1, 050	85	52. 5	Do.
74	12	11 N.	24 W.	Flows..............	1, 000	78	76. 9	Makes considerable sand. Oil very gassy.
Average, 74 measurements							48. 4	

TABLE 10.—*Geothermal gradient in the central part of the Sunset-Midway field.*

[Based on temperature of oil produced by wells more than 2 miles and less than 4 miles east of the outcrop of the lowest producing oil sand.]

No.	Well.				Mean depth of oil sand.	Temperature of oil.	Depth per degree of increase in temperature.	Remarks.
	Location.			How operated.				
	Sec.	T.	R.					
					Feet.	° *F.*	*Feet.*	
75	24	31 S.	22 E.	Pumped............	2, 000	93	71. 4	Makes considerable sand.
76	10	32 S.	23 E.	.....do.............	2, 830	84	149. 0	Makes some water, probably from above the oil.
77	1	32 S.	23 E.	Flows..............	3, 175	98	96. 1	Makes much gas.
78	13	32 S.	23 E.	Pumped............	2, 950	90	118. 0	Makes no sand.
79	24	32 S.	23 E.	.....do.............	2, 270	94	78. 2	Oil gassy.
80	19	32 S.	24 E.	....	2, 270	89	94. 6	Makes little sand.
81	32	32 S.	24 E.	Pumped............	2, 940	101	81. 8	Makes some sand.
81A	25	12 N.	24 W.	Flows..............	2, 225	92	82. 4	"Wild" gusher.
82	26	12 N.	24 W.	Pumped............	1, 950	87	88. 8	Makes very little sand.
83	36	12 N.	24 W.	.....do.............	1, 980	92	73. 4	
84	36	12 N.	24 W.	.....do.............	1, 700	90	68. 0	
85	33	32 S.	24 E.	.....do.............	2, 450	100	70. 0	
86	25	12 N.	24 W.	.....do.............	2, 180	95	72. 7	
87	25	12 N.	24 W.	.....do.............	2, 260	83	125. 5	
88	6	11 N.	23 W.	.....do.............	2, 580	84	135. 8	
89	31	12 N.	23 W.	.....do.............	1, 860	86	88. 6	Oil gassy.
90	31	12 N.	23 W.	.....do.............	1, 625	91	62. 5	Do.
91	32	12 N.	23 W.	.....do.............	1, 820±	97	56. 9	Considerable water.
92	32	12 N.	23 W.	.....do.............	2, 600	93	92. 9	
93	32	12 N.	23 W.	Flows..............	2, 560	89	106. 5	High gas pressure.
94	32	12 N.	23 W.	.....do.............	3, 120	115	62. 4	High gas pressure. Makes practically no sand.
95	5	11 N.	23 W.	Pumped............	2, 400	100	68. 5	
96	4	11 N.	23 W.	Flows..............	3, 015	98	91. 3	"Wild" gusher, making about 40,000 barrels of fluid, about 75 per cent emulsion. Temperature measured in ditch 100 feet from well.
Average, 22 measurements							88. 7	

TABLE 11.—*Geothermal gradient in the eastern part of the Sunset-Midway field.*

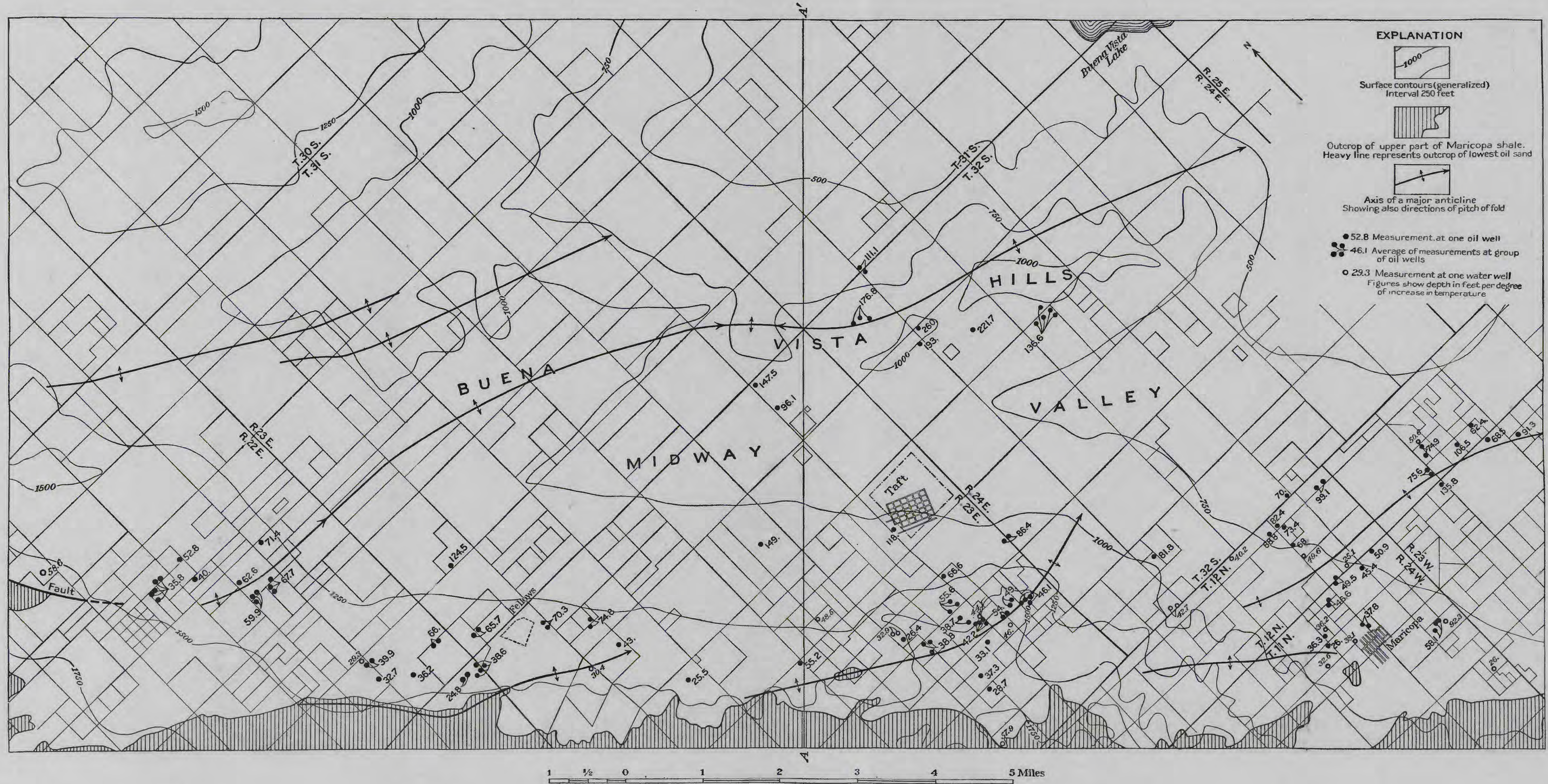
[Based on temperature of oil produced by wells more than 4 miles east of the outcrop of the lowest producing oil sand.]

No.	Well.				Mean depth of oil sand.	Temperature of oil.	Depth per degree of increase in temperature.	Remarks.
	Location.			How operated.				
	Sec.	T.	R.					
					Feet.	°*F.*	*Feet.*	
97	1	32 S.	23 E.	Flows	2,660	83	147.5	Makes much gas and considerable sand.
98	6	32 S.	24 E.	Pumped	2,430	79	173.5	Makes considerable gas and very little sand.
99	6	32 S.	24 E.	Flows	2,380	75	238.0	Makes much gas and some sand.
100	6	32 S.	24 E.	do	2,375	85	118.8	Makes much gas and very little sand.
101	32	31 S.	24 E.	do	3,000	91	115.4	Makes much gas. Temperature measured after oil had passed through gas trap.
102	5	32 S.	24 E.	do	2,990	93	106.8	Makes considerable gas.
103	7	32 S.	24 E.	do	2,510	78	193.0	Do.
104	8	32 S.	24 E.	do	2,600±	75	260.0	Makes a great deal of gas and some sand.
105	8	32 S.	24 E.	do	2,660	77	221.7	Makes a great deal of gas.
106	16	32 S.	24 E.	do	2,780±	88	120.9	Oil gassy.
107	9	32 S.	24 E.	do	2,575	79	183.9	Makes a little sand.
108	16	32 S.	24 E.	Pumped	2,650±	82	155.9	Makes very little sand.
109	16	32 S.	24 E.	Flows	2,575	89	107.3	Oil very gassy. Makes some sand.
110	16	32 S.	24 E.	do	2,640	88	114.8	Oil very gassy. Makes little sand.
Average, 14 measurements							161.2	

TABLE 12.—*Geothermal gradient in western part of Sunset-Midway field.*

[Based on temperature of water produced by 20 water wells. Wells operated by compressed air except as otherwise indicated.]

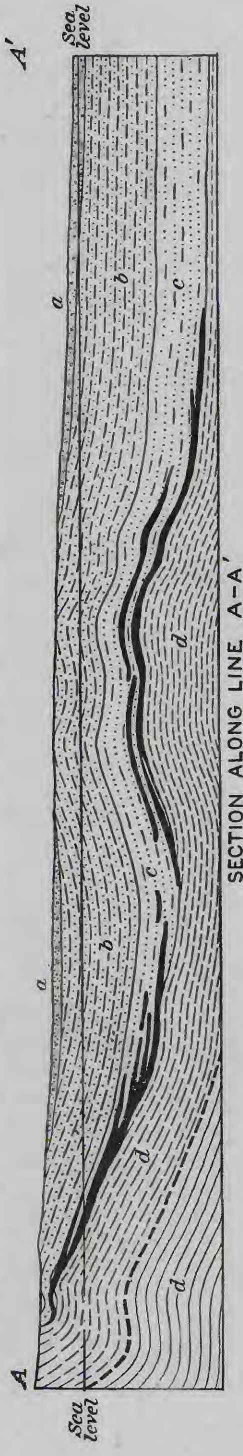
No.	Well.	Location.			Mean depth of water sand.	Temperature of water.	Depth per degree of increase in temperature.	Remarks.
		Sec.	T.	R.				
					Feet.	°*F.*	*Feet.*	
111	General Petroleum (Carnegie).	9	31 S.	22 E.	3,870	131	58.6	
112	Associated No. 1	35	31 S.	22 E.	1,610	120	29.3	
113	Stratton No. 3	7	32 S.	23 E.	760±	90	30.4	Probably a mixture of waters from above and below the oil.
114	General Petroleum (Foxtail) No. 2.	15	32 S.	23 E.	1,790	102	48.5	
115	Traders No. 71	23	32 S.	23 E.	1,300	99	38.2	Makes about 10 per cent oil. Water has probably migrated up from lower bed.
116	Traders No. 81	23	32 S.	23 E.	1,100	101	30.6	Makes about 5 per cent oil. Water has probably migrated up from lower bed.
117	Mascot No. 17	26	32 S.	23 E.	1,500	99	44.1	
118	Crescius No. 6	25	32 S.	23 E.	1,470	97	46.0	
119	August (California Amalgamated) No. 2.	35	32 S.	23 E.	1,100	84	57.9	Sulphur water. Probably includes considerable water from shallow depths.
120	August No. 3	31	32 S.	24 E.	1,480	105	37.0	
121	August No. 4	31	32 S.	24 E.	1,500±	94	51.8	Probably mixed with upper waters.
122	Standard (Monarch) C	26	12 N.	24 W.	2,170	119	40.2	
123	Standard (M. & M.) No. 7	36	12 N.	24 W.	2,630±	118	49.6	Water from sands between 2,385 and 2,870 feet.
124	Standard (Wellman)	36	12 N.	24 W.	1,080	108	25.1	Makes considerable oil.
125	Midway Northern No. 5	32	12 N.	23 W.	2,530	115	50.6	Water flowing between casings
126	Standard (Occidental) No. 4.	2	11 N.	24 W.	1,520	107	36.2	Water from sands between 1,485 and 1,556 feet.
127	Ida May	2	11 N.	24 W.	1,600±	114	32.6	Well pumped. Exact depth of water sand unknown.
128	Adeline No. 31	2	11 N.	24 W.	1,865	114	38.1	
129	Good Roads No. 14	12	11 N.	24 W.	3,600	104	92.3	Flowing between casings and probably cooled during ascent.
130	Union (Diamond) No. 2	13	11 N.	24 W.	650	90	26.0	Sulphur water. Well pumped.
Average, 20 measurements							43.2	
Average of Nos. 111, 112, 114, 118, 120, 122, 123, 126, and 128, assuming that temperature of water has been lowered 2° by the compressed air.							41.0	



1 ½ 0 1 2 3 4 5 Miles

MAP SHOWING RATE OF TEMPERATURE INCREASE WITH DEPTH IN DIFFERENT PARTS OF THE SUNSET-MIDWAY FIELD.

Based on temperature of fluid at mouth of well and therefore only approximate. Geology adapted from Plate III, Professional Paper 116.



SECTION ALONG LINE A–A'

a Alluvium *b* Paso Robles ("Tulare") formation *c* Etchegoin formation (contains chief petroleum reservoirs of the district) *d* Maricopa shale

The foregoing figures are of interest as showing (1) the wide variation in the gradient in different parts of the field, and (2) the fact that this variation appears to bear a definite relation to distance from the outcrop of the oil sands. Thus, in the zone within 2 miles of the outcrop the calculated rate of temperature increase averages 48.4 feet per degree; in the zone between 2 and 4 miles away the average rate is 88.7 feet; and in the zone more than 4 miles away it is 161.2 feet. These data are presented graphically in Plate I, which shows the temperature gradient in different parts of the field. Owing to the small scale on which the map is reproduced, measurements made at adjoining wells have been averaged and are not shown separately. The map brings out strikingly the decrease in the calculated gradient with distance from the outcrop and shows that despite local irregularities the variation as a whole is surprisingly uniform. This variation is probably due largely to incidental factors which have affected the accuracy of the observations but in part to chemical reactions which have raised the gradient in the zone along the outcrop.

The following table, inserted for purposes of comparison, shows the rate of temperature increase in some other oil fields and in several districts in which the gradient is supposed to be "normal." Each of the oil-field measurements cited was selected as typical of a number of observations in the locality, and the list is probably a representative one of recorded gradients in oil fields. The gradients in the other regions cited were selected chiefly because they are based on fairly accurate measurements in deep wells and are apparently not affected by any abnormal conditions. It happens that all but one of the gradients cited are rather closely concordant and average about 61 feet per degree, but this may or may not represent the true normal gradient for the globe.

TABLE 13.—*Geothermal gradient in oil fields and in other regions.*

	Depth of well.	Temperature at bottom.	Depth per degree of increase in temperature.	Remarks.	Observer.
Oil fields:	*Feet.*	*°F.*	*Feet.*		
Sunset-Midway, Calif.	1, 470–3, 870	97–131	41. 0	Based on average of corrected temperature of water in 9 wells in western part of field.	Rogers.
Bartlesville, Okla.	1, 275	84	51. 0	Oil well	Woodruff.[a]
Batson, Tex.	1, 100	101	34. 5	Oil and water well	Fenneman.[b]
Florence, Colo.	....	....	44. 0	Based on average temperature of oil produced by many wells.	Washburne.[c]
Findlay, Ohio	3, 000	82. 1	95. 8	Precise measurements	Johnston.[d]
Wheeling, W. Va.	4, 462	110. 15	75. 2	Precise measurements in dry hole	Hallock.[e]
Vera Cruz, Mexico	2, 276	122. 9	48. 6	Furbero oil field	Mühlberg.[f]
Pechelbronn, Alsace	1, 692	....	25. 3–38. 3	Asphaltic shale oil	Branca.[g]
Campina, Rumania	2, 726	99. 3	54. 7	Dry hole	Tanasescu.[h]
Lucacesti-Zemes, Rumania.	1, 575	70. 7	69. 8	Oil and water well	Do.
Bibi-Eibat, Apsheron Peninsula, Russia.	2, 695	114. 5	47. 7	Thermometer submerged for 11 hours in oil well.	Goloubjatnikov.[i]
Samarinda, Borneo	2, 214	....	51. 0	Oil well producing light paraffin oil.	Mühlberg.[f]
Echigo, Japan	2, 381	118. 6	39. 2	....	Kawamura.[j]
Other districts:					
Bay City, Mich.	3, 455	97. 0	68. 5	....	Lane.[k]
Charleston, S. C.	2, 001	99. 7	57. 5	Temperature of outflowing water	Knapp.[l]
Ames, Iowa	2, 100	63. 4	129. 6	Precise measurements	Beyer.[m]
Maris, Holland	4, 265	138	50. 5	do	(n)
Schladebach, Germany	5, 630	133. 9	67. 2	do	Dunker.[o]
Paruschowitz, Germany	6, 427	156. 7	62. 1	do	Henrich.[p]

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[a] Personally communicated by N. H. Darton.

[b] Fenneman, N. M., Oil fields of the Texas-Louisiana Gulf Coastal Plain: U. S. Geol. Survey Bull. 282, p. 56, 1906.

[c] Washburne, C. W., The Florence oil field, Colo.: U. S. Geol. Survey Bull. 381, p. 530, 1910.

[d] Johnston, John, and Adams, L. H., On the measurement of temperatures in bore holes: Econ. Geology, vol. 11, p. 741, 1916.

[e] Hallock, William, Deep well at Wheeling, W. Va.: Am. Jour. Sci., 3d ser., vol. 43, pp. 234–236, 1892; School of Mines Quart., vol. 18, pp. 148–153, 1897.

[f] Konigsberger, J., and Mühlberg, M., On measurements of the increase of temperature in bore holes: Inst. Min. Eng. (England) Trans., vol. 39, pp. 617–644, 1910.

[g] Branca, W., Ver. Naturkunde in Württemberg Jahreshefte, 1897, p. 42.

[h] Tanasescu, I., Étudés préliminaires sur le régime thermique: Inst. Geol. Romanei Annarul, vol. 5, fasc. 1a, p. 111, 1912.

[i] Goloubjatnikov, D., Observations géothermiques à Bibi-Eibat et Sourakhany [in Russian]: Com. géol. Mém., nouv. sér., livr. 141, p. 32, 1916. The observation cited is close to the average of several hundred careful measurements. The average gradient in the neighboring Sourakhany field is 44.5.

[j] Kawamura, On the geothermic gradient in the Echigo oil fields, Japan [in Japanese]: Geol. Soc. Tokio Jour., vol. 19, pp. 179–185, 222–227, 1912.

[k] Lane, A. C., The geothermal gradient in Michigan: Am. Jour. Sci., 4th ser., vol. 9, p. 435, 1900.

[l] Stephenson, L. W., A deep well at Charleston, S. C.: U. S. Geol. Survey Prof. Paper 90, p. 70, 1915.

[m] Beyer, S. W., Iowa Agricultural College water supply, pp. 13–14, Ames, 1897.

[n] Temperatur-Metingen in diepe Boorgaten: Ryksopsporing van Delfstoffen Jaarverslag, 1912, pp. 27–28.

[o] Dunker, E., Ueber die Temperatur-Beobachtungen im Bohrloche zu Schladebach: Neues Jahrb., 1889, Band 1, pp. 29–47.

[p] Henrich, F., Ueber die Temperaturverhältnisse in dem Bohrloch Paruschowitz V: Zeitschr. prakt. Geologie, vol. 12, pp. 316–320, 1904.

It will be noted that the oil-field gradients shown in Table 13 differ widely and are not very much higher than those in regions in which no oil occurs. The high gradient at Batson, Tex., is due to the fact that the oil field is on a salt dome and the water has probably ascended steeply from a considerable depth. The Ohio and West Virginia measurements, which are representative of a large number of very careful observations in the Appalachian fields, are unusually low. The gradient in the Alsace fields appears to be unusually steep, to judge from the many measurements that have been made, but that in the Rumanian fields approximates the average in non oil-bearing regions. The measurements in Russia and Borneo indicate a gradient slightly higher than normal, and those in Japan show a rather steep gradient. Although the average of the oil-field gradients is probably somewhat higher than normal, it appears improbable that the difference is great enough or regular enough to make temperature measurements of much practical value in prospecting for oil.

FACTORS AFFECTING ACCURACY OF OBSERVATIONS.

Several factors injure the value for geothermal calculations of measurements of the temperature of fluid made at the mouth of a well. This is particularly true of oil wells, on account of the cooling effect of the expanding gas. The method by which the fluid is brought to the surface also affects the temperature. Furthermore, calculations of the geothermal gradient based on such measurements are generally open to the criticism that the depth from which the fluid is derived can not be determined within many feet.

Measurements of the temperature of water generally represent more nearly the true earth temperature than those of oil. Tests made on wells by Fuller[1] "show that with a steady and moderately rapid flow of water through a pipe with a diameter of one-half inch the change in temperature due to a difference of 15° in the surrounding material amounts to only about 1° for 1,000 feet." As the pipes through which the water is conducted to the surface in the wells examined by the writer are generally between 3 and 6 inches in diameter, they carry a much larger volume of water, which would retain its heat longer, and the loss of heat during ascent in such pipes is probably negligible. The temperature of the water produced by a flowing well should therefore furnish a fairly satisfactory basis for calculating the gradient, provided the source of the water is definitely known and no surface drainage is included. Nearly all the wells listed in Table 12, however, were operated by compressed air, which doubtless lowers the temperature of the water somewhat. The writer's observations were made in August, 1914, when the normal air temperature was 100° or more. As the air is generally compressed and delivered immediately to the well, it probably loses little heat on the way, and after expanding in the well is only slightly below its original temperature. The water is doubtless cooled somewhat by the air during ascent, but as the temperatures of the two are not very different, the loss is probably small. If the measured temperature of the water at the surface is increased by 2° or 3°, the true temperature at its original horizon will probably be closely approximated.

Most of the oil wells in the Sunset-Midway field, especially in the western and central portions, are operated by pumping, and as the loss in mechanical efficiency of the pump is converted into heat the temperature of the oil is thereby raised to some extent. Furthermore, most of the wells make more or less sand, which must increase the friction somewhat, despite the fact that the pump is working in a lubricating medium. The oil in wells making a large quantity of sand is generally a few degrees warmer than that in wells making no sand, though the observed relation is vague. Even if the loss in mechanical efficiency of the pump is 50 per cent, the oil theoretically will be heated less than 5°. This factor has doubtless operated to raise the apparent gradient in the zone nearest the outcrop, but the modification in the gradient as measured in wells of average depth in this district would seldom amount to more than 10 feet per degree.

The greatest alteration in the temperature of oil during its ascent to the surface is effected by expanding gas, and variations in the amount

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[1] Fuller, M. L., Amount of free water in the earth's crust: U. S. Geol. Survey Water-Supply Paper 160, p. 64, 1906.

of gas doubtless account for much of the variation in the gradient in different parts of the field. (See Pl. I.) Nearly all the wells in the Buena Vista Hills (Table 11) were flowing when visited by the writer and naturally made large quantities of gas, whereas nearly all of those near the outcrop (Table 9) were pumped and made relatively little gas. Little information is available as to the proportions of oil and gas made by any of the wells, but those in the Buena Vista Hills probably averaged between 400 and 800 cubic feet of gas per barrel of oil, and those in the western part of the field probably averaged only one-fifth or one-tenth as much. Furthermore, as the gas pressure in the Buena Vista Hills was still high, the expansion of the gas in the wells was greater than in the older territory in the western part of the field.

The cooling effect of expanding gas is theoretically great, especially if part of the gas is dissolved in the oil. To what extent the oil in the Sunset-Midway field is actually cooled by the expanding gas, however, is not clear. Certainly in the western part of the field its temperature can not have been greatly altered, for the average gradient calculated from measurements at 74 oil wells is only slightly lower than that based on 20 water wells which are unaffected by gas. Furthermore, measurements 93, 94, and 96 (Table 10) were made at wells flowing more than 7,000 barrels a day of very gassy oil, yet the gradients based on these measurements are not nearly as low as those based on apparently similar observations made at the Buena Vista wells. On the other hand, measurements 98 and 108 (Table 11) were made in the Buena Vista Hills at wells in which the gas pressure had diminished so much that the well no longer flowed, yet the gradients based on these observations approximate the average of those at neighboring wells.

Although experimental data on the cooling effect of gas are scanty, a direct observation, kindly communicated by Mr. C. E. Van Orstrand, is of interest. Mr. Van Orstrand, in the course of a very careful study of the geothermal gradient in the Appalachian oil fields, measured temperatures at various depths in a well making about 1 barrel of oil and 570,000 cubic feet of gas a day. At the point at which the flow of gas entered the well he observed an abrupt drop in temperature of 9° F., and he concludes that this represents practically all the cooling powers of the gas under a decrease in pressure of several hundred pounds. In some other wells which made both gas and oil the drop in temperature amounted to only 5° or 6°.

In view of the considerations set forth above it seems probable that in the Buena Vista Hills the extra loss in temperature due to the expansion of gas does not exceed 10° F. If 10° is added to the temperature of the oil at the wells listed in Table 11, the average gradient for the 14 wells becomes 97 feet instead of 161 feet. This gradient, however, is still far below that derived from wells near the outcrop (48.4 feet) or even that shown by wells in the intermediate zone (88.7 feet), and the increment of heat due to pump friction accounts for only a small fraction of the difference. It is evident that a much more liberal correction might be made for the cooling effect of gas in the Buena Vista Hills without entirely wiping out the difference in the calculated gradients.

CHEMICAL REACTIONS AFFECTING THE GEOTHERMAL GRADIENT.

Although the influence of many factors on the geothermal gradient has been recognized in one place or another, the data are yet too scanty to permit a satisfactory evaluation of their relative importance. In most oil fields the most obvious cause of high gradients—proximity to recently intruded igneous rocks, or the presence of thermal (magmatic) ascending waters—need not be considered. Rise in temperature due to orogenic movements may, however, be an important factor in Tertiary oil fields which have suffered recent deformation. Tanasescu[1] suggests that as petroleum [oil and gas] is compressible it may suffer considerable reduction in volume through orogenic movement, and that this reduction in volume would be transformed into heat—in other words, that the heating of the rocks by earth movements is accentuated if petroleum is present. He calculates that if a deposit of oil and gas is subjected to sufficient pressure to cause a reduction to two-thirds of its original volume its temperature will be raised 120° F., and that reduction to one-third of its original volume will raise the temperature 327° F. It is very improbable that so great a reduction in volume could be brought about by earth strains, for movements

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[1] Op. cit.

of the fluids would probably take place and hydrostatic equilibrium would be restored; but it does seem possible that earth movements in comparatively recent geologic time may still affect the gradient in some oil fields. This possibility may in part explain the fact that the gradient in the Appalachian fields, which are in Paleozoic rocks that have undergone no recent deformation, is unusually low, whereas the gradient in the other oil fields studied, which are in more or less deformed Tertiary or Cretaceous rocks, is unusually high.

If oil-field gradients in general prove to be high it is possible that radioactivity has been a factor. Boyle[1] has shown that radium emanation is about fifty times as soluble in crude oil as in water and that thorium emanation is also considerably more soluble. Oil may thus tend to concentrate whatever radium and thorium emanation may be present in the rocks, and the heating effects of these substances might be sufficient to cause a perceptible increase in the geothermal gradient. Although little weight can yet be attached to this suggestion, it would seem that an investigation of the radioactivity of crude oils might be of value.

Variation in the gradient within the limits of a field must, however, be ascribed to other causes, the most effective of which is probably the heat of chemical reaction. It has already been shown that both the oil and the water have undergone certain chemical changes, which have been and probably are now most vigorous in the zone nearest the outcrop. Some of these reactions are perhaps endothermic, absorbing heat; others are exothermic, generating heat. As the series of reactions as a whole is certainly exothermic, the higher gradient near the outcrop seems to be adequately explained. Among the chief reactions involved are these:

1. Reduction of sulphate to sulphide and oxidation of hydrocarbon to carbonate. As the exact course of this reaction is unknown its thermal value can not be determined. The reaction as written on page 27 would, according to Wells,[2] yield several hundred calories and would therefore be weakly exothermic.

2. Oxidation of hydrogen sulphide to sulphur. This reaction is strongly exothermic, yielding 59,100 calories.[3]

3. Reaction of the oil with sulphur, leading to the formation of sulphur compounds. The thermal character of this reaction is unknown.

4. Oxidation of the oil by oxygen-bearing waters, probably a rather strongly exothermic reaction.

5. Condensation or polymerization of the hydrocarbon molecule through the action of sulphur or oxygen, or in other ways. According to Berthelot[4] the polymerization of acetylene (C_2H_2) to benzene (C_6H_6) produces 163 calories, and other similar changes are also known to be exothermic. In Stremme's opinion[5] such reactions may account for a higher geothermal gradient in oil fields.

As the net thermal value of these reactions is unknown, it is impossible to estimate their quantitative effect. It is significant, however, that oil nearest the outcrop and highest in sulphur is almost invariably hotter in proportion to its depth than that farther away. Similarly, water containing hydrogen sulphide (sulphur water) is in general abnormally warm unless it is mixed with shallow (sulphate) waters. On the other hand, the oil low in sulphur and the water from which all sulphate and hydrogen sulphide have been removed are usually much cooler in proportion to their depth. Though much or most of the difference in the calculated gradient in different parts of the field is undoubtedly due to incidental factors, as already explained, the conclusion that the geothermal gradient has been affected by chemical reactions seems unavoidable.

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[1] Boyle, R. W., Note on the solubility of radium emanation in liquids: Royal Soc. Canada Trans., 3d ser., vol. 3, sec. 3, p. 75, 1909. See also McLennan, J. C., On the radioactivity of natural gas: Nature, vol. 70, p. 151, 1914; Burton, E. F., A radioactive gas from crude petroleum: Philos. Mag., 6th ser., vol. 8, p. 498, 1904; Himstedt, F., Über die radioaktive Emanation der Wasser- und Ölquellen: Annalen der Physik, 4th ser., vol. 13, p. 573, 1904; also in Physikal. Zeitschr., vol. 5, p. 210, 1904.

[2] Wells, R. C., personal communication.

[3] Becker, G. F., Geology of the quicksilver deposits of the Pacific slope: U. S. Geol. Survey Mon. 13, p. 254, 1888.

[4] Berthelot, M., Thermo-chimie, vol. 1, pp. 486-492, 1897.

[5] Stremme, H., Das polymerisierende Erdöl als Wärmquelle im Erdboden: Centralbl. Mineralogie, 1908, p. 271.

OIL-FIELD WATERS.

SCOPE OF DISCUSSION.

One of the most important problems in the development of the California oil fields is that of determining the position of the water-bearing strata in relation to those that carry the oil. In most localities several water-bearing sands are intercalated in the sediments above the oil measures, and water sands also occur some distance below; in many places one or more of the sands in the oil measures are occupied by water, though some distance away the sand at the same horizon contains oil. In sinking a well through this complex it is difficult to prevent the water, which may be under a high head, from entering the oil sands, and if it does it may drive the oil some distance back and so ruin a considerable tract of land. Although difficulty in shutting out the water is experienced in every oil field it seems to be accentuated in the California fields by the practically unconsolidated nature of the sediments, and at the same time, perhaps because of the chemical character of the oil itself, the invasion of water into the oil sands in those fields seems to exercise a particularly harmful effect on production.

Oil-field waters may be studied from several different points of view, each of which leads to conclusions of value. Determination of the position of the principal water sands with relation to the oil, which is usually possible from a study of the well logs, is of course of primary importance. Investigations of the chemical character of the waters have also proved to be of direct value, for it has been found that the source of a water is indicated in a general way by its composition. Studies of the manner in which water gains access to the oil sands and of its effect on the productivity of the sands are concerned partly with geologic and partly with technologic factors. Investigations of the best methods of excluding water from the well, which are of most immediate interest to the operator, are strictly technologic.

The stratigraphic position of the main water sands in relation to that of the oil sands is discussed by Mr. Pack in Part I of this report, and the chemistry of the water will be discussed in this chapter. Although the field work on which this report is based also included a survey of water conditions throughout the field, it is felt that details of the appearance, source, effects, etc., of water in individual wells have little permanent interest. The constantly changing water conditions are being closely watched by officials of the California State Mining Bureau,[1] whose reports contain much detailed information on the subject. Accordingly only the general principles governing the invasion of water and its effects on production will be considered here. These matters and also the problem of shutting out the water from the wells have been discussed in several reports of the Bureau of Mines,[2] and of the California State Mining Bureau, as well as in numerous recent papers in the periodical press.

HYDROLOGIC RELATIONS OF THE FIELD.[3]

The Sunset-Midway field lies on the west side of San Joaquin Valley, which is a portion of the great nearly level floored depression that lies in the central part of California. The northern two-thirds of the valley is drained by San Joaquin River, but the southern, more arid third has no surface outlet under normal conditions, and the surface waters accumulate in the depressions occupied by Buena Vista Lake, just east of the field, and Tulare Lake, some 50 miles to the north. The streams that drain into the valley from the Sierra Nevada on the east carry about all the surface water that reaches it, for the streams on the west side are shorter and practically dry during the greater part of the year.

A large portion of the water that drains into San Joaquin Valley sinks into the sand and silt of the valley floor and joins the under-

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[1] McLaughlin, R. P., California State Min. Bur. Bull. 73, 1917; Bull. 82, 1918.

[2] Lewis, J. O., and McMurray, W. F., The use of mud-laden fluid in oil and gas wells: Bur. Mines Bull. 134, 86 pp., 3 pls., 18 figs., 1916.

Tough, F. B., Methods of shutting off water in oil and gas wells: Bur. Mines Bull. 163, 122 pp., 20 pls., 7 figs., 1918.

Arnold, Ralph, and Garfias, V. R., The cementing process of excluding water from oil wells, as practiced in California: Bur. Mines Tech. Paper 32, 12 pp., 1 fig., 1913.

Pollard, J. A., Arnold, Ralph, and Garfias, V. R., The prevention of waste of oil and gas from flowing wells in California, with a discussion of special methods used: Bur. Mines Tech. Paper 42, 15 pp., 2 pls., 4 figs., 1913.

Pollard, J. A., and Heggem, A. G., Mud-laden fluid applied to well drilling: Bur. Mines Tech. Paper 66, 21 pp., 12 figs., 1914.

Arnold, Ralph, and Garfias, V. R., Methods of oil recovery in California: Bur. Mines Tech. Paper 70, 57 pp., 7 figs., 1914.

[3] For a complete account of the underground waters of San Joaquin Valley see Mendenhall, W. C., Dole, R. B., and Stabler, Herman, Ground water in San Joaquin Valley, Calif.: U. S. Geol. Survey Water-Supply Paper 398, 1916.

ground circulation, which follows the surface flow in general direction but at a far slower rate. The rate of movement of underground water is governed by several factors, important among which are the gradient of the slope, the shape and size of the materials through which the water must flow, and the freedom of the outlet by which it escapes. In San Joaquin Valley all these factors militate against rapid flow; the gradient is low, the materials are generally fine, and the outlet at San Francisco Bay is narrow. As a result of these conditions the ground-water circulation is abnormally sluggish, the deeper waters being highly mineralized and practically ponded, especially near the north end of the valley.

As the west side of the valley is a region of very scanty rainfall, practically all the drainage sinks beneath the surface before reaching the valley proper and circulates through the great thickness of sedimentary formations described by Mr. Pack in Part I of this report. These strata contain a large amount of disseminated gypsum and other sulphates, which are readily dissolved by the waters leaching through them. All the water that drains from the west side of the valley is therefore high in mineral matter, predominantly sulphates. Many of the shallower waters in the Sunset-Midway field are notable for their very high proportion of sulphate.

Rain water falling on the upturned and truncated edges of the sedimentary formations in the Temblor Range, west of the Sunset-Midway district, naturally tends to enter the strata and percolate down into San Joaquin Valley, becoming a part of the underground circulation of the valley and finally reaching the ocean at San Francisco. Inasmuch, however, as underground water in a region of sedimentary rocks tends to follow the bedding planes, the structure of the rocks has an important effect on the freedom of circulation. Rain water falling on the northeast slope of the Elk Hills or the Buena Vista Hills, for example, enters the beds and presumably finds a relatively free passage down into the valley. Water falling in the western part of the main field, however, enters the strata and percolates down into the Midway syncline, where its farther passage is impeded and at least temporarily blocked by the Buena Vista and other anticlines that separate the syncline from the main valley trough. The degree of completeness with which the water is ponded in the synclinal trough is somewhat increased by the fact that this trough pitches in general toward the southeast, whereas the trend of the circulation in the valley below is toward the northwest. If a sufficient hydrostatic pressure accumulates a part of the water trapped in the syncline will of course be forced around the end of the barrier or will be forced over it, presumably at some structurally low point. It is obvious that a certain amount of meteoric water is practically ponded in the syncline, and it is furthermore believed that a part of the connate water (sea water that the beds contained when they were deposited) has never been driven out. The belief that the oil-field waters consist in part of rain water and in part of slightly altered sea water is borne out, as will be shown later, by the chemical character of the waters in different parts of the field.

OCCURRENCE OF THE OIL-FIELD WATERS.

GENERAL DISTRIBUTION.

It is generally assumed that ground water exists as a fairly continuous body saturating all rocks down to an indefinite depth. The upper limit of the body of ground water is known as the water table; it follows in a general way the configuration of the surface but in arid regions may lie at a depth of several hundred feet. Although this conception is valuable in a broad study, investigation shows that the water table is generally irregular and that numerous local accumulations of ground water, known as perched water tables, occur above it. Furthermore, although all the strata below the main water table are believed to be saturated with water the facts that the head of water varies in different strata and that circulation is confined largely to certain beds are of course of great practical importance. The layers in which the water will circulate are determined by a variety of factors, most of which, though generally unknown in advance of drilling, are well understood. There is no intrinsic difference between a water sand and any other sand.

WATER SANDS.

As water flows most readily through rocks of uniformly coarse grain it tends to circulate chiefly in the sandy layers or "water sands."

The amount and pressure of the water in a sand depend largely on local conditions, but if these were uniform water would normally be found in greater available quantity and under higher head in coarse sand than in tight sand or sandy shale. Moreover, as few beds of sand are entirely uniform in grain the water is generally concentrated to some extent in the coarser layers, which are analogous to the "paystreaks" in an oil sand. In some sands the coarser portions are not true layers extending across the sand body but are simply streaks or channels having a comparatively small width. Hence, of several neighboring wells penetrating the same sand, one may encounter an unusually open or porous streak which yields a large flow, whereas the others may penetrate the tighter portion of the sand and obtain a much smaller volume of water, perhaps so small that the driller fails to recognize the bed as a water sand at all.

Although the grain of the rocks is important in determining which beds the drainage follows, an equally effective factor in lenticular material is the freedom of inlet and outlet of the lens itself. It is evident that water will not circulate in a bed unless the water entering at the outcrop can escape at the lower end of the lens, either into another lens or through some practicable channel. If the upper end is open and the lower end sealed, water will accumulate only up to the absorptive capacity of the sand, and if the hydrostatic head of the water thus trapped is not great enough to force an outlet movement will cease until the pocket is opened by the drill. The structure of the rocks may exercise an entirely similar effect in preventing circulation, so that water may be trapped in a syncline or a basin. If a lens is effectually sealed on all sides, there can be no movement even when it is penetrated in drilling, unless the rock pores are partly filled with air or gas under pressure; under such conditions the expansion of the gases may displace some of the water.

Although water sands are so termed because they are the principal channels of circulation, it must not be supposed that the surrounding rocks are dry. Coarse, open sand, through which flow is most rapid, has an average pore space or absorptive capacity of 32 to 37 per cent; unsorted or tighter sand, 38 to 42 per cent; and clay, 44 to 47 per cent.[1] Clay may thus contain nearly half as much water again as sand, though the important practical consideration is that sand yields its water readily because more fluid can easily take its place, whereas movement is slower in clay and much of the water it contains is probably held by capillary attraction. A sandy shale or a tight sand may also contain considerable water that will not be apparent in drilling because it escapes too slowly from the bed. If the strata penetrated by an ordinary oil well could be carefully examined, however, all those below the ground-water level probably would be found to contain more or less water.

It is thought by some drillers that water sands have a peculiar texture by which they may be distinguished from oil sands. It is variously held that the grains are sharper or more angular, or that they are smaller, or that water sand contains grains of mica, whereas oil sand does not. Any of these distinctions may be valuable locally, and some sands may be traced for a considerable distance by their texture and mineral character, but to assume that water sands and oil sands are essentially different in grain or mineral composition is to overlook entirely the principles that govern the movement of water and oil.

DRY SANDS.

In most well logs an attempt is made to differentiate water sands and "dry" sands, the dry sands being those which yield no water or which, on the contrary, absorb it. The distinction is valuable in so far as it records the horizons at which the greatest volumes of water were encountered, though none of the beds below the ground-water level are actually dry. A so-called dry sand may contain a large proportion of water under low hydrostatic head which it may yield under favorable conditions. Emphasis on this point is by no means academic. In the early history of an oil field water under low hydrostatic head may be unimportant, but at a later period, after the gas pressure has diminished and a considerable portion of the oil has been removed, the oil sands constitute a con-

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[1] King, F. H., Principles and conditions of the movements of ground water: U. S. Geol. Survey Nineteenth Ann. Rept., pt. 2, pp. 209-215, 1899.

venient reservoir, and such water may enter them and do considerable damage. The facility with which water under low head may enter practically exhausted oil sands has been strikingly exemplified in parts of the Sunset-Midway and Coalinga fields.

In the standard or cable-tool method of drilling it is customary to maintain a certain depth of water in the drill hole. If the water level rises when a sand is encountered the bed is logged as a water sand, and if it remains stationary or falls the sand is logged as dry. However, a column of drilling water 1,000 feet high exerts a pressure of 434 pounds to the square inch at the bottom of the hole, and if the hydrostatic pressure in the sand is lower than the weight of the column of drilling water the water level will sink and most of the water may be absorbed. Thus, sands that rapidly absorb the drilling water and are therefore logged as dry sands might yield considerable water if the drill hole were dry. In the rotary method of drilling mud is continually pumped into the hole under considerable pressure and it is even more difficult to estimate the water-yielding capacity of a sand. If the bed is pervious and carries water under a low head its presence is easily recognized by the fact that the pump pressure necessary to force the mud into the hole is suddenly decreased. If, however, the sand contains water under a high head the difference between its upward pressure and the downward pressure of the column of drilling mud may be so small that it is not shown by the pump gage, and the sands that contain the most water may thus be missed.

HEAD OR PRESSURE.

The head or pressure of the water is different in different sands, owing chiefly to variations in porosity and in freedom of circulation. As a general rule, however, it increases with depth; and similarly in any one sand it is generally greater farther down the dip. Many waters that flow at the surface have been encountered in the Sunset-Midway field, some above and others below the oil measures. The head in most of the sands reported by drillers as water sands is more than 200 feet, and many sands that are reported as dry probably carry water under a head of more than 50 feet.

The water pressure in the Sunset-Midway field is, in general, highest in Midway Valley and on Maricopa Flat. The pressure in most sands, however, is not constant and diminishes noticeably a short time after the sand is tapped. Waters that flow for months or years finally cease to flow, and the head of waters that rise but do not reach the surface is also known to decrease. The rate of decrease in any particular sand depends on local conditions and may differ widely among neighboring wells, but the general decrease in the field as a whole is striking.

The fact that the water pressure increases roughly as the depth indicates that it is mainly hydrostatic in general character. Hydrostatic pressure is caused by the weight of the downward-bearing column of water, and its amount at any place is controlled by the difference in elevation between that point and the point at which the water enters the bed, and by the fineness of the material through which the pressure is transmitted. There is a difference in elevation of 800 to 1,000 feet between the extreme western part of the field and Midway Valley, and although this head is largely destroyed by the friction incident to the passage of water through the sand in the 4 miles between these points, enough head usually remains to raise the water almost to the surface in Midway Valley and in some places to cause it to flow. So far as hydrologic conditions are concerned the Midway syncline constitutes an excellent artesian basin, though the rainfall is small and much of the head is lost because of the lenticularity of the sands.

The unusually low head of water in the so-called dry sands may be due to a variety of conditions. If the sand is fine or irregular in grain, most of the normal head will be lost through friction and the movement of water through it will be very slow. Similarly, if the sand is in the form of a lens sealed on all sides by shale it can neither give nor take up water when penetrated by the drill. On the other hand, if the sand has a free intake above and a free outlet below and if it is coarse and open grained, so that the water percolates through it readily, only a small head is developed, for the water will follow the path of least resistance. If the sand is sealed at the upper end but has a free outlet at the lower end, a negative head or partial vacuum might conceivably be created, and such a sand might take up drilling water as fast as it could be poured into the well.

Another factor which is supposed by many to exert a notable influence on the movement of underground water is rock pressure. Rock pressure, strictly defined, is the weight of the overlying column of rock which exerts a compressive effect on the beds beneath it. During the deposition of the sediments the pressure of the upper layers undoubtedly leads to closer packing of the grains in the lower layers and to the expulsion of some of the connate water. Pressure due to strains produced during uplift and deformation, which may also be called rock pressure, is doubtless an important agent in forcing water out of the beds or causing it to migrate to other parts of the formation or series.[1] The past and present effects of rock pressure can not be disregarded, but their magnitude is generally an unknown quantity.

Although in the Sunset-Midway field the water pressure in many of the sands is probably wholly artesian, the influence of gas must be taken into account, especially in considering the pressure in the lower sands. In general the gas pressure in any sand is less than the weight of an overlying column of water, but there are sands in which it is greater and in which, therefore, its influence must be considered. If a sealed sand lens is filled partly with water and partly with gas under pressure, the water may flow out under great apparent head when the sand is tapped. In addition to the pressure exerted by a body of gas, the influence of gas liberated from solution in causing water to flow is also important. Hydrocarbon gas is dissolved in some waters, and many others contain carbon dioxide and hydrogen sulphide. These gases are partly liberated at the foot of the well and act somewhat like an air lift in causing the water to flow. Their action is feeble compared with the propulsive effect of a body of compressed gas, but it is doubtless more widespread and causes some waters to flow that might not otherwise reach the surface.

TEMPERATURE.

The temperature of a few of the waters was measured by the writer and found to range between 84° and 131° F. The temperature of water from sands more than 1,200 feet deep is generally greater than 100°, but it is doubtful if any waters yet encountered in the field are much hotter than 131°, though reports to this effect are sometimes heard. The measurements and a discussion of the factors that cause variation in temperature are given on pages 37–42.

Although variation in temperature is due to several causes, the gradient is usually fairly regular, so that the source of the water is indicated in a general way by its temperature. A sand that receives much surface drainage is generally abnormally cool, and several waters which seemed cool in proportion to their supposed depth were found by chemical analysis to be mixed with waters from higher levels. Similarly, a mixture of oil and bottom water is generally 5° to 10° hotter than clean oil produced from the same depth by neighboring wells, a fact which suggests that the water in migrating up from the lower water sand is carrying its original temperature with it. Whether edge water or top water close to the oil could be distinguished by their temperature is not known, for the measurements made by the writer are neither sufficiently numerous nor sufficiently precise to indicate the significance of slight variations in temperature. It is interesting to note, however, that in the Baku fields of Russia, where invasion of water into the oil sands has long been a source of great trouble and expense, an effort has been made to use temperature measurements in determining the bed or horizon from which the water comes. Goloubjatnikov,[2] who has made several hundred fairly precise measurements of the temperature of the oil and water in wells in the Bibi-Eibat and Sourakhany fields, states that the horizon of the water may be estimated rather closely from its temperature, and that observations of temperature are therefore of considerable practical value in determining the source of the water flooding a well.

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[1] For an ingenious speculative discussion of this process, see Daly, M. R., The diastrophic theory: Am. Inst. Min. Eng. Bull. 115, pp. 1137-1157, 1916.

[2] Goloubjatnikov, D., Observations géothermiques à Bibi-Eibat et Sourakhany [in Russian]: Com. géol. Mém., nouv. sér., livr. 141, p. 32, 1916.

RELATION TO THE OIL.[1]

The Paso Robles and Etchegoin formations, which overlie and include the productive oil measures in the Sunset-Midway field, contain a number of sands that carry water. Most of these sands are irregular and discontinuous and can be traced only within small areas. In some localities where an unusually extensive sand offers a favorable channel or reservoir for the water the circulation is localized, but in general there are many lenticular sands and all of them contain more or less water. The Maricopa shale, which unconformably underlies the oil measures, also includes a number of lenticular water sands. Some waters thus occur above the oil sands, others below, and still others in the same sands but farther down the dip, and it is customary to designate them top waters, bottom waters, and edge waters, respectively. It is natural for the driller who is interested primarily in the position of the oil itself to classify waters according to their position with regard to the oil, but his terminology is often ambiguous. The bottom water of an upper oil sand may be the top water of a lower sand. An edge water may be either top water or bottom water or both. These terms are too commonly used and too convenient to discard, but the term top water should be restricted to water above the highest producing oil sand, and bottom water to that below the lowest oil sand. The waters within the oil zones themselves may in general be regarded as edge waters.

As numerous factors influence the distribution of the water and the course of its circulation, it is impossible to predict in advance of drilling exactly where the largest flows will be found, though certain useful generalizations can easily be made. The general groundwater level in the field varies from place to place but is usually within 500 feet of the surface. Between this water table and the horizon of the oil from one to half a dozen or more top waters are found, the number depending chiefly on the depth of the oil zone. Along the hilly western portion of the field the groundwater level is of course particularly low and in some localities there is little water above the oil zone. In many of the wells within 1,000 or 1,500 feet of the outcrop and also in those along the crests of several of the shallow anticlines no top water was found and only a single string of casing is set. Tar sands that occur above the productive oil measures, however, usually carry some water—commonly sulphur water—and although this water is generally under low head it is likely to become troublesome after the gas pressure has decreased and the oil sands are partly exhausted. In Midway Valley the ground-water level is generally within 200 feet of the surface and a large number of top waters are encountered. Some of the deeper waters flow at the surface and would yield large supplies if pumped. These waters are strongly saline and of little value, however, and as most of the wells in this district are drilled to a level near the oil horizon by the rotary method, no accurate record of the top waters is kept. Conditions in the Buena Vista Hills are similar, though the ground-water level there is of course somewhat deeper than in the valley. In general, top water may be expected to occur down within 100 or even 50 feet of the highest oil sand everywhere except along the western edge of the field, though in parts of the Buena Vista Hills no top water is definitely reported within 300 feet of the oil.

The waters that have proved most troublesome are those occurring in or below the productive oil measures. As shown in Part I (Prof. Paper 116), the plane of unconformity separating the Maricopa shale from the Etchegoin formation has greatly influenced the accumulation of the oil and has also indirectly affected the distribution of the water. In the extreme western part of the field, where the Etchegoin formation is thin, the productive oil measures are comprised in zone A, but farther down the dip zone B appears and then zone C, the upper or western edges of these zones abutting against the irregular surface of the Maricopa shale. Near the line along which zone C becomes recognizable, however, zone A ceases to be productive, its sands being occupied by tar and water and farther down the dip by water alone. Similarly, water sands appear in zone B still farther down the dip, and near the axis of the Midway syncline practically all the sands in this zone are occupied by water, though on the flanks of the

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[1] The positions of the water sands in the various parts of the field have been described by Mr. Pack in Part I of this report (Prof. Paper 116), and many of the statements in the following account are based on the details there given.

Buena Vista anticline, to the east, zone B again becomes productive. Zone C, in the lower part of the Midway syncline, contains some water sands but is recognized as a productive oil zone across the syncline and becomes wholly occupied by water only on the farther flank of the anticline to the east.

As zones A and B both become filled with water down the dip, it is evident that the belts or strips of territory in which the transition takes place are likely to be critical with reference to water conditions. In these belts some operators are likely to attempt to produce from the upper zone, while others drill to the deeper sands and case off the less productive upper sands. The operators who produce from the upper zone thus have to contend not only with the water originally present there, but also with that let into the zone by the neighboring deeper wells. As pointed out by Mr. Pack in Part I of this report, water is likely to be very troublesome throughout these transition belts and as time passes will become more so.

As shown on Plate III, Professional Paper 116, zone A is recognized only in certain localities in the western portion of the field. Near the outer or eastern edge of the areas for which this zone is shown by contours on the map water sands appear, and beyond the area contoured the zone consists almost entirely of water sands. The transition belt for this zone, which is fairly narrow and well defined, thus surrounds the area in which the zone is contoured. The waters occurring at the same horizon farther down the dip are true edge waters of zone A, though they are generally referred to as the top waters of zone B.

The transition belt in zone B is broader and more poorly defined. Water sands appear in this zone well up on the structure along the west side of the field, though some sands carry oil far down the dip toward the Midway syncline. In the northern part of the field zone B becomes filled with water and wholly nonproductive within a few miles of the outcrop. In the southern part its productive area extends much farther east, though in most of the deeper territory the zone includes one or more water sands. Where the waters occur near the top of the zone they are usually treated as top water and cased off, and where they occur well down in the zone they are usually regarded as bottom water. On Maricopa Flat, however, where all the productive measures are referred to zone B, there are several well-recognized water sands lying between productive oil sands, and this condition has rendered extraction of the oil with exclusion of water very difficult. Although on the southwestern limb of the Midway syncline water sands in zone B generally extend well up the slope, on the farther or northeastern limb the water, according to Mr. Pack, extends a much shorter distance, except in the northern part of the field. In the central and southern parts of the Buena Vista Hills zone B is productive in a broad strip and extends well down the farther flank of the anticline before again becoming filled with water.

Zone C in several parts of the field includes water sands, some of which occur at the base of the productive measures and may therefore properly be termed bottom waters. Thus in practically all the productive territory in T. 31 S., R. 22 E., water occurs at or below the base of the oil zone, and this water sand, or series of sands, constitutes one of the most persistent water carriers in the field. Farther southeast, or along the syncline in T. 32 S., R. 23 E., water also occurs in the lower part of zone C or at its base. In some localities water sands also occur higher in zone C, a conspicuous example being the water closely underlying the gusher oil sand north of Fellows. In the northern part of the Buena Vista Hills the zone includes one or more water sands, and down on the northeastern limb of the Buena Vista anticline the zone finally becomes nonproductive.

In some parts of the field true bottom water is found only in the Maricopa shale. As the bedding in this formation is unconformable with that in the overlying oil measures the water is not encountered at any special depth or horizon below the oil but occurs in sandy beds that are apparently lenticular. In the eastern part of the field the Maricopa shale has not been explored, but in the western part many wells have penetrated it and have found water at varying depths beneath its upper surface. Several wells along the western edge of the field obtain from this formation large quantities of water, which is sold for boiler use.

In some localities water from the Maricopa shale has probably, according to Mr. Pack, migrated up into the overlying oil measures. In the area northwest of Fellows and also on Twenty-five Hill the producing oil zone (A) rests directly on the Maricopa shale. In narrow belts in these localities a strong bottom water is encountered, apparently at the very base of the oil measures. This water is believed to have migrated up from a Maricopa water sand, truncated along the plane of unconformity that marks the top of that formation, or, in other words, to have followed the course originally taken by the oil. As the basal oil sands become exhausted this water may spread farther through them and thus become an edge water, working down the dip instead of following the oil up the slope in the normal way.

ANALYSIS OF WATER AND INTERPRETATION OF RESULTS.

MINERAL CONSTITUENTS IN WATER.

Natural waters are essentially solutions of mineral substances that have been derived from the rocks or other material with which the waters have come into contact. The amount and character of these substances vary greatly and depend on many factors, chief among which are the chemical character and physical condition of the materials encountered, the heat and pressure, the duration of the contact, and the amount and character of the substances previously dissolved. If two waters that carry different salts in solution come into contact a chemical reaction may take place and some of the dissolved material may be precipitated.

The common mineral constituents of natural waters may be divided into two groups—those which have definite chemical relations with some other constituent and those which are probably present as colloids. The colloid group comprises silica, iron oxide, and alumina. These substances, like those in the other group, may perhaps be held in solution in some waters, but ordinarily they are considered to be not in actual solution and are conventionally reported as the oxides silica (SiO_2), ferric oxide (Fe_2O_3), and alumina (Al_2O_3). The constituents of the other group are of two kinds—the positive radicles or bases, chiefly sodium, potassium, calcium, and magnesium, and the negative or acid radicles, chiefly sulphate, chloride, carbonate, and bicarbonate. The several constituents of each kind have different but definite capacities for reacting with or holding in solution constituents of the other kind. The two kinds of constituents in a water are always in chemical equilibrium—that is, the sum of the reaction capacities, or "reacting values," of the positive radicles is equal to the sum of the reacting values of the negative radicles. In addition to the colloidal material and the dissolved mineral solids most waters contain dissolved gases, chiefly nitrogen, oxygen, and carbon dioxide, and also carry clay and other material in suspension.

COLLECTION OF SAMPLES.

In most districts the collection of water samples for analysis is a simple matter, but in oil fields, where the universal aim is to shut the water out of the wells, it is often very difficult. In wells used to supply water for industrial purposes the depth of the water sands is generally known and samples can of course be easily taken, but the waters that can be sampled in this way are few. Some of the oil wells produce water which is known to come from a certain depth, but generally its exact source is unknown. In the Sunset-Midway field, where sharp variations in the character of the water may occur within short vertical distances, too much care can not be exercised in the collection of samples. After a sufficient number of authentic samples in any area have been collected and analyzed it will be possible, by comparison with these standards, to form an estimate of the probable source of any water found later in the same area.

Usually authentic samples can be taken only while the well is being drilled or repaired. Flowing waters can of course be easily sampled, and the only precaution necessary is to let the water flow long enough before sampling to insure complete washing out of the drilling water from the hole. The collection of samples from a well that is being drilled by the standard method is not especially difficult, and samples uncontaminated by water from upper sands can generally be obtained after the drilling water has been bailed out. Under some conditions it is possible to obtain a fairly satisfactory sample merely by running the bailer to a point near that at which the water is entering the drill hole. When the circulating or the rotary system of drilling is used the proper collection of samples is often difficult or even impossible. Waters that flow when the pressure is released may be sampled at the expense of a little trouble, and if a string of casing is to be set within a short distance of a strong water sand, a sample of this water may be obtained while drilling is suspended. However, the rotary drill tends to mud up or plaster the walls of the hole and thus shut off flows of water, and if one of these flows breaks forth later the driller is likely to suppose that it comes from a deeper sand.

In view of these uncertainties it is evident that unless the location of the water can be positively determined its analysis should not be used as a standard for exact comparison. For this reason it is the more desirable to collect samples carefully and label them accurately whenever good ones can be obtained, as when a flowing water is encountered.

CHEMICAL ANALYSIS.

CONSTITUENTS TO BE DETERMINED.

The number of constituents to be determined in the analysis of water and the accuracy with which the work is done differ with the use to which the analysis is to be put, but in general the following determinations are desirable: Sodium (Na), potassium (K), calcium (Ca), magnesium (Mg), iron (Fe), aluminum (Al), sulphate radicle (SO_4), chloride radicle (Cl), nitrate radicle (NO_3), carbonate radicle (CO_3), bicarbonate radicle (HCO_3), silica (SiO_2), and total solids at 180° C. It is well also to test waters from oil fields for sulphide (S) and for the gases hydrogen sulphide (H_2S) and carbon dioxide (CO_2). The quantity of suspended matter and the quantity of organic matter also are usually determined.

In industrial analyses, iron and aluminum are usually precipitated and weighed together and reported as the oxides ($Fe_2O_3+Al_2O_3$), and carbonate and bicarbonate are often not distinguished from each other. The laborious determination and separation of sodium and potassium is omitted in many industrial analyses, and the content of these two substances together is calculated, after the acids and the other bases have been determined, by assuming the presence of sufficient sodium and potassium to complete the balance of reacting values between the bases and the acids. This practice unfortunately conceals all analytical error and makes it impossible to ascertain the accuracy of the analysis from the reported figures.

STATEMENT OF ANALYSIS.

In analyzing a natural water the chemist can determine only the proportions of the mineral substances that it holds in solution. He can not determine what compounds have been dissolved, nor can he ascertain by the ordinary methods of analysis what compounds, if any, exist in the solution; his work is limited for the most part to the determination of the parts of compounds that are known as ions or radicles. Despite this limitation it is common practice to report not the radicles actually determined but the compounds of which they are thought to be a part, and these hypothetical combinations may be calculated by several methods, founded on different theories or devised from different points of view. As a result of this difference of opinion it is impossible to compare the results of one chemist with those of another until the analytical data have been reduced to a statement of all the radicles actually determined.

As there is no valid reason for reporting analyses in hypothetical combinations and as it is impossible to compare analyses so reported by different chemists, the analyses in this report have been calculated to the ionic form in order to show the amounts of the radicles actually found by the analyst. They have also been calculated to parts per million, the proportion most suitable for comparison, in order to avoid confusion due to the use of different units, such as grains per United States gallon, percentage, and parts per hundred thousand.[1]

REACTING VALUES.

The statement of a water analysis in ionic form in parts per million shows numerically the relative proportions of the several radicles by physical weight, in terms of gravity, and therefore is not a numerical representation of the water as a chemical reagent. A form of statement more convenient for study and comparison is that in reacting values, which shows numerically the relative proportions of the

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[1] The following factors are used in transforming results to parts per million: 1 grain per United States gallon=17.1 parts per million: one part per hundred thousand=10 parts per million; 1 gram per liter=1,000 parts per million; 1 per cent=10,000 parts per million.

radicles by chemical weight—in terms of reaction capacity. It is possible to calculate either form of statement from the other, because for each radicle there is a fixed ratio between physical weight and chemical reaction capacity, though the ratios for the several radicles are different and the relation between the two forms of statement is therefore complex.

In order to translate an analysis from the ionic form into a form which expresses the chemical balance of the radicles, it is convenient to calculate the reacting values of the radicles. Stabler[1] has suggested that this be done by multiplying the weight of each radicle by its "reaction coefficient," which he defines as the chemical reacting power of a unit weight of the radicle. The reaction coefficient of a radicle in numerical value is the valence of the radicle divided by its weight on the atomic scale. The following table shows the reaction coefficients of the positive and negative radicles most commonly found in waters:

Reaction coefficients of radicles commonly found in waters.

Positive radicles.		Negative radicles.	
Sodium (Na)	0.0434	Sulphate (SO_4)	0.0208
Potassium (K)	.0256	Chloride (Cl)	.0282
Calcium (Ca)	.0499	Nitrate (NO_3)	.0161
Magnesium (Mg)	.0821	Carbonate (CO_3)	.0333
Hydrogen (H)	.992	Bicarbonate (HCO_3)	.0164
		Sulphide (S)	.0622

The coefficients of silica, iron, and aluminum have been omitted from this table, as it is generally assumed that these substances are present as oxides in the colloidal state and therefore take no part in the chemical system of acids and bases. Stabler prefixes the letter *r* to the symbol of a radicle to designate its reacting value, and the same symbolization will be followed in this report.

When the weights of the radicles have been translated into their reacting values the chemical nature of the whole system becomes apparent. Comparison is further facilitated, however, if the reacting values are reduced to a percentage basis, and this computation has been applied to all the analyses here discussed. It will be observed that inasmuch as the sum of the positive radicles (bases) must be chemically equivalent to the sum of the negative radicles (acids), the reacting values of the two groups should be the same, each making up 50 per cent of the total.

As the figures representing the reacting values of the radicles have a greater chemical significance than those representing their weight, it is generally preferable to use the reacting values in comparing or studying analyses. Hence, statements in this report regarding the percentage of radicles present in waters refer to the percentage by reacting value, unless otherwise stated.

PROPERTIES OF REACTION.

Chase Palmer[2] has proposed a system for the classification and comparison of natural waters based on certain well-known properties of the solution as a whole, and his system is adopted in this report. The writer has found this mode of interpretation very valuable, for it sums up the detailed analytical statements in terms of a few properties, which furnish a convenient basis for the comparison of a large number of analyses. Although the properties are ordinarily calculated from the analytical statement, they may also be determined directly by testing the solution; hence they not only sum up the detailed analyses but also serve to bring out certain true chemical differences between waters which are fundamental in their geologic and industrial bearing.

When different salts are dissolved in water they impart different qualities to the solution. A simple solution of sodium carbonate, for example, is soft and alkaline; one of sodium chloride is neither alkaline nor acid, being neutral or saline; and one of calcium chloride is hard and saline. If the separate salt solutions are mixed the resulting solution still has definite properties acquired from those of its constituents. In a mixed solution, however, it is no longer possible to state how much of each salt is present; reactions have taken place, and different combinations have resulted, and there is no possible way in which these combinations can be actually determined. The properties of the solution as a whole may be determined, however, or the amounts of the various radicles present may be determined by analysis and the properties

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[1] Stabler, Herman, The mineral analysis of water for industrial purposes and its interpretation by the engineer: Eng. News, vol. 60, p. 355, 1908; also chapter on the industrial application of water analyses in U. S. Geol. Survey Water-Supply Paper 274, pp. 165–181, 1911.

[2] Palmer, Chase, The geochemical interpretation of water analyses: U. S. Geol. Survey Bull. 479, 1911. Rogers, G. S., The interpretation of water analyses by the geologist: Econ. Geology, vol. 12, pp. 56–88, 1917.

deduced from them. The reactive properties of the solution therefore depend essentially on the chemical balance existing between the radicles themselves.

In order to sum up the detailed analytical statement, radicles that are similar chemically and that impart similar properties to the solution are grouped together. Thus sodium and potassium fall in the alkali group, and calcium and magnesium in the group of alkaline earths. The common acid radicles are grouped as strong acids (chloride and sulphate) and weak acids (carbonate, bicarbonate, and sulphide). The balances that may exist between each two of these basic and acidic groups impart different properties to the solution. The presence of salts of the strong acids leads to salinity and that of salts of the weak acids to alkalinity. If the strong acids are in equilibrium with alkalies the salinity may be called primary salinity; if they are in balance with alkaline earths it may be called secondary salinity; similarly the balance between the radicles of the weak acids and the alkalies may be called primary alkalinity, and that between the radicles of the weak acids and the alkaline earths secondary alkalinity. Most of these properties have long been recognized by water chemists; thus secondary salinity is synonymous with permanent hardness, secondary alkalinity is practically equivalent to temporary hardness, and primary alkalinity has been called permanent negative hardness.

A water containing only one basic and one acidic group would evidently be characterized by only one property, but as most waters contain the members of all four groups, the equilibria existing between them must be considered. Inasmuch as strong acids or bases "displace" weak acids or bases under ordinary conditions, the several groups may be balanced against one another in the order of their chemical strength or reactive power. In other words, the strong bases (alkalies) are balanced against the strong acids; the excess of either group is balanced against the weak bases or acids; and finally the remaining weak acids and bases are balanced together. A water containing members of all four groups will therefore be characterized by primary salinity and secondary alkalinity. If the strong bases exceed the strong acids and are therefore in equilibrium with weak acids the water will have primary alkalinity; but if the reverse is true, the strong acids being in excess of the alkalies and therefore in equilibrium with alkaline earths, the water will have secondary salinity. These two properties are therefore incompatible; nearly all waters are characterized by one or the other, but no water can exhibit both.

The grouping of all waters as those having primary alkalinity (softness) or secondary salinity (permanent hardness) is one of the most valuable features of Palmer's system. This distinction is important in the study of the industrial value of waters and is also of geologic significance. The surface waters and the shallow ground waters in the Sunset-Midway field contain little carbonate but a high proportion of sulphate, balanced against roughly equal values of alkalies and alkaline earths, and they therefore invariably show secondary salinity. The waters associated with the oil in the western part of the field contain no sulphate but a high proportion of carbonate and of alkalies and are waters of primary alkalinity. The deeper waters in the central and western parts of the field contain no sulphate but are higher in alkaline earths and very low in carbonate and are waters of secondary salinity. By a study of the properties of the waters all the stages in their alteration and mixing can be traced and distinctions become apparent that do not suggest themselves in a study of the detailed analyses.

In addition to the three properties of reaction two other criteria for comparison are available. One of them is the ratio of the chloride to the sulphate radicles, for in Palmer's system these radicles are classed together as strong acids. As the strong acids give rise to salinity, chloride salinity and sulphate salinity may be distinguished, and these properties may conveniently be expressed as percentages of the total salinity. The other criterion is the concentration of the solution, or the total amount of dissolved solids. In general, the concentration of oil-field waters of any one type is fairly constant, but it may vary widely and therefore should not be lost sight of. For some waters it may also be desirable to determine the ratio of sulphate to carbonate, though in general this ratio is adequately expressed by the proportions of the properties of reaction.

SOURCE OF ANALYSES IN THIS REPORT.

In the tables given in the following pages the analyses of 74 waters from the Sunset-Midway region are given. These include all that the writer has been able to collect with the exception of a few that are duplicates or are obviously incorrect.

Of the 74 analyses given 29 were made by the Geological Survey, 27 by the Standard Oil Co. and the Kern Trading & Oil Co., and 18 by industrial chemists. In most of those made by the Survey all the reported constituents were determined and the percentage of error may be computed. The others are partial analyses, the alkalies having been calculated by difference. The analyses made by the Standard Oil Co. and the Kern Trading & Oil Co. may be accepted as reliable and accurate within close limits. The remaining analyses are believed to be reliable, but they were doubtless made according to different standards of accuracy. They afford a good idea of the general character of the water, and in most of them the error is probably less than 5 per cent.

TYPES OF OIL-FIELD WATERS.

CRITERIA FOR COMPARISON.

The chemical character of the substances dissolved in natural waters differs widely and several different types of water may be found in nearly every region. Owing to this wide variation in character it is often difficult to distinguish, without careful study, the significant differences from those that are more or less fortuitous, or more properly the differences that are due to determinable and fixed conditions from those which result from changing or indeterminable conditions. Moreover, waters may be classified from several different points of view, and in each classification the significance of different constituents may be emphasized.

Although the chemical character of oil-field waters has, in general, received little attention, several investigators in the Sunset-Midway and other fields have studied the waters and have attempted to classify them. E. A. Starke, of the Standard Oil Co., who has made the most comprehensive study, recognized several years ago that waters associated with the oil contain no sulphate and are likely to be high in carbonate. Other investigators have used as criteria for comparison such features as the concentration of the waters, the proportion of chloride, the ratio of calcium to magnesium, and the presence or absence of rarer mineral constituents, or of constituents derived from the petroleum itself, such as naphthenic acid. Some of these features are obviously poor criteria for scientific comparison, for they are controlled by factors that are indeterminable and that have no apparent relation to the presence of oil; others may in the future prove of value, but the data at hand are not sufficient to permit an estimate of their reliability. The carbonate and sulphate values used by Starke furnish a rational basis for the classification of the oil-field waters and at present constitute the most trustworthy indexes of their position with regard to the oil.

It should be emphasized, however, that no single isolated constituent or ratio affords a sufficient basis for studying and comparing the oil-field waters; rational conclusions must be based on a study of the complete analysis. The distribution and significance of all the common constituents of the oil-field waters are accordingly outlined in the following section.

DISTRIBUTION AND SIGNIFICANCE OF THE CONSTITUENTS.

Alkalies.—The alkalies (sodium and potassium) are by far the most abundant bases in the oil-field waters, and in the deeper waters from the west side of the field they and their equivalent acidic radicles constitute over 95 per cent of the total mineral content. In the deeper waters from the Midway syncline the alkalies are somewhat less prominent. They usually predominate over the alkaline earths in all waters from depths of more than 300 feet, though in most surface waters the alkaline earths are present in slight excess.

Alkaline earths.—In many of the surface waters and some of the shallow ground waters of the Sunset-Midway field the alkaline earths (calcium and magnesium) exceed the alkalies, but in all the deeper waters their relative proportion is low, not only because of the high concentration of the alkalies, as already explained, but also because the alkaline earths themselves are generally present only in small actual amounts. Large amounts of the earths can not be retained in waters in which more than a certain proportion of carbonate or bicarbonate is present, and if this proportion is exceeded alkaline-earth carbonates are precipitated from the solution. In most of the shallower waters sulphate is high and carbonate low, and alkaline earths are therefore abundant constituents, but in the waters near the oil zone carbonate is high and the earths are accordingly low.

Sulphate.—In the normal ground waters everywhere on the west side of San Joaquin Valley sulphate is the predominating acid radicle, especially near the surface. In some of the shallow waters from the Sunset-Midway field sulphates constitute over 70 per cent of the total mineral content. Outside of the oil field most of the deeper ground waters also show a high concentration of sulphate, though the amount bears no constant relation to depth. Within the field, however, sulphate decreases with increasing depth and practically disappears at a certain distance above the oil zone. Many of the waters associated with the oil do not contain even a trace of sulphate, and most of them carry less than 0.2 per cent. The tables of analyses in this report show the ratio of sulphate to sulphate plus chloride by reacting value in all the waters discussed and also the ratio of sulphate to carbonate in many of these waters.

The decrease of sulphate in the waters near the oil measures and its absence from the waters most closely associated with the oil are believed to be the result of chemical reaction with constituents of the oil or gas. The sulphate is probably reduced to sulphide or hydrogen sulphide, which may either escape as gas or undergo oxidation to free sulphur and so be lost by precipitation. The reduction of the sulphate is presumably attended by the oxidation of an equivalent portion of the hydrocarbon material to carbonate or carbon dioxide. These reactions are discussed in more detail on pages 60–61.

Chloride.—Chloride is a widespread constituent of terrestrial waters, but its concentration varies greatly. As the chlorides of all the common bases are highly soluble in water they are not important as rock-forming constituents and are concentrated chiefly in the ocean. A high concentration of chloride in ground water usually indicates that the water is partly of oceanic origin or that it has leached saline deposits.

The chloride in the Sunset-Midway waters is believed to be of oceanic origin, and its concentration depends on the extent to which the connate sea water has been admixed with meteoric water carrying sulphate or carbonate. This admixture is controlled largely by the freedom of the circulation. In the Midway syncline, where the geologic structure impedes circulation, the deeper waters are very salty. Near the surface, however, and on the west side of the field, near the outcrop of the beds, the connate water has been largely replaced by meteoric water and the concentration of chloride is therefore much lower.

Carbonate and bicarbonate.—In most industrial analyses no distinction is made between carbonate and bicarbonate, the two being grouped under the head of carbonate. Under ordinary conditions the two are more or less interchangeable; carbonate may be regarded as the primary radicle from which, in the presence of carbon dioxide, bicarbonate is derived. If a sufficient amount of carbon dioxide is present all of the carbonate radicle may be converted to bicarbonate, but a slight increase in temperature or decrease in pressure may drive part of the carbon dioxide from the solution, and thus cause a reversion to carbonate. A solution of calcium bicarbonate, for example, yields calcium carbonate on boiling. The bicarbonates of calcium and magnesium are relatively soluble in water, whereas the normal carbonates are almost insoluble; hence, when the bicarbonate solutions are boiled and, by release of carbon dioxide, normal carbonate is formed, most of the normal carbonate is thrown out as a precipitate or "scale." As most surface waters can dissolve enough carbon dioxide from the air to form bicarbonate exclusively, it is generally assumed that practically all the carbonate reported in analyses of surface water and shallow ground water represents bicarbonate in the solution.

Carbonate and bicarbonate are subordinate in amount to sulphate in most of the surface water on the west side of San Joaquin Valley and are generally present in minor amount in the normal ground water. In the waters associated with the oil, however, they are generally more abundant, and when chloride is low carbonate and bicarbonate constitute the chief acidic radicles.

Bromine and iodine.—Bromine and iodine have been detected in some of the oil-field brines, and iodine was determined quantitatively in one sample (analysis 9, p. 65) and found to amount to 29 parts per million. Many years ago Watts[1] reported 19.8 parts per million of iodine in water from one of the old Jewett & Blodgett wells in the Sunset field and stated that water from several other wells gave a "strong reaction" for iodine.

The presence of iodine and bromine in salty oil-field waters is usually regarded as an indication that the waters have been derived from sea water. Ordinary sea water, however, contains 1,880 parts per million of bromine and only 2 to 2.4 parts per million of iodine, so that the proportion of the iodine in the oil-field waters has evidently been considerably raised. Mrazec,[2] the foremost authority on the Rumanian oil fields, finds that all the waters in those fields contain appreciable amounts of iodine, whereas salty waters from nonoil-bearing regions carry bromine but little or no iodine. This relation appears to hold so widely in the Rumanian and neighboring oil fields that Mrazec regards the presence of iodine in water as an indication of the presence of oil. He explains the high concentration of iodine in oil-field water as compared with ordinary sea water on the ground that the sea water in which the petroliferous sediments were laid down must have been rich in certain organisms that are known to extract iodine from sea water and thus cause a local concentration. It is unfortunate that more attention has not been paid to the iodine and bromine in the Sunset-Midway waters, for if these constituents have a more or less definite relation to the oil a study of their distribution should be of direct economic value.

Sulphide.—Sulphide occurs in small amounts in many of the waters above the oil zone, and the presence of hydrogen sulphide has long been recognized by drillers as indicating a top water. The manner in which the sulphide is held in solution is usually not determined, but it is highly probable that in primary alkaline waters some of the sulphide is held in equilibrium by alkalies and perhaps by alkaline earths. In some waters the acid sulphide (bisulphide) radicle (HS) is doubtless present. Both the normal and acid sulphide, however, tend to form the gas hydrogen sulphide (H_2S), which is easily recognized by its odor and to which directly the term sulphur water is due.

Sulphide in the oil-field waters of San Joaquin Valley is probably formed by the reduction of sulphate. This reaction generally takes place a short distance above the main oil zone, and whether the sulphide radicle is first formed or not it is certain that hydrogen sulphide is produced in notable amounts. As hydrogen sulphide is a gas, it tends to rise to higher waters or to the surface, if it is free to migrate at all, and the current belief that "sulphur waters" are top waters is therefore well founded. Like most generalizations, however, it must be applied with discretion, for when sulphate encounters small amounts of oil or gas the sulphate may be partly reduced to sulphide and a sulphur water thus formed far below the oil zone.

Minor mineral constituents.—Iron and aluminum differ from the constituents already discussed in that they occur in most waters simply as hydrated oxides, which are supposed to be in the colloidal state rather than in true solution. They are rarely present in large amounts and generally do not affect the chemical aspects of the water.

Silicon is nearly always present as the colloidal oxide (silica) and may therefore be disregarded in a study of the reactive properties of the water. In waters of primary alkalinity it may enter the solution as silicate but probably soon breaks down into the colloidal form (SiO_2). It varies greatly in amount in the oil-field waters but averages higher in waters showing primary alkalinity than in brine.

Small amounts of several other constituents such as nitrate, phosphate, boron, and lithium are probably present in some of the waters, but they do not materially affect the character of the water and their determination is not essential to a study of the relations of the water to petroleum. Twenty-nine of the samples whose analyses appear in Tables 14 to 27 were tested for nitrate, but only six, of which four were surface waters, were found to contain it. A small quantity of boron was found in the only sample tested for it.

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[1] Watts, W. L., The gas and petroleum yielding formations of the San Joaquin Valley of California: California State Min. Bur. Bull. 3, pp. 90–91, 1894.

[2] Mrazec, L., L'industrie du pétrole en Roumanie, p. 20, Bucharest, 1910.

Total mineral solids.—The total mineral solids present in a given quantity of water, or the concentration of the solution, varies widely in the different waters. Most of the surface waters in the vicinity of the field contain at least 1,000 parts per million, and most of the shallower ground water contains between 1,000 and 3,000 parts. The concentration in general increases with depth but is governed to a considerable extent by the freedom of circulation. As the distribution of chloride is also affected by this condition marked variation in the total concentration of the deeper waters is usually associated with variation in the proportion of chloride. Thus the waters along the western edge of the field, where chloride is lowest, contain an average of about 10,000 parts per million of total mineral solids, whereas the waters of the Midway syncline, which are high in chloride, average about 30,000 parts. Although the concentration of the different types of water is fairly regular, individual samples may show considerable variation.

In the tables of analyses given in this paper the concentration is represented simply by the totals of the constituents reported except where bicarbonate is shown. Bicarbonate is unstable and tends to break down into carbonate when the solution is evaporated to dryness; hence, in accordance with convention, the bicarbonate radicle is not given its full value in the total but appears as carbonate.

Petroleum constituents.—In most industrial analyses petroleum constituents are not determined, but under the heading "Organic and volatile matter" is given the loss in weight when the solid matter obtained on evaporation of the water is heated to redness. The material thus lost includes whatever organic or hydrocarbon matter was present in the water but generally consists chiefly of carbon dioxide.

Certain minor constituents of petroleum or natural gas are soluble in water and have been observed in oil-field waters from several regions. Aside from the scientific interest that attaches to these substances they may in some places be of practical use, for their presence in a water has been taken by some to indicate that the water has been closely associated with oil or gas. The petroleum constituents soluble in water are of two kinds—simple light hydrocarbons, such as methane, and complex hydrocarbon derivatives, such as the naphthenic acids.

Methane and ethane are the predominating constituents of most natural gas, and water that has been in contact with gas is therefore likely to contain these hydrocarbons in solution. Their presence in water that is flooding an oil well is of little value in determining the source of the water, as they are apparently rapidly soluble and may be taken up by the water while it is being raised to the surface. Their presence in the water from a wildcat well in which no oil or gas has yet been found might be taken as a suggestion of the proximity of petroleum but certainly could not be considered conclusive evidence.

The more complex hydrocarbon derivatives that are soluble in water are chiefly compounds containing oxygen, the commonest of which are probably the naphthenic acids. These compounds are the oxygen derivatives of the naphthenes (polymethylenes) and have the general formula $C_nH_{2n-2}O_2$. In alkaline waters these acids are doubtless present as alkali salts rather than as free acids.

So far as the writer is aware no attempt has been made to study the petroleum acids in California oil-field waters, although W. E. Perdew, formerly with the Kern Trading & Oil Co., and others have detected them in certain waters from the Sunset-Midway and Coalinga fields. The answer to the question whether the presence or absence of these substances in a water may serve to determine the position of the water with respect to the oil zone obviously depends on the ease and rapidity with which water can dissolve the acids from the petroleum. If top water leaking down behind the casing and mixing with the oil can dissolve petroleum acids before it is pumped out such a distinction would be entirely misleading. It is probable that the chemical character of the water has much to do with its ability to dissolve the acids. As the alkali salts of the naphthenic acids are readily soluble in water, it may be inferred that alkali carbonate water of the type associated with the oil in the western part of the Sunset-Midway field is readily able to dissolve the acids when brought into contact with oil containing them. The acids are practically insoluble, however, in strong solutions of sodium sulphate, and therefore they are probably much less readily soluble in the strongly sulphate top waters. Until the rapidity with which naphthenic acids are extracted by different types of water is investigated their value as indicators of the original position of a water with respect to the oil is open to question.

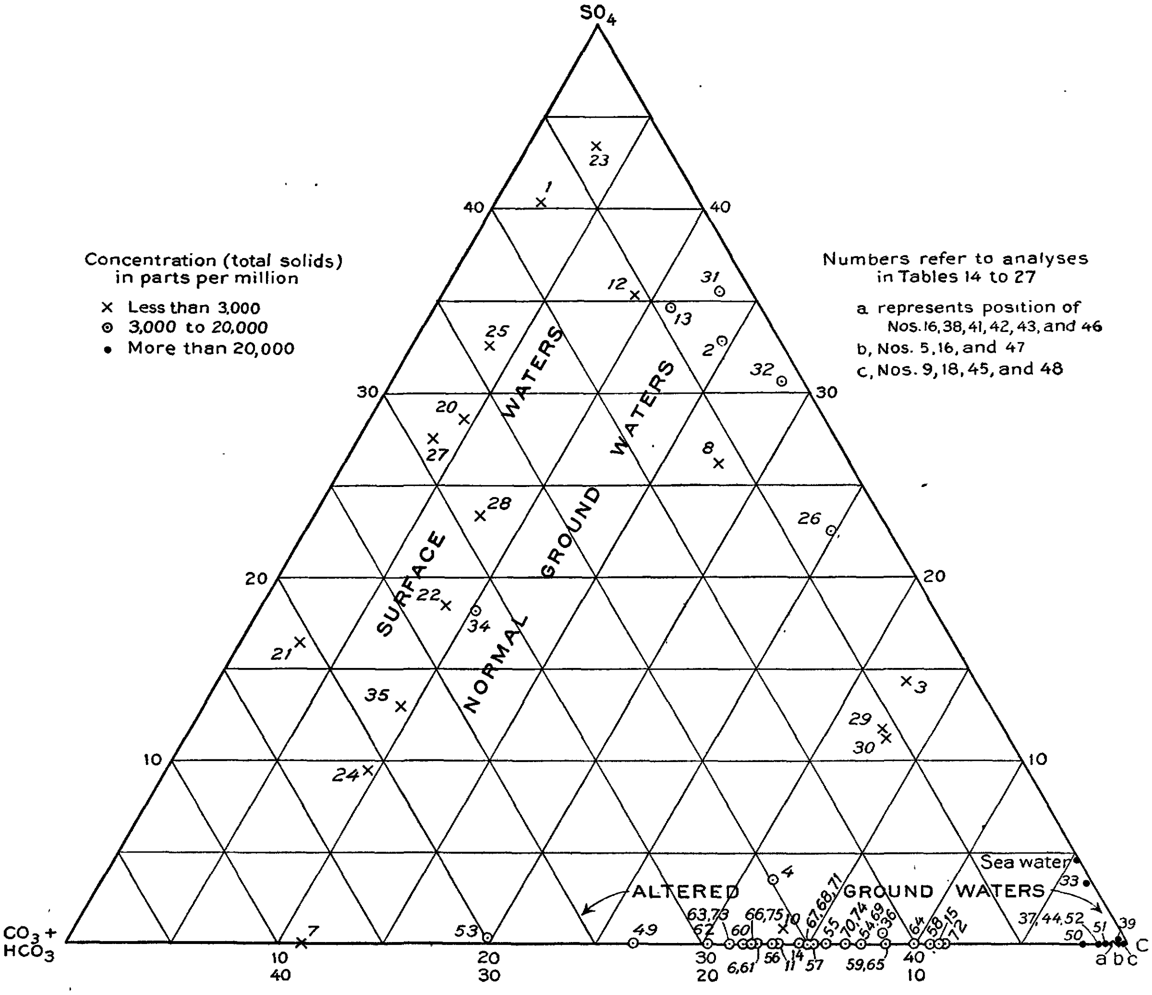

FIGURE 4.—Diagram showing proportions of sulphate (SO_4), carbonate and bicarbonate ($CO_3 + HCO_3$), and chloride (Cl) in the oil-field waters. The proportions of each constituent are plotted in percentage reacting values and therefore aggregate 50 per cent.

The presence of organic acids in alkaline waters may be determined by acidulating the water. Organic acids, if present in moderate amounts, appear as a milky precipitate, but in some waters they are so abundant that they separate out in large oily globules. Many of the waters near the oil measures respond to this reaction. The following more conclusive test, devised by Kharitschoff,[1] may be of value to those who desire to examine oil-field waters for petroleum acids:

> The water to be tested is first acidulated with hydrochloric acid and well shaken with benzine, which extracts all organic acids, leaving all the sulphur behind. The benzine solution is then separated, repeatedly washed with warm water, and filtered. To the filtrate is added a few cubic centimeters of a solution of copper sulphate and three or four drops of piridine or of a strong ammoniac solution, and the mixture is well shaken. A green coloration of the benzine on top of the testing tube shows the presence of petroleum acid in the tested water, and the degree of coloration allows to judge of its quantity.

GENERAL CLASSIFICATION.

As all natural waters are mixtures, it is impossible to classify them rigorously, and any system of classification is a matter of convenience rather than of fixed principles. It is evident that for practical convenience oil-field waters should be classified as far as possible according to their position in relation to the oil. As the surface or shallow ground waters, together with the deeper ground waters

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[1] Kharitschoff, K. V., Petroleum acids in boring waters: Petroleum Rev., vol. 28, p. 380, 1913.

outside the oil fields, are high in sulphate, whereas waters close to the oil are practically free from sulphate, the proportion of sulphate furnishes the most rational single basis for classification. On this basis waters high in sulphate and evidently unaffected by contact with oil may be called normal waters and those free from sulphate may be called altered waters. It is convenient also to recognize an intermediate group which may be called modified waters.

When sulphate is removed from a water through reaction with oil carbonate is apparently introduced, and if the waters contained only these two acid radicles the ratio between the two would furnish an adequate basis for classification. As most oil-field waters, however, contain large amounts of chloride the proportion of this constituent must generally be taken into account. Figure 4 shows the proportions of sulphate, carbonate (and bicarbonate), and chloride in all the waters whose analyses are given in this report. This three-cornered diagram is based on the fact that as sulphate, chloride, and carbonate constitute the only acid radicles in most waters their reacting values must equal the sum of the reacting values of the basic radicles.[1] A water consisting entirely of sulphates would fall at the upper apex of the triangle; one consisting entirely of carbonates and bicarbonates would fall at the lower left-hand apex, and one consisting of sulphates, carbonates (or bicarbonates), and chlorides in equal proportions would fall at the center of the triangle. All the surface and shallower ground waters in the Sunset-Midway field and the deeper ground waters outside of the field therefore fall in the upper or central part of the triangle, whereas the altered waters that contain no sulphate fall on the base line. It is evident that chloride is the predominating constituent in most of the altered waters and that it can not properly be ignored in classifying them.

Although the three-cornered diagram affords a convenient means of comparing the proportions of the three acidic radicles in waters, a more complete classification may be made on the basis of the properties of reaction. Practically all the waters high in sulphate are low in carbonate and high in alkaline earths and are therefore characterized by secondary salinity. As the sulphate diminishes and the carbonate increases the secondary salinity decreases to zero and primary alkalinity appears. Normal waters therefore have secondary salinity, whereas modified and altered waters may have either primary alkalinity or secondary salinity, their character depending on the proportions of carbonate and chloride. All the waters containing more than 8 per cent of carbonates (see fig. 4) have primary alkalinity, whereas those consisting almost entirely of chlorides have secondary salinity. Without considering for the present the conditions that govern the respective proportions of carbonate and chloride, the altered waters containing no sulphate may be divided into two groups—the brine, which is high in chloride and shows secondary salinity, and the mixed waters, which contain less chloride and show primary alkalinity. The chemical characteristics of representative waters of these classes are considered in the following section.

WATERS OF THE NORMAL TYPE.

To the normal type belong the surface waters and the shallow ground waters of the Sunset-Midway field and the deeper ground waters outside the field. As the chief criterion of a normal water is by definition a high content of sulphate, it is apparent that waters of more or less diverse composition in other respects may be grouped under this head. Within the field, however, the type is very distinct. Normal waters are characterized by the presence of secondary salinity; by a high percentage of sulphate, with carbonate and chloride generally subordinate; by alkaline earths about equal to or predominating over the alkalies; and generally by a concentration of less than 3,000 parts per million.

Analyses 1 and 2, Table 14 (p. 63), are representative waters of the normal type. Analysis 1 represents spring water issuing from the Maricopa shale in the hills a short distance west of the field. The sulphate salinity, or the percentage of rSO_4 in rSO_4+rCl is very high, and the ratio of carbonate to sulphate is very low. The water shows very strong secondary salinity and has a fairly high proportion of secondary alkalinity—in other words, the strong acids (SO_4 and Cl) exceed the weak acids (CO_3) in

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[1] This type of diagram has been used by W. H. Emmons in discussing mine waters. (The enrichment of ore deposits: U. S. Geol. Survey Bull. 625, pp. 83-86, 1917.)

reacting value, and the alkaline earths exceed the alkalies. The concentration of this water, 2,334 parts per million, is very high for surface waters in most regions but is not much higher than the average in the Sunset-Midway field. Other analyses of this type of water are shown in Table 18 (p. 81).

Analysis 2 represents water from a shallow-water well at the east end of the Buena Vista Hills. The carbonate-sulphate ratio is even lower than in the spring water represented by analysis 1, being only 0.09. The sulphate salinity is also slightly lower, but this is due to the increase of chloride rather than to decrease of sulphate. As the concentration is about double that of the shallower water the actual amounts of most of the constituents are higher, but the most marked rise is in the chloride. The alkaline earths are lower in relative proportion, and the alkalies are correspondingly higher. These variations are summed up in the properties of reaction. The primary salinity in analysis 2 is considerably higher than in analysis 1 owing to the increase of chloride and the alkalies; the secondary salinity is somewhat lower, and the secondary alkalinity is very much lower owing to the decrease in carbonate and alkaline earths. Other analyses of this type of water are shown in Tables 15 (p. 65) and 19 (p. 82).

WATERS OF THE MODIFIED TYPE.

The modified type includes the waters lying below those of the normal type and above those of the altered type, or, in general, the waters several hundred feet or more away from the oil measures. The type is characterized by low secondary salinity or by primary alkalinity; by a lower ratio between sulphate and both carbonate and chloride than in the normal type, and by the predominance of alkalies over alkaline earths.

Analysis 3, Table 14, represents a slightly modified water. The sulphate salinity is much lower than in the normal waters, being only 30.6 per cent, and hydrogen sulphide, which indicates alteration, is present. The secondary salinity of this water is very low in comparison with that of the normal waters; in other words, the water is characterized by lower sulphate and alkaline earths and by higher chloride and alkalies. As the water is derived from a depth of 1,090 feet the increase in chloride is to be expected, though the total concentration of the water is unusually low.

Analysis 4 represents a very strongly modified water that is more typical of the modified group. This water is still lower in sulphate and is higher in carbonate, the sulphate salinity being only 10.3 per cent and the carbonate-sulphate ratio being 4.2. This water, like No. 3, contains hydrogen sulphide. The alkaline earths are much lower than in the shallower waters, and the alkalies are much higher. These changes are summed up in the properties of alteration; the water is one of primary alkalinity and not of secondary salinity like those discussed above and is characterized by moderate primary salinity and low secondary alkalinity. The concentration of this water, 7,040 parts, is about the average for a water of this type. Analyses of other modified waters are given in Table 20 (p. 83).

WATERS OF THE ALTERED TYPE.

All the waters occurring in or vertically below the oil measures belong to the altered group, and the waters for some distance above the oil are usually also altered. The distance to which the zone of alteration extends above the oil depends largely on the local geology. Waters occurring a short distance above oil zone A are in general strongly modified but are not completely altered. The waters occurring in zone A (edge waters) are of the altered type, however, and as these waters replace the oil entirely down the dip they become the top waters of zone B. Similarly, the edge waters of zone B may, farther down the dip, become the top waters of zone C. It is evident, therefore, that waters several hundred feet above the producing zone in the central part of the field may in reality be edge waters of a higher oil zone and therefore just as completely altered as if they occurred in or below the producing zone itself. Hence along the western edge of the field, where the zone of alteration extends only a short distance above the oil sands, top waters may readily be identified by their chemical character, but in the central part, where the zone of alteration extends much higher, only those top waters occurring 700 feet or so above the oil can be so identified.

TABLE 14.—*Types of ground water from Sunset-Midway field.*

	Normal.		Modified.		Altered.		
	1	2	3	4	5	6	7
PROPERTIES OF REACTION IN PER CENT.							
Primary salinity	14.4	54.0	90.2	70.2	86.6	65.0	22.4
Secondary salinity	70.4	40.4	3.4	0	12.2	0	0
Primary alkalinity	0	0	0	27.2	0	32.2	60.4
Secondary alkalinity	15.2	5.6	6.4	2.6	1.2	2.8	17.2
Per cent of rSO_4 in rSO_4+rCl	94.9	70.8	30.6	10.3	0	0.3	Trace.
Ratio of rCO_3+rHCO_3 to rSO_4	.19	.09	.22	4.2	∞	17.5	8
CONSTITUENTS IN PARTS PER MILLION.							
Sodium (Na)	117	[a] 867	911	[a] 2,710	11,160	3,747	[a] 1,011
Potassium (K)			8.4	....	124	99	....
Calcium (Ca)	444	404	23	40	848	40	56
Magnesium (Mg)	107	144	39	15	425	35	77
Iron oxide (Fe_2O_3) and alumina (Al_2O_3)	....	22	....	....	....	11	....
Sulphate (SO_4)	1,393	2,205	605	420	0	22	Trace.
Chloride (Cl)	50	671	1,013	2,660	20,694	3,924	421
Nitrate (NO_3)	8	60	....	....	....	....	....
Carbonate (CO_3)	0	[b] 116	0	[b] 1,100	48	0	[b] 1,236
Bicarbonate (HCO_3)	335	....	175	....	359	3,672	....
Silica (SiO_2)	50	....	32	90	102	122	Trace.
	2,334	4,489	2,717.4	7,040	33,578	9,807	2,800
Hydrogen sulphide	0	0	Present.	Present.	0	0	Present.
REACTING VALUES IN PER CENT.							
Alkalies:							
Sodium (rNa)	7.2	[b] 27.0	44.7	[a] 48.7	43.0	47.8	[a] 41.4
Potassium (rK)			.4		.3	.8	
Alkaline earths:							
Calcium (rCa)	30.7	14.5	1.3	.8	3.7	.6	2.6
Magnesium (rMg)	12.1	8.5	3.6	.4	3.0	.8	6.0
Strong acids:							
Sulphate (rSO_4)	40.2	32.9	14.3	3.6	0	.1	....
Chloride (rCl)	2.1	13.6	32.5	31.5	49.4	32.4	11.2
Nitrate (rNO_3)	.1	.7	....	....	....	....	....
Weak acids:							
Carbonate (rCO_3)	0	[b] 2.8	0	[b] 15	.1	0	[b] 38.8
Bicarbonate ($rHCO_3$)	7.6	....	3.2	....	.5	17.5	....

[a] Reported and calculated as sodium but includes potassium.
[b] Reported and calculated as carbonate but probably in part bicarbonate.

1. Crocker Spring, sec. 18, T. 31 S., R. 22 E. Spring issues from Maricopa shale. Sampled by G. S. Rogers, September, 1915. Analyst, S. C. Dinsmore.
2. Pyramid Oil Co., water well, 80 feet deep, in sec. 18, T. 32 S., R. 25 E. Analyst, Kern Trading & Oil Co.
3. August Water Co., California Amalgamated well 2, sec. 35, T. 32 S., R. 23 E. Sulphur water from depth of 1,090 feet in Maricopa shale and therefore below oil measures. Sampled by G. S. Rogers, July, 1914. Analyst, Chase Palmer.
4. Ida May water well, SW. ¼ sec. 2, T. 11 N., R. 24 W. Sulphur water, chiefly from depth of about 1,500 feet (in Maricopa shale) but probably in part from depth of about 500 feet, or above highest oil sand. Analyst, F. T. Green, August 27, 1912. Authority, Ida May Oil Co.
5. Mays Consolidated Oil Co., well 6, sec. 28, T. 31 S., R. 23 E. Flowing water from depth of 3,000 feet, or a short distance beneath oil sand in upper part of zone C. Sampled by G. S. Rogers, September, 1915. Analyst, S. C. Dinsmore.
6. Tamalpais Oil Co., well 3, sec. 25, T. 32 S., R. 23 E. Water pumped with oil; probably edge water in upper part of zone A (1,223 feet). Sampled by G. S. Rogers, August, 1914. Analyst, S. C. Dinsmore.
7. Potter Oil Co., well 2, sec. 15, T. 31 S., R. 22 E. Water from lower part of tar sand zone. Analyst, Smith, Emery & Co., May, 1915. Authority, Potter Oil Co.

Analyses 5, 6, and 7, Table 14, represent waters of the altered type. These waters differ in many respects from one another, but their common and most striking characteristic is the practical absence of sulphate.

Analysis 5 represents a brine of the type associated with the oil throughout the central and eastern parts of the field. This water is very different from those already described, having a very high content of chloride and alkalies. Alkaline earths are fairly high, and carbonate is very low. The water is therefore characterized by secondary salinity, with high primary salinity and very low secondary alkalinity. The concentration of waters of this type usually ranges between 30,000 and 40,000 parts per million. Other analyses of such waters are given in Tables 21, 22, and 23 (pp. 84–86).

Analyses 6 and 7 represent altered waters of the mixed type. These waters are much less concentrated than the brine and show proportionately lower chloride and alkaline earths and much higher carbonate. They are, therefore, waters of primary alkalinity. No. 6 is a good example of the type of water associated with the oil along the western edge of the field; No. 7 has more pronounced primary alkalinity and has been recognized only in the northern part of this belt. Many other analyses of waters of the mixed type are given in Tables 24 to 27 (pp. 88–91).

ORIGIN AND RELATIONS OF THE TYPES.

ORIGIN OF THE ALTERED (SULPHATE-FREE) WATER.

Inasmuch as the normal ground waters everywhere on the west side of San Joaquin Valley show a high content of sulphate and the only known waters containing no sulphate are those associated with the oil, it is reasonable to suppose that the sulphate-free waters have been derived from the others through chemical reaction with the oil. The reactions that may take place and the corroborative evidence afforded by a study of the changes in the character of the oil itself have been discussed on pages 26–32. The sulphate is supposed to be reduced to sulphide by certain constituents of the oil, which are themselves simultaneously oxidized to products that eventually yield carbonate. The action of oil upon water may therefore be considered roughly as resulting in the substitution of carbonate for sulphate.

Although no suites of analyses showing the complete alteration of waters are available, analyses of water from different depths in three wells are given in Table 15. Nos. 8 and 9 and Nos. 10 and 11 represent waters from different depths in two oil wells, and Nos. 12 and 13 represent waters from a well outside the oil field and therefore show the normal change in depth in waters unaffected by oil or gas. Analysis 8 represents water occurring between 350 and 790 feet, and analysis 9 the water occurring at 2,505 feet, or below the top oil sand, in the same well. No. 8 is an ordinary water of the normal type, having sulphate considerably in excess of chloride and greatly in excess of carbonate. As the alkaline earths in this water are unusually low, the water shows a slight degree of primary alkalinity. No. 9 is an ordinary altered brine of the type associated with the oil everywhere in the central and eastern parts of the field. Its concentration is about 15 times as great as that of the upper water, and all the constituents are present in correspondingly greater amount, except sulphate, which is completely lacking, and carbonate, which has about the same value. These two waters, which are vertically about 2,000 feet apart, thus represent the extremes, and analyses of the modified waters that undoubtedly occur at the intermediate levels are unfortunately not available.

Analyses 10 and 11 represent waters of the mixed type found along the western edge of the field. No. 10 is a modified water occurring below tar sands but 600 feet above the highest oil sand; No. 11 is an altered water occurring 30 feet above the highest oil sand, or 570 feet vertically below No. 10. As would be expected, the differences between these waters are much less marked than those between Nos. 8 and 9, which occur 2,000 feet apart, though the character of the changes is the same. The per cent of sulphate decreases from 0.8 in the upper water to 0.1 in the lower, the sulphate salinity decreases from 2.3 to 0.2, and the ratio of carbonate to sulphate increases from 20 to 165. The properties of reaction show only a slight change, though the concentration of the lower water is more than double that of the upper. Water from beds below the lowest oil sand in the section to the west is practically identical with No. 11, except that sulphate is completely lacking and that the total concentration may be higher. (See Tables 25 and 26, pp. 89–90.)

TABLE 15.—*Analyses of ground water from different depths, showing change in character as oil is approached, and normal change with depth.*

	Wells in oil field.				Well in which no oil or gas has been found.	
	8	9	10	11	12	13
PROPERTIES OF REACTION IN PER CENT.						
Primary salinity	87.4	83.6	68.6	67.0	64.6	91.2
Secondary salinity	0	16.0	0	0	24.0	0
Primary alkalinity	3.4	0	28.6	31.8	0	6.6
Secondary alkalinity	9.2	.4	2.8	1.2	11.4	2.2
Per cent of rSO_4 in rSO_4+rCl	60.2	0	2.3	0.2	80.0	76.0
Ratio of rCO_3+rHCO_3 to rSO_4	.29	....	20	165	.16	.13
CONSTITUENTS IN PARTS PER MILLION.						
Sodium (Na)	719	11,176	[a] 1,059	[a] 2,809	[a] 544	[a] 3,000
Potassium (K)	9.5	86	....	....	....	....
Calcium (Ca)	39	1,100	11	26	124	28
Magnesium (Mg)	22	503	9.6	2.9	82	19
Iron (Fe)	....	....	1.7	....	....	Trace.
Sulphate (SO_4)	879	0	38	8.7	1,243	4,421
Chloride (Cl)	429	20,421	1,125	2,920	232	1,040
Iodide (I)	....	29	....	....	....	....
Nitrate (NO_3)	....	45	....	....	....	....
Carbonate (CO_3)	32	0	[b] 443	[b] 1,226	[b] 125	[b] 355
Bicarbonate (HCO_3)	170	162	....	....	....	....
Silica (SiO_2)	44	....	12	17	57	29
	2,257.5	33,440	2,699.3	7,009.6	2,407	8,892
REACTING VALUES IN PER CENT.						
Alkalies:						
Sodium (rNa)	45.0	41.6	[a] 48.6	[a] 49.4	[a] 32.3	[a] 48.9
Potassium (rK)	.4	.2	....	....	....	....
Alkaline earths:						
Calcium (rCa)	2.8	4.7	.6	.5	8.5	.5
Magnesium (rMg)	2.6	3.5	.8	.1	9.2	.6
Strong acids:						
Sulphate (rSO_4)	26.3	0	.8	.1	35.3	34.6
Chloride (rCl)	17.4	49.7	33.5	33.4	9.0	11.0
Nitrate (rNO_3)	....	.1	....	....	....	....
Weak acids:						
Carbonate (rCO_3)	1.5	0	[b] 15.7	[b] 16.5	[b] 5.7	[b] 4.4
Bicarbonate ($rHCO_3$)	4	.2	....	....	....	....

[a] Reported and calculated as sodium but includes potassium.
[b] Reported and calculated as carbonate but probably in part bicarbonate.

8, 9. Midway Northern Oil Co. well in sec. 32, T. 12 N., R. 23 W. Sampled by G. S. Rogers, August, 1914. Analyst, Chase Palmer. 8, Water from sands between 350 and 790 feet; 9, water from sand at depth of 2,505 feet, or below top oil sand and about 100 feet above second oil sand.

10, 11. Standard Oil Co. well in sec. 30, T. 32 S., R. 24 E. Sampled while drilling and analyzed by Standard Oil Co. 10, Water from depth of 1,380 feet, or below tar sands of zone A and 600 feet above top of highest oil sand in zone B; 11, water from depth of 1,947 feet, or 30 feet above top of highest oil sand in zone B and 120 feet above top of main producing oil sand.

12, 13. Standard Oil Co. well Domengine No. 1, several miles north of the Coalinga oil field. No. 12 represents water from depth of 370 feet; No. 13, water from depth of 3,700 feet, at which no oil or gas had been encountered. These analyses probably represent the normal changes that occur with increasing depth in waters unaltered by oil. Analyst, Standard Oil Co.

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Analyses 12 and 13 represent waters encountered at 370 and 3,700 feet, respectively, in a well drilled several miles north of the Coalinga oil field. No oil or gas was encountered in the well, which was drilled to a depth several hundred feet below the level of the lower water. Both waters are unaffected by hydrocarbons, and their analyses may therefore be considered as showing the normal changes that take place with increasing depth. It will be noted that although the concentration of the lower water is nearly four times that of the upper, the proportion of sulphate is almost exactly the same; the sulphate salinity of the upper water is 80 per cent and that of the lower 76 per cent, and the carbonate-sulphate ratio in the upper water is 0.16 and in the lower 0.13. There is a slight difference in the properties of reaction, owing to the fact that the alkaline earths are lower in the deeper water, but the similarity in sulphate content despite the great change in concentration is striking.

Analyses of water from other deep wells outside the oil fields are not available, but Dole,[1] after a careful chemical study of the waters of San Joaquin Valley, finds that although the proportion of sulphate bears no constant relation to depth, the deep as well as the shallow waters on the west side of the valley are invariably high in sulphate.

ORIGIN OF THE BRINE.

Owing to the fact that underground waters in a region of sedimentary rocks tend to follow the bedding planes, the structure of the rocks has a considerable effect on the freedom of the circulation, which in turn influences the chemical character of the waters themselves. If salt water, for example, is present in the strata before they are folded, some of it may be trapped in structural troughs or basins and held there indefinitely. Although all the water in the Sunset-Midway field is more or less salty, the very salty water belonging to the well-defined chemical type here called brine occurs only in the Midway syncline or on the anticline to the east—localities in which the circulation is naturally restricted. This water may be regarded as fossil sea water, entrapped in the sediments when they were laid down and only slightly altered by contact with the surrounding rocks.

When sediment is deposited on the floor of the sea it is saturated with sea water, which remains in the pores until it is elevated to form land. The compacting of the material necessarily forces out a large quantity of this water, but that remaining ordinarily fills the pore spaces of the rocks after they have assumed their normal bulk. Uplift, however, causes circulation of the water to commence, and meteoric or rain water falling on the newly elevated land surface enters the beds and tends to dilute and force out the connate water—the sea water entrapped in the sediments. This replacement takes place with considerable rapidity under some conditions, but under others the connate water may remain trapped for long periods of time. The freedom of the outlet by which the salt water may escape is the chief factor, for water trapped in a lens of sand entirely inclosed by shale might remain there indefinitely. Similarly, as circulation follows bedding planes, if the strata are folded into a closed basin or trough, some of the water will accumulate in its deepest portion and remain there. Where the outlet is not entirely closed but is merely restricted other conditions have an influence, such as the volume and the head of the meteoric waters that are tending to drive out the connate water, the porosity of the materials through which the waters must pass, and the dip of the rocks and the distance from their outcrop. Even where all the conditions are favorable to the retention of the salt water it is evident that some of it near the surface will be leached out and that, other things being equal, the largest proportion will be retained at the greatest depths. In a region of lenticular beds, however, irregularities are to be expected, for the freedom of circulation differs from bed to bed and therefore some sands will retain their salt water much longer than others.

It has already been pointed out that in a hydrologic sense the most important structural feature of the Sunset-Midway field is the Midway syncline, which with the Buena Vista and associated anticlines to the east forms a deep wrinkle or crenulation in the general mono-

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[1] For a complete account of the underground waters of San Joaquin Valley, see Mendenhall, W. C., Dole, R. B., and Stabler, Herman, Ground water in San Joaquin Valley, Calif.: U. S. Geol. Survey Water-Supply Paper 398, 1916.

clinal slope of the west side of San Joaquin Valley. If the valley is regarded as a great open trough with these folds perched high on its western rim, it becomes evident that the syncline constitutes a trap which acts not only to pond water within itself but also to impede circulation across the anticline to the east. As the Maricopa and Etchegoin formations were laid down in salt water and were thoroughly saturated with it when they were elevated above the sea, it is entirely reasonable to suppose that some of this water would be trapped in the syncline when the beds were folded and would remain there indefinitely. Rain water falling in the western part of the field and entering the beds has naturally driven out most of the salt water in the belt along the outcrop and has mingled with and partly replaced the salt water in the belt still farther from the outcrop, but it has apparently never penetrated to the deeper portion of the trough. A large volume of rain water acting through a long period of time might eventually replace the connate water entirely, but it must be remembered that the region is arid and that the beds are geologically young.

As water in contact with rock tends to change in character, it can not be expected that fossil sea water will long retain exactly its original composition. Water entrapped in the older rocks, such as the Paleozoic strata of the Appalachian oil fields, may have changed so materially that its origin, so far as chemical evidence goes, may be in doubt, but the salt water in the Midway syncline is so similar to sea water that there can be little doubt that it is fossil sea water. The principal differences in composition are due entirely to the removal of the sulphate through the action of oil.

The reaction between sulphate-bearing water and petroleum results essentially in the substitution of carbonate for sulphate, and although the exact proportion between the sulphate removed and the carbonate introduced is not known, it may be assumed for the present that the values are equivalent. In unaltered sea water sulphate and chloride exceed the alkalies in reacting value and are therefore partly in equilibrium with the alkaline earths; hence if carbonate is substituted for the sulphate the alkaline earths will be partly in equilibrium with carbonate. Only a small amount of earths and carbonate can be retained in solution, even in the presence of an excess of carbon dioxide, and if this amount is exceeded alkaline-earth carbonates will be formed and then lost through precipitation. In a concentrated solution like sea water the maximum of alkaline earths balanced by carbonate that can be retained represents only a very small percentage of the total concentration, and if the sulphate is entirely replaced by carbonate a large proportion of this carbonate, with an equivalent value of earths, will be precipitated.[1] The effect on the properties of reaction of this substitution and consequent loss therefore consists in a decrease in secondary salinity and an increase in secondary alkalinity limited by the solubility of the alkaline-earth carbonates. Sea water has 21.1 per cent of secondary salinity, of which 9.3 per cent is contributed by sulphate; hence the removal of the sulphate will effect a substantial reduction in the secondary salinity. The increase in secondary alkalinity, however, will be slight, so that if the properties are expressed in percentages the primary salinity will be raised. If it is assumed, first, that the sulphate in sea water is entirely removed and an equal proportion of carbonate introduced, and second, that 8.0 per cent, or 2,800 parts per million, of alkaline-earth carbonates is lost through precipitation, the properties will change as follows:

Changes in properties of sea water through substitution of carbonate for sulphate.

	Primary salinity (per cent).	Secondary salinity (per cent).	Secondary alkalinity (per cent).	Concentration (parts per million).
Normal sea water (see analysis 19, Table 16)	78. 6	21. 1	0. 3	35, 000
Sea water in which all SO_4 is calculated as CO_3	78. 6	11. 8	9. 6	35, 000
Same after precipitation of assumed excess of alkaline-earth carbonates	85. 4	12. 8	1. 8	32, 200

The similarity between the properties of the altered sea water, as thus deduced, and those of the oil-field brines leaves little doubt that the brines are simply fossil sea water modified chiefly through the removal of sulphate and the accompanying precipitation of alkaline-

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[1] Murray, John, and Irvine, Robert, On the chemical changes which take place in the composition of the sea water associated with blue muds on the floor of the ocean: Roy. Soc. Edinburgh Trans., vol. 37, p. 481, 1893.

earth carbonates. The properties of some of the brine samples analyzed check almost exactly with those of the altered sea water. (See analysis 5, p. 63.) Most of the samples, however, show 1 or 2 per cent more secondary salinity than simple altered sea water, an excess which may indicate that the value of the carbonate introduced is not quite equivalent to that of the sulphate removed. Any attempt to reduce these reactions to exact figures, however, is admittedly speculative. It would be strange indeed if the properties of the brines were identical with those of altered sea water, as calculated above, for the figures used represent the average composition of sea water from all parts of the world. The waters of a deep embayment, such as the San Joaquin Valley was during the middle Tertiary time, are almost certain to depart somewhat from this average. If the region is arid the waters may become more concentrated through evaporation and may deposit calcium carbonate and gypsum, whereas if many rivers empty into the basin, its waters may become more dilute and may be locally modified in composition by admixture with the river water.

There are two minor differences in composition between the brines and sea water, which are not explained by the removal of the sulphate, namely, the deficiency in the brines of potassium and magnesium, as compared with sodium and calcium, respectively. The average ratio by reacting value of sodium to potassium in sea water is 48, whereas in the oil-field brines it is about 165. The deficiency of potassium in the brine is accounted for by the fact that clays and silts extract potassium from water by a process of absorption, whereas they have little effect on sodium. The ratio of magnesium to calcium in normal sea water is about 5, but in the oil-field brines it averages less than 1, and this discrepancy can not be so easily explained. At moderately high temperatures magnesium is rapidly deposited from solution as basic carbonate or hydrate,[1] and it is possible that the temperatures of 100° to 130° F., which prevail at depths of 1,000 to 4,000 feet, have had some effect in lowering the concentration of the magnesium. It is also possible that magnesium is removed under some conditions as magnesium silicate. Kharitschoff[2] in his experiments on the reduction of sulphates by petroleum found that magnesium sulphate apparently underwent somewhat more reduction than sodium sulphate, and if this observation is well founded it may also partly account for the deficiency of magnesium in the oil-field waters.

RELATIONS OF THE MIXED TYPE.

VARIATION IN CHLORIDE.

No matter how effectively fossil sea water may be trapped in a structural trough, such as the Midway syncline, it is evident that near the surface of the ground and also around the edges of the trough, where the rocks crop out, there will be a certain admixture of meteoric or rain water, which is constantly tending to drive out and replace the connate water. The extent to which this replacement of salt water by fresh has progressed may be studied by observing the increase of chloride with depth beneath the surface and with distance from the outcrop. Chloride forms a good index of the extent of the replacement, for it is not removed through reaction with the rocks or with petroleum, nor are there any salt deposits known which could increase the concentration of chloride in the waters near them.

The increase of chloride with depth beneath the surface has already been illustrated by the analyses in Table 15 and need not be considered further. Practically all the other analyses given also show a similar and fairly regular increase in the chloride with depth, the extremes being represented by the surface waters, which carry less than 300 parts per million, and the brines in the deeper part of the Midway syncline, which carry about 20,000 parts.

The increase in chloride with distance from the outcrop is also fairly regular, within certain limits, throughout the field. In order to illustrate this increase four sets of analyses of waters occurring at different distances from the outcrop have been plotted in the four diagrams in figure 5. In these diagrams the hori-

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[1] Davis, W. A., Studies of basic carbonates: Soc. Chem. Industry Jour., vol. 25, p. 796, 1906.

[2] Kharitschoff, K. V., The waters in petroleum wells: Petroleum Rev., vol. 29, p. 368, 1913.

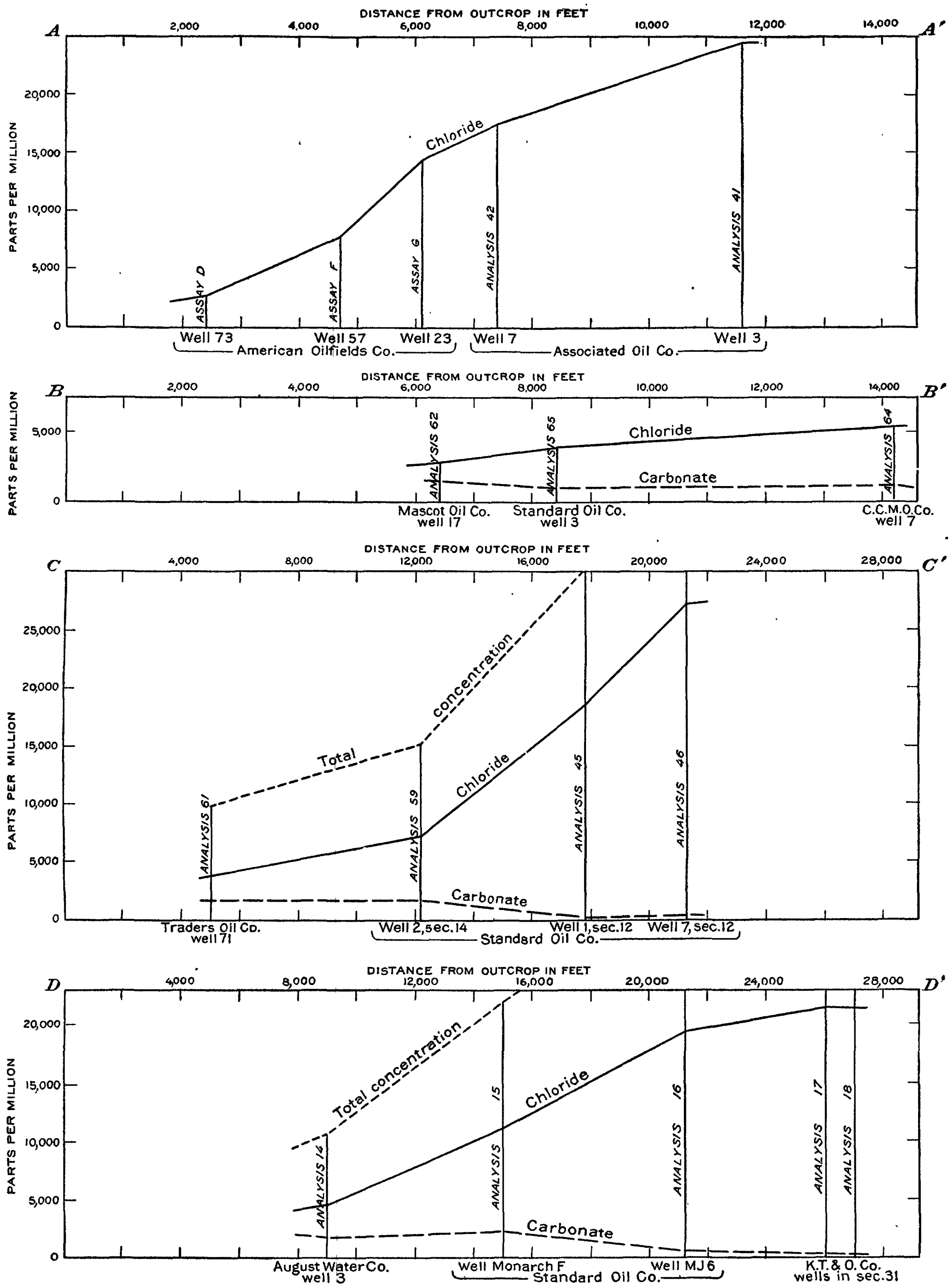


FIGURE 5.—Diagrams showing increase in chloride and decrease in carbonate in waters with distance from the outcrop. For location of sections see Plate II.

zontal scale represents the distance from the outcrop of the well from which the samples were taken, and the vertical scale the concentration of chloride and other constituents. The first three diagrams represent waters along lines about parallel to the dip of the rocks, but the line of the fourth is from east to west and therefore oblique to the dip. (See Pl. II.) All four diagrams, however, bring out the decrease in chloride with increasing proximity to the outcrop, and if analyses of waters obtained still nearer the outcrop could be added they would doubtless show still less chloride. The first, third, and fourth diagrams show the gradation from waters low in chloride and evidently largely of meteoric origin to the very salty brines of the Midway synclines. As these brines have about the composition and density of ocean water, analyses of water still farther from the outcrop would show no further increase in chloride. In the second diagram, however, all three waters represented are of the mixed type, the zone of brines not being reached in the distance plotted.

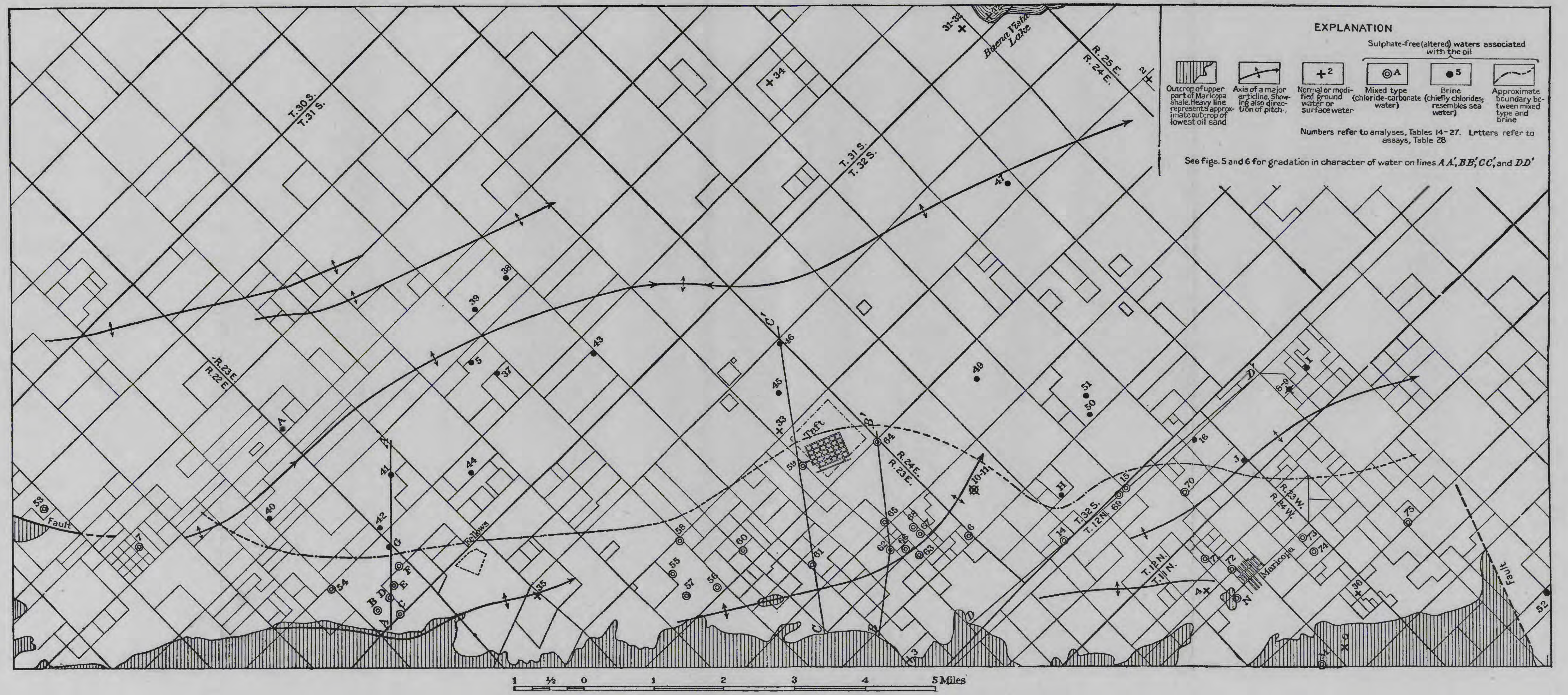
Although all the waters plotted in figure 5 are of the type of altered waters more or less closely associated with the oil, they are not all exactly from the same bed or horizon, a fact which is suggested by the slight irregularities in the curves. As already explained, the oil zone in the Midway syncline is several hundred feet stratigraphically lower than the oil zone in the western part of the field and also, because of the dip, is much deeper beneath the surface. Thus of the waters represented in diagrams AA′ and BB′ those nearest the outcrop are probably 500 feet or so stratigraphically higher than those farthest from the outcrop. The same is true of the waters represented in diagram CC′, except that the third water from the outcrop occurs 1,500 feet above the horizon of the productive zone and is therefore as high as the waters nearest the outcrop, if not higher. Of the water represented in diagram DD′, however, the first two occur in the Maricopa shale several hundred feet below the oil measures, whereas the three farthest from the outcrop are either in or slightly above zone B. (See Table 16, p. 72.) The fact that the gradation shown by this diagram is similar to that shown by the others indicates that the exact vertical or stratigraphic position of the water is of little significance and that the gradation is essentially horizontal and is controlled by distance from the outcrop.

VARIATION IN THE PROPERTIES OF REACTION.

Besides causing a simple variation in the chloride content the mingling of connate salt water and meteoric rain water leads to a series of reactions between the other constituents and produces corresponding changes in the properties of the waters. The fact that the water along the western edge of the field is of the chloride-carbonate type whereas that farthest east is a brine showing secondary salinity is due to the entrance of meteoric water at the outcrop, and the gradations that may be traced between this mixed type and the brine afford an interesting study of the mixing of meteoric and connate waters.

It has already been shown that the action of oil upon a sulphate-bearing water results in the removal of the sulphate and the substitution of carbonate and that when sea water undergoes this alteration alkaline-earth carbonates are formed and precipitated. As a result the reactive properties of the sea water become almost identical with those of the oil-field brines—that is, the sea water loses its secondary salinity, gains in primary salinity, and gains in secondary alkalinity only slightly because of the small solubility of the alkaline-earth carbonates. If the normal surface waters of the region, consisting almost entirely of sulphates, are subjected to this change it is evident that they will become practically pure carbonate waters. As a result of this change a considerable proportion of alkaline-earth carbonates will be lost through precipitation, but as these waters are generally not very highly concentrated, a considerable proportion will be retained. The alteration of such waters, therefore, results in a change from primary and secondary salinity to primary and secondary alkalinity, though the percentage of the last property is only moderate.

If the changes induced in the properties of waters by the substitution of carbonate for sulphate and the consequent precipitation of alkaline earths are understood, the relations of the chloride-carbonate type of water become



MAP OF SUNSET-MIDWAY FIELD SHOWING LOCATION OF WATER SAMPLES ANALYZED AND AREAL DISTRIBUTION OF THE BRINE AND MIXED TYPES OF WATER.

clear. This type is derived through the mixing of the altered meteoric waters, which show strong primary alkalinity and contain chiefly sodium carbonate, with the brine or altered sea water, which still shows some degree of secondary salinity. The reaction that ensues when the two are mixed may be written thus:

$$\underset{\text{Secondary salinity}}{CaCl_2} + \underset{\text{primary alkalinity}}{Na_2CO_3} = \underset{\text{primary salinity}}{2NaCl} + \underset{\text{secondary alkalinity}}{CaCO_3}$$

The addition of a water that has primary alkalinity to a brine increases the alkalies without corresponding increase in strong acids and therefore reduces the secondary salinity of the brine. It is evident that if a sufficient amount of sodium carbonate water is added all the secondary salinity will be destroyed and the water will then be characterized by only two properties, primary salinity and secondary alkalinity. Any further increment of sodium carbonate water will then introduce primary alkalinity, which will continue to increase as more of the carbonate water is added. The average concentration of most of the brines is about 35,000 parts, whereas that of the altered surface waters is only about 2,000 parts; hence the concentration of the mixed water will be represented by some intermediate figure, depending on the proportions of the mixture. If the brine component predominates primary salinity and the concentration will be high and primary alkalinity low, as in analysis 58 (p. 88), but as more and more of the meteoric water is added primary alkalinity will increase and primary salinity and concentration will decrease, as in analysis 53 (p. 88).

The transition from brine to the mixed type is shown in figure 6, in which are plotted the reaction properties of the waters from five wells. Complete analyses of the waters are given in Table 16, and the simple variation in chloride and carbonate is shown in figure 5.

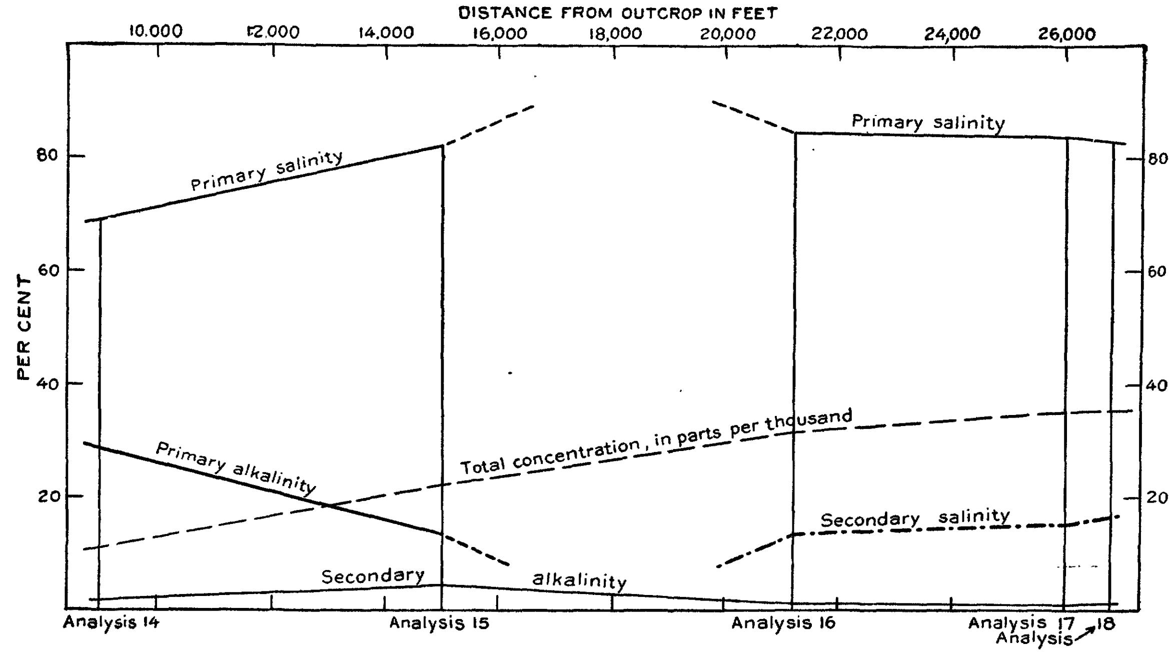


FIGURE 6.—Diagram showing change in properties of waters with distance from the outcrop along line D-D′, Plate II. (See Table 16, p. 72.) Analyses 14 and 15 represent waters of the mixed type; analyses 16, 17, and 18 represent brines.

As shown in figure 6, the waters of the two wells near the outcrop are primary alkaline, whereas those farther east are brines. With increasing distance from the outcrop there is a marked decrease in primary alkalinity, which if continued would lead to the total disappearance of this property at some point between the second and third wells. In the same direction there is a corresponding rise in primary salinity indicating that at some point the water is characterized by only two properties. East of this point primary salinity decreases and secondary salinity appears, rising to 16.2 per cent in the water farthest from the outcrop. The concentration curve shows a steady rise

TABLE 16.—*Analyses showing gradation from the high carbonate water (mixed type) occurring along the western side of the field to the brine occurring in Midway syncline, and the similarity of the brine to ocean water.*

[See fig. 5, D-D¹, and fig. 6.]

	14	15	16	17	18	19
PROPERTIES OF REACTION IN PER CENT.						
Primary salinity	69.0	82.0	84.6	84.0	83.4	78.6
Secondary salinity	0	0	13.8	15.2	16.2	21.1
Primary alkalinity	29.2	13.8	0	0	0	0
Secondary alkalinity	1.8	4.2	1.6	.8	1.4	.3
Per cent of rSO_4 in rSO_4+rCl	.1	Trace.	.20	0	Trace.	9.
CONSTITUENTS IN PARTS PER MILLION.						
Sodium (Na)	4,188	8,437	10,548	[a] 11,955	[a] 11,656	10,710
Potassium (K)	52		72			390
Calcium (Ca)	31	163	772	1,391	1,281	420
Magnesium (Mg)	21	94	570	320	443	1,300
Iron (Fe)	Trace.	....	.1	[b] 63	....	....
Aluminum (Al)	5.2	....	8.4	....	....	....
Sulphate (SO_4)	11	3	34	Trace.	4.3	2,700
Chloride (Cl)	4,593	11,123	19,624	21,646	21,415	19,410
Carbonate (CO_3)	108	0	0	[c] 148	[c] 90	[c] 70
Bicarbonate (HCO_3)	3,477	4,270	573	....	....	....
Silicia (SiO_2)	125	108	43	26	39	....
	10,846.2	22,031	31,953.5	35,549	34,928.3	35,000
REACTING VALUES IN PER CENT.						
Alkalies:						
Sodium (rNa)	48.8	47.9	42.1	[a] 42.0	[a] 41.7	38.5
Potassium (rK)	.3		.2			.8
Alkaline earths:						
Calcium (rCa)	.4	1.1	3.5	6.0	5.3	1.8
Magnesium (rMg)	.5	1.0	4.2	2.0	3.0	8.9
Strong acids:						
Sulphate (rSO_4)	.1	Trace.	.1	....	....	4.6
Chloride (rCl)	34.4	41.0	49.1	49.6	49.8	45.2
Weak acids:						
Carbonate (rCO_3)	.9	0	0	[c] .4	[c] .2	[c] .2
Bicarbonate ($rHCO_3$)	14.6	9.0	.8	....	....	....

[a] Reported and calculated as sodium but includes potassium.

[b] $Fe_2O_3+Al_2O_3$.

[c] Reported and calculated as carbonate but probably in part bicarbonate.

14. August Water Co. well 3, sec. 31, T. 32 S., R. 24 E. Water from sands between 1,334 and 1,609 feet, or more than 200 feet below top of Maricopa shale. Sampled by G. S. Rogers, July, 1914. Analyst, S. C. Dinsmore.

15. Standard Oil Co. well Monarch F, sec. 26, T. 12 N., R. 24 W. Flowing water from depth of 2,540 to 2,560 feet, or about 650 feet below top of Maricopa shale. Sampled by G. S. Rogers, July, 1914. Analyst, S. C. Dinsmore.

16. Standard Oil Co. well M. J. 6, sec. 36, T. 12 N., R. 24 W. Flowing water from depth of 2,270 feet, or about 250 feet below top of zone B and 250 feet above top of Maricopa shale. Sampled by G. S. Rogers, June, 1914. Analyst, S. C. Dinsmore.

17. Kern Trading & Oil Co. well in NE. ¼ sec. 31, T. 12 N., R. 23 W. Flowing water from depth of 2,990 feet, or 450 feet below top of zone B and 200 feet above main producing oil sand. Analyst, Kern Trading & Oil Co.

18. Kern Trading & Oil Co. well in NE. ¼ sec. 31, T. 12 N., R. 23 W. Flowing water from depth of 2,924 feet, or about 350 feet below top of zone B and 125 feet above main producing oil sand. Analyst, Kern Trading & Oil Co.

19. Ocean water. Interpretation of the mean of 77 analyses by W. Dittmar of sea water collected by the *Challenger* expedition (*Challenger* Rept., Physics and chemistry, vol. 1, p. 203, 1884).

with increasing distance from the outcrop, and in the distance covered by the figure it more than trebles. It will be noted that there is much less difference between the waters of the three wells farthest from the outcrop than between those of the two wells nearest, indicating that beyond a certain point the infiltration of meteoric water is negligible. Beyond the farthest well the brine shows no further changes and is fairly uniform in composition, but between the first well and the outcrop the water probably increases rapidly in primary alkalinity.

COMPARATIVE VALUE OF THE TYPES FOR INDUSTRIAL AND TECHNOLOGIC PURPOSES.

SOURCES OF WATER SUPPLY.

As the Sunset-Midway field is in an arid region in which there are no perennial streams, the problem of developing an adequate water supply has always been pressing. The ground waters of the region are in general so highly mineralized as to be entirely unfit for domestic purposes and unsuited even for making steam, yet because of the lack of better supplies these waters have been widely used. In the early days drinking water was hauled into the field in tank wagons, and later it was brought in by railroad from the east side of San Joaquin Valley. During this period most of the boiler water used was of the highly mineralized type supplied by wells along the western edge of the field, and it was not until the Western Water Co. completed its system that water suitable for boilers became cheap enough for general use. Owing to the increasing use of electricity and of natural gas in pumping wells, the demand for steam has decreased somewhat in the last few years, though it will doubtless always be strong.

At present the bulk of the water used in the field, both for domestic purposes and for use in boilers, is supplied by the shallow wells of the Western Water Co. near the north end of Buena Vista Lake. This is a rather hard water containing about 900 parts per million of mineral solids, of which over 600 parts are sodium and chloride. (See analyses 29 and 30, p. 82.) Several of the larger oil companies have developed better water supplies of their own, using either spring or lake water or water from shallow wells. The Western Minerals Co., in the southern part of the Sunset field, is supplied by springs which issue close to a fault contact between the sedimentary rocks and granite. This water, as shown by analysis 24 (p. 81), contains only about 300 parts per million of mineral solids and although somewhat hard makes an excellent boiler water. The Honolulu Consolidated Oil Co. uses the water of Buena Vista Lake, which resembles the water of Kern River but is somewhat more concentrated. According to analysis 22 the lake water contains 309 parts of mineral solids and, unlike the other surface waters on the west side of San Joaquin Valley, is not characterized by permanent hardness (secondary salinity). The Standard Oil Co. pipes water for its own use from the east side of San Joaquin Valley, and this water is doubtless one of primary alkalinity and contains an even smaller amount of mineral solids than the lake water. The Chanslor-Canfield Midway Oil Co. uses the water furnished by shallow wells in the Santa Maria Valley, southwest of McKittrick. This is a hard water containing a high proportion of sulphate, though its total concentration is but 526 parts per million. (See analysis 27, p. 82.) Other companies have drilled shallow wells in various parts of the field but have found only moderate supplies of the hard and highly mineralized water which constitutes the normal ground water of the region. Thus analysis 2, representing water from a well 80 feet deep, shows 4,489 parts per million of total solids; analysis 8, from a well 790 feet deep, 2,575 parts; and analysis 31, from a well 170 feet deep, 4,534 parts.

In the early days, when water of any kind was scarce, a few fairly deep water wells were drilled at or beyond the western edge of the field and a number of unsuccessful oil wells were also converted to produce water. The wells drilled primarily for water produce a modified water high in mineral content. (See analyses 3 and 35, pp. 63, 83.) The converted oil wells produce an altered water of the mixed (chloride-carbonate) type, which is even higher in mineral solids but which has the advantage of showing only temporary hardness. (See Tables 23 to 28.) Waters of these types were widely used in boilers for a number of years and are still used to a considerable extent. The highly concentrated brines associated with the oil in the central part of the field are so undesirable that they have apparently never been used in boilers, though abundant supplies could be obtained.

FACTORS DETERMINING VALUE FOR MAKING STEAM AND FOR DOMESTIC USE.

Mineral content.—Although some constituents are much more objectionable than others in water for either domestic or industrial use, a rough index of the value of a water is afforded by its concentration, or content of mineral solids. This is particularly true if, as in the Sunset-Midway field, all the waters belong to several well-defined chemical types. No rigid classification can be made on the basis of mineral content, however, for waters that would in the humid parts of the country be considered unfit even for making steam, are commonly used for domestic purposes in the more arid regions. Although 250 parts per million of chloride makes a water "salty," waters containing 1,500 parts of chloride and 2,000 parts of other constituents have been used for domestic purposes in San Joaquin Valley. Dole,[1] in discussing the ground waters of this region, classifies waters containing less than 150 parts of total solids as low in mineral matter, those containing 150 to 500 parts as moderate, those containing 500 to 2,000 parts as high, and those carrying more than 2,000 parts as very high. According to this classification the waters used by several of the larger oil companies mentioned above would be characterized as having a moderate content of mineral matter, the ordinary water supply of the field as high, and the normal ground water of the region as very high.

Hardness.—Calcium and magnesium are the chief constituents that cause hardness in waters, but the kind of hardness depends on the proportions of the other radicles. Waters in which the alkalies exceed the strong acids have only temporary hardness, or hardness which is mostly removed by boiling. In such waters the calcium and magnesium must be held in equilibrium by the weak acids, carbonate and bicarbonate, and the hardness is therefore equivalent to the property of secondary alkalinity. When the solution is boiled the bicarbonate is converted into carbonate, and as only a small quantity of calcium and magnesium can be retained in solution in the presence of carbonate the excess is thrown down as a precipitate or scale and most of the hardness is thus removed. Waters in which the strong acids exceed the alkalies, however, have permanent hardness. This property, which is synonymous with secondary salinity, is due to the balance between the alkaline earths and strong acids and can be removed only by the addition of a precipitating agent, such as sodium carbonate or lime.

Hard water is objectionable for domestic use and for making steam, because it consumes soap and deposits scale in kettles and in boilers. The hardness of a water may be measured directly by its soap-consuming power or may be calculated from the complete analysis. It may be calculated in percentage as secondary salinity and secondary alkalinity, as already explained, but is usually expressed in parts per million as total hardness in terms of $CaCO_3$, and may be derived by the following formula:

$$\text{Total hardness as } CaCO_3 = 2.5\ Ca + 4.1\ Mg$$

According to Whipple[2] 1 pound of ordinary soap is consumed or wasted in softening about 25 gallons of water having a total hardness of 200 parts per million. As shown in Table 17 (p. 78), the best waters obtainable for domestic use in the Sunset-Midway field range in hardness between 110 and 383 parts, for although some of the deeper waters are less hard they have other qualities that are still more objectionable.

Formation of scale.—The readiness with which water deposits scale when heated in a boiler is determined to some extent by its hardness, for waters that have a high percentage of temporary hardness deposit a large amount of scale. However, when the water is heated to a high temperature in a boiler and concentrated, some of the mineral solids not involved in hardness are also precipitated and most of the suspended and colloidal matter is deposited. These deposits increase the consumption of fuel and, as they have to be removed, increase the cost of repairs; if they are allowed to accumulate the boiler capacity is decreased, the boiler shell is likely to become blistered, and a disastrous explosion may occur.

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[1] Dole, R. B., Ground water in San Joaquin Valley, Calif.: U. S. Geol. Survey Water-Supply Paper 398, p. 82, 1916.

[2] Whipple, G. C., The value of pure water, p. 26, New York, 1907.

The scale or incrustation formed includes practically all of the suspended matter or mud; also the silica, which is precipitated as SiO_2; the iron and alumina, which appear as Fe_2O_3 and Al_2O_3; the magnesium, which appears chiefly as MgO; and the calcium, which appears as $CaCO_3$ and $CaSO_4$. As calcium and magnesium are usually present in much greater amounts than the other scale-forming constituents their compounds generally constitute over 90 per cent of the deposit. A water high in calcium and carbonate is likely to yield a rather powdery scale, which is not difficult to remove, whereas one high in magnesium and sulphate may yield a hard, cement-like deposit.

Stabler[1] has devised a series of convenient formulas for estimating the action of waters under boiler conditions. The formulas, as modified by Dole[2] for estimating in parts per million the scale-forming ingredients and the probable hardness of the scale formed, are as follows:

$$(1)\qquad s = Sm + Cm + 2.95\ Ca + 1.66\ Mg$$

$$(2)\quad h = SiO_2 + 1.66\ Mg + (1.92\ Cl + 1.42\ SO_4 - 2.95\ Na)$$

In formula 1 s = scale-forming ingredients, Sm = suspended matter, and Cm = colloidal matter. In most of the waters under consideration Sm may be neglected and Cm (chiefly SiO_2, Fe_2O_3, and Al_2O_3) may be assumed to be about 30 in the shallower waters unless actual determination shows a higher figure. Formula 2 is designated for calculating the quantity of hard-scale ingredients, the most abundant of which appear as silica, magnesia, and calcium sulphate. Hence if the value in the parentheses in this formula exceeds 1.42 SO_4 or 3.4 Ca, it should be reduced to the smaller of the two, and if it is a minus quantity, as in some of the deeper waters, it should be neglected. If the ratio of h, as thus estimated, to s is greater than 0.5 the scale formed may be considered hard, and if it is less than 0.25 it may be called soft. These values have been computed for some of the waters here discussed and are shown in Table 17 (p. 78).

Foaming.—Foaming, or the formation of bubbles upon and above the surface of the water, is one of the least understood of boiler phenomena. It is usually ascribed to the existence of dissolved matter, which increases the surface tension of the liquid and impedes the breaking of the steam bubbles and thus under certain conditions causes the water to pass from the boiler with the steam. As the chief constituents remaining dissolved in water under boiler conditions are the alkalies, and as the concentration of these constituents constantly increases as fresh water is added and converted into steam, the foaming tendency of a water is usually measured by its content of alkali salts. The presence of suspended matter and of organic matter also increases the tendency to foam, and some of the precipitated matter or scale probably has a similar effect. It is recognized, however, that the most potent factor in foaming consists in the design of the boiler, its condition, and the method of handling it, and in comparison with this factor the effects of any of the constituents of the water, except the alkalies, are probably very small. Accordingly, the foaming tendency of a water may be derived from the following simple equation:[3]

$$f = 2.7\ Na$$

As shown by Table 17 (p. 78) the value of f is moderate in only three of the waters commonly used in the field, and it is exceedingly high in all the deeper waters. The excessive tendency to foam of the chloride-carbonate water associated with the oil in the western part of the field is its only really bad quality for boilers, but unfortunately the foaming tendency can not be overcome by chemical treatment.

Corrosion.—The corrosion of metal by water is caused chiefly by the solvent action of acids, which may be originally present in the water or may be formed in a boiler. Acid waters are, generally speaking, not common, but many of the deeper oil-field waters contain naphthenic and other organic acids that may become corrosive under some conditions. Other waters contain the gas hydrogen sulphide, which oxidizes readily to sulphurous acid or sulphuric acid, both powerful corroding agents.

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[1] Stabler, Herman, Some stream waters of the western United States, with chapter on sediment carried by the Rio Grande and the industrial application of water analyses: U. S. Geol. Survey Water-Supply Paper 274, p. 165, 1911. See also Eng. News, vol. 60, p. 355, 1908.

[2] Mendenhall, W. C., Dole, R. B., and Stabler, Herman, Ground water in San Joaquin Valley, Calif.: U. S. Geol. Survey Water-Supply Paper 398, p. 65, 1916.

[3] As devised by Stabler (op. cit.) and modified by Dole (op. cit.).

Sulphur waters are probably active in the corrosion of casing in oil wells, but when sulphur water is introduced into a boiler most of the hydrogen sulphide gas probably escapes before it is oxidized to acid and its action is generally not pronounced. Similarly the dissolved gases, oxygen and carbon dioxide, promote corrosion, but they are generally soon driven from the water.

Under boiler conditions, however, a neutral or alkaline water may become acid and corrosive. As already stated, magnesium, iron, and aluminum are deposited as scale and appear as hydrates or oxides; consequently the acidic radicles with which these bases had previously been in equilibrium are left to become free acids. If these bases had been held in balance by the carbonate radicle, carbonic acid would be liberated and would pass off as water and carbon dioxide, but if they had been in equilibrium with sulphate, for example, sulphuric acid would be formed. If calcium in the water were being deposited as calcium carbonate, the acid would doubtless attack it first, forming calcium sulphate and carbonic acid, but if an excess of sulphuric acid were set free it would attack the boiler. These relations are expressed by Stabler in the following formula:[1]

$$C = 1.008(rH + rAl + rFe + rMg - rCO_3 - rHCO_3)$$

which may in general be simplified as follows:

$$C = rMg - rCO_3 - rHCO_3, \text{ or}$$
$$C = 0.0821\ Mg - 0.0333\ CO_3 - 0.0164\ HCO_3$$

If c is positive the water will certainly corrode the boiler. If $c + rCa$ (or $c + 0.0499\ Ca$) is negative the mineral constituents of the water will not cause corrosion, but whether organic matter or irregularities will cause it is uncertain. If c is negative but $c + rCa$ is positive corrosion may or may not occur. The probability of corrosive action of some of the representative waters is shown in the table on page 78.

WATER SOFTENING.

Hard waters, which are objectionable both for domestic use and in boilers, may be softened and improved in several ways. Waters that have temporary hardness (secondary alkalinity) may be improved simply by heating, and if they do not have permanent hardness (secondary salinity) also most of the hardness can thus be removed. The heating simply decomposes the bicarbonate radicle and precipitates calcium carbonate and magnesium carbonate, basic carbonate, or hydrate up to the limit of solubility of these salts. It is generally accomplished in water for boiler use by means of preheaters, which utilize exhaust steam or flue gases to heat the water before it is fed into the boiler. The extent to which the oil-field waters can be improved by preheating is indicated roughly by the percentage of secondary alkalinity and the total concentration, both of which are given in the analytical tables.

Waters that have permanent hardness (secondary salinity) must be chemically treated in order to soften them and remove the scale-forming ingredients, and as the elimination of temporary hardness is hastened by the addition of a precipitant, the two processes are often effected together. As secondary salinity is caused by an excess of strong acids (SO_4 and Cl) over alkalies, it may be removed by the addition of a weak acid salt, such as sodium carbonate (soda ash). It is thus converted into secondary alkalinity, and calcium and magnesium carbonates are precipitated. If lime in the hydrated form ($Ca(OH)_2$) is also added, practically complete elimination of the magnesium as magnesium hydroxide is effected, but at the same time it may be necessary to add an excess of sodium carbonate in order to precipitate the extra calcium thus introduced. Stabler employs the following formulas to determine the weight in pounds of 90 per cent lime (CaO) and 95 per cent soda ash (Na_2CO_3) that must be added to soften 1,000 gallons of water:

Lime required $= 0.26(rFe + rAl + rMg + rH + rHCO_3 + 0.0454CO_2) = 0.00931Fe + 0.0288Al + 0.0214Mg + 0.258H + 0.00426HCO_3 + 0.0118CO_2$.

Soda ash required $= 0.465\ (rFe + rAl + rCa + rMg + rH - rCO_3 - rHCO_3) = 0.0167Fe + 0.0515\ Al + 0.0232Ca + 0.0382Mg + 0.462H - 0.0155\ CO_3 - 0.00763HCO_3$.

The application of these formulas to analysis 29 (p. 82), for example, indicates that 0.56

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[1] Stabler, Herman, op. cit.

pound of lime and 0.84 pound of soda ash are required to soften 1,000 gallons of the water. The ordinary ground water, represented by analysis 2 (p. 63), requires 4.09 pounds of lime and 13.07 pounds of soda ash, whereas the primary alkaline water represented by analysis 54 (p. 88) requires 7.36 pounds of lime but no soda ash.

It is interesting to note that the addition of soda ash to a permanently hard water is entirely analogous to the mixing of waters that have primary alkalinity with waters that have secondary salinity, a process which has evidently occurred naturally in the western part of the field. (See p. 51.) It would therefore be entirely practicable to soften such waters as Nos. 1 and 2 (p. 63) by the addition of such water as No. 7 and thus save the cost of the soda ash. Most of the waters that have primary alkalinity are much more concentrated than No. 2, however, and although mixing them with the ordinary dilute surface waters would remove the permanent hardness of the surface waters, the resulting mixture might be so concentrated that the undertaking would prove unprofitable. On the other hand, highly concentrated waters that have primary alkalinity are commonly used in the field for making steam and they would be diluted and thus improved by being mixed with a less concentrated but permanently hard water, which could not be used alone without chemical treatment. Under certain conditions this method might prove economically successful.

The soda-lime method of softening water removes the chief scale-forming ingredients, calcium and magnesium, and the chief constituent involved in corrosion, magnesium, but on the other hand it increases the chief foaming ingredient, sodium. The addition of soda ash may therefore simply convert a scale-forming and corrosive water into a foaming water, and there is no way in which the foaming tendency may be reduced.

The softening of water may also be accomplished by other chemicals, but none has proved more efficient or economical than soda and lime. Substances of another class, mostly organic, are occasionally used, not to prevent the formation of scale but to soften it and render it easily removable. Most of the boiler compounds on the market consist chiefly of soda ash and of organic substances, and their chief function is to prevent corrosion and to facilitate removal of the scale. In general it is far better to have the water analyzed and to treat it with a calculated amount of well-known chemicals, such as soda ash and lime, before it is fed. into the boiler, than to experiment with expensive boiler compounds of unknown composition.

COMPARISON OF REPRESENTATIVE WATERS.

The accompanying table gives the main factors in the industrial values of a few representative waters. All these waters, with the probable exception of Nos. 5 and 12, are used in boilers.

The first four waters are used also for domestic purposes and are commonly regarded as the best waters obtainable in the field. If suspended and organic matter is ignored, the Buena Vista Lake water is evidently the best. Nos. 2, 3, and 4 are all permanently hard waters, deposit a considerable amount of medium or hard scale, and are semicorrosive. The normal ground water of the field, represented by No. 5, is evidently undesirable in every respect, and the brine, No. 12, shows the same bad qualities in much greater proportion.

The waters of primary alkalinity, represented by Nos. 7 to 11, are not permanently hard or corrosive, their chief undesirable quality being the large proportion of foaming ingredients. As this proportion can not be reduced by chemical treatment, such waters can be improved only by mixing them with the more dilute shallow waters.

TABLE 17.—*Industrial values of representative waters from the Sunset-Midway field.*

[Parts per million except as otherwise designated.]

	Analysis No.	Mineral content.	Total hardness as $CaCO_3$.	Scale-forming ingredients (s).	Character of scale.	Foaming ingredients (f).	Probability of corrosion (c).
Surface and shallow waters used for domestic and industrial purposes:							
1. Buena Vista Lake	22	309	119	145	Soft	178	Noncorrosive.
2. Kern County Land Co.'s spring	24	314	206	248	Medium	62	Uncertain.
3. Chanslor-Canfield Midway Oil Co.'s water wells.	27	526	383	367	Hard	49	Probably corrosive.
4. Western Water Co.'s water wells	29	899	177	216	do	686	Uncertain.
Normal ground water:							
5. Pyramid Oil Co.'s well, depth 80 feet.	2	4,489	1,611	1,454	do	2,343	Corrosive.
Modified ground water used for making steam:							
6. August Water Co.'s California Amalgamated well, depth 1,090 feet.	3	2,717	684	165	do	2,485	Do.
7. Stratton Water Co.'s well, depth 915 feet.	35	1,959	262	284	do	1,760	Noncorrosive.
Water associated with the oil, used for making steam:							
8. General Petroleum Co.'s Carnegie well, depth 3,880 feet.	53	5,179	93	149	do	5,562	Do.
9. Associated Oil Co.'s well, depth 1,727 feet.	54	7,940	38	73	do	8,543	Do.
10. August Water Co.'s well, depth 1,609 feet.	14	10,846	164	246	do	11,450	Do.
11. Northern Oil Co.'s water well, depth 1,423 feet.	73	9,602	289	308	Medium	10,236	Do.
Brine associated with the oil:							
12. Mays Consolidated Oil Co.'s well, depth 3,000 feet.	5	33,578	3,862	3,307	Soft	30,467	Corrosive.

ACTION OF OIL-FIELD WATERS ON CEMENT.

Because of the extent to which cement is used as a means of excluding water from the wells, any action that the various types of water may have on cement is of considerable importance. The process of placing or pumping the cement into the well and forcing it through the lower end of the casing and up around its outer side is a difficult one, in which failures are not uncommon, and these failures are often ascribed to the chemical action of the mineralized waters, especially sulphate or "alkali" waters. The action of various types of water on cement has not been extensively investigated and, being purely a technologic problem, falls outside the scope of this report; but it may be helpful at least to point out the chemical character of the waters to which the cement is likely to be exposed. It is assumed that the cement is mixed with fresh water low in mineral content and that the hole is flushed with similar water before the cement is introduced.

The deeper wells in the field are now finished with at least two and generally three or four strings of casing, and some operators cement not only the water string—the line of casing landed as close as possible above the oil sand—but also one or more of the outer strings. Even where this is done, however, the principal effective shut-off is the one at the end of the water string, for this directly protects the oil sand. Under especially favorable conditions the cement may be forced up on the outside of the casing for as much as 1,000 feet, but in the majority of the wells little of the cement reaches more than 300 or 400 feet from the top of the uppermost producing oil sand. As already pointed out, the waters within this distance of the top of the oil measures in the Sunset-Midway field contain practically no sulphate, and if they affect the setting of the cement their action must be ascribed to some other constituent. Moreover, Oatman[1] has shown that solutions containing even 5 per cent of sodium sulphate do not affect the setting of cement, though they may cause disintegration after a period of months or years.

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[1] Oatman, F. W., Water intrusion and methods of prevention in California oil fields: Am. Inst. Min. Eng. Trans., vol. 48, p. 527, 1914.

In the central and eastern parts of the field cement placed near the oil measures is exposed to the action of a brine which, except for its lack of sulphate, closely resembles sea water in both strength and composition. (See Table 22, p. 85.) In the same area the waters for 1,500 feet above the oil measures are very similar in character except that they contain a little sulphate, but none of them more than sea water. (See analysis 33, p. 83.) In a recent investigation[1] by the Bureau of Standards it was found that sea water has no appreciable effect on a good cement, provided that the cement is properly handled and placed and that it is not exposed to successive wetting and drying. The action of many other solutions on cement was also studied and it was found that although nearly all of them attack ground cement in the laboratory, their action on masses of cement in the field is practically negligible, probably because of the early formation of a lime coating which prevents further reaction. Cement in oil wells several thousand feet deep is of course exposed to considerable hydrostatic pressure, which would tend to force the water into its pores, but as the pressure is not differential and the water is not actually moving through the pores, its effect is doubtless of little importance.

In the western part of the field cement placed near the oil measures is exposed to a less concentrated water containing, roughly, 7,000 parts per million of sodium chloride and 3,000 parts of sodium carbonate. (See Table 25, p. 89.) Water of this type extends at least as far above the producing oil sands as the tar-sand zone, though waters above this zone usually contain considerable proportions of sulphate. Sodium carbonate waters are active in the solution of silica, and in the laboratory they rapidly remove lime from ground cement. Water of this type thus has a somewhat more injurious effect than the brine, though to judge from the field studies of the Bureau of Standards its action is probably not serious.

The oil-field waters to which cement is chiefly exposed are therefore not of such a character as to interfere with the setting of cement or to cause rapid disintegration afterward. Cement, in fact, is more resistant to the action of the oil-field waters than the casing itself and forms an excellent protective covering for it. A factor more important than chemical character is the temperature of the waters, for increase in temperature hastens the time of setting. According to Oatman,[2] a temperature of 110° F. decreases the normal time of setting by about one-third; and as already shown, the temperature of the oil-field waters is generally at least 100° and may reach 130°. Another important geologic factor is the presence of gas. Escaping gas may keep the cement mixture agitated and so prevent its setting; and as gas occurs at many localities above the oil measures it has probably been the cause of failures in cementing water strings. Oil is of less importance, for although it retards the time of setting considerably it does not seem to affect the strength of cement.[3] It is highly probable, however, that a great majority of the failures in cementing are due to faulty technologic methods rather than to any of the geologic factors discussed above.[4]

CORROSION OF WELL CASING BY WATERS

It is now well recognized that both iron and steel casing deteriorate when placed in the ground and after a varying period may become riddled with holes and thus useless as a means of excluding water. The life of the casing apparently depends on many conditions; in some wells or fields the casing is strong enough to be withdrawn from the ground after 10 or 15 years, whereas in others it may become extensively corroded within a year. The photographs reproduced in Plate XLV, *A*, *B*, of Part I (Professional Paper 116) show the corrosion of casing that had been in the ground for about four years in a well in the Buena Vista Hills. This corrosion is supposed to have been caused by a water which occurs between 1,700 and 1,900 feet and which is probably similar in character to the waters whose analyses appear in Table 22 (p. 85).

The causes of the corrosion of casing are difficult to study and are not thoroughly understood. Acid waters are of course strongly

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[1] Bates, E. H., Phillips, A. J., and Wig, R. J., Action of the salts in alkali water and sea water on cements: Bur. Standards Tech. Paper 12, 1913.

[2] Oatman, F. W., op. cit.

[3] Page, L. W., Oil-mixed Portland cement, mortar, and concrete: Min. and Sci. Press, vol. 103, Nov. 4, 1911, p. 580.

[4] Arnold, Ralph, and Garfias, V. R., The cementing process of excluding water from oil wells as practiced in California: Bur. Mines Tech. Paper 32, 1913.

corrosive, but waters containing free mineral acids are not encountered in the Sunset-Midway field, and whether the weaker organic acids that some waters contain cause corrosion is conjectural. When water is heated in a boiler certain mineral salts, especially magnesium salts, hydrolyze and liberate free acid, and although little hydrolysis takes place in a cold solution, it is possible that sufficient takes place at temperatures of 100° or so to cause perceptible corrosion. Corrosion due to the hydrolysis of magnesium salts would occur only in the central and eastern parts of the field, where the water is a brine carrying considerable quantities of magnesium and chloride. Dissolved gases are generally thought to be the chief agency of corrosion by nonacid waters. Hydrogen sulphide, though in itself a reducing agent, is regarded as especially harmful because of its tendency to oxidize to sulphurous or sulphuric acid. Carbon dioxide, or carbonic acid, is also corrosive, and its activity is usually accounted for by the theory that electrolytic action takes place and that the hydrogen ions formed are easily replaced by the iron. The iron goes into solution as ferrous carbonate, but if oxygen is present it is oxidized and precipitated as ferric hydroxide, thus releasing the carbon dioxide again to attack fresh iron. Oxygen is probably not abundant in the deeper oil-field waters, however, and in the absence of oxygen the corrosive action of carbon dioxide is not so pronounced.

A probable factor in the corrosion of oil-well casing which is often overlooked is electrolysis due to stray electric currents. The electrolytic corrosion of gas mains and similar pipes buried at shallow depth has long been recognized, and with the increasing use of electricity as a source of power in oil-field operations the possibility of the action of stray currents following the casing has become too great to be ignored. The corrosion would occur at the point at which the low-density stray current leaves the casing, which in oil wells would generally be at the point of contact with a water-bearing sand. The presence of any dissolved salts in the water would increase the electrolytic action, and the strong brines in the central and eastern parts of the field would be especially favorable as electrolytes.[1] Another well-recognized cause of corrosion is the presence of impurities or inclusions, such as slag, cinders, or sulphides in the casing itself, which probably set up local galvanic action.

ANALYSES OF OIL-FIELD WATERS.

GENERAL STATEMENT.

In the following pages are given a number of other analyses of water from different parts of the field. These waters are all members of the several classes already defined and differ from the types shown in Table 14 only in detail. As the origin and relations of these types have already been discussed and as the location of the water sands from which the samples were taken have been described in Part I of this report, no further comments on the particular analyses will be necessary.

Tables 18 and 19 contain analyses of surface waters and shallow ground waters, Table 20 analyses of modified waters, Tables 21, 22, and 23 analyses of altered brine, and Tables 24 to 27 analyses of altered waters of the mixed type. Within each group the samples analyzed are arranged in order, according to their location from north to south. Table 28 contains a few miscellaneous assays or partial analyses which were made with a reasonable degree of accuracy and which afford a general indication of the type of water represented. The locations of the wells from which most of the samples were taken are shown on Plate II.

The analyses should be of value to those who desire to study the chemical character of the waters in connection with the horizon at which they occur and to utilize the data thus obtained in determining the source of the water flooding a well. The analyses given are sufficient to establish the principles that control the character of the water, to permit the recognition of all the main types, and to establish the distribution of these types, though for detailed work in any particular section many more analyses would have to be made. The waters from any one sand or zone seem to be unusually uniform and constant in composition, but few sands can be definitely traced very far, and a single analysis can not be used as a standard for comparison except within a small area

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[1] McCollum, B., and Logan, K. H., Electrolytic corrosion of iron in soils: Bur. Standards Tech. Paper 25, 1913.

SURFACE WATERS AND SHALLOW GROUND WATERS.

Table 18 contains analyses of six surface waters and spring waters from the Sunset-Midway district. All these waters except No. 22 show strong secondary salinity and all contain a high proportion of sulphate. No. 22, the water of Buena Vista Lake, resembles the waters of the east side of San Joaquin Valley, as would be expected from the fact that the lake water is derived largely from the overflow of Kern River. No. 23, the water of Bitterwater Creek, is by far the most concentrated of those shown in the table, though No. 25, which represents the water of San Emigdio Creek, also contains a very high proportion of solids.

Table 19 contains analyses of water from shallow water wells. Nos. 26, 31, and 32 represent the normal ground water of the region, which shows strong secondary salinity and is high in sulphate and highly concentrated. Analysis 2 (p. 63) and analyses 8 and 12 (p. 65) represent other waters of the same type. The remaining analyses in Table 19 represent waters that for one reason or another are more dilute than the average and better suited to commercial use.

TABLE 18.—*Analyses of surface and spring water from the Midway-Sunset region.*

	20	21	22	23	24	25
PROPERTIES OF REACTION IN PER CENT.						
Primary salinity	44.4	15.6	54.6	45.4	19.6	28.4
Secondary salinity	22	23	0	48	18.8	43.6
Primary alkalinity	0	0	0	0	0	0
Secondary alkalinity	33.6	61.4	45.4	6.6	61.6	28.0
Per cent of rSO_4 in rSO_4+rCl	86.1	85.5	68.1	93.4	66.1	90.5
Ratio of rCO_3+rHCO_3 to rSO_4	.59	1.86	1.22	.08	3.21	.44
CONSTITUENTS IN PARTS PER MILLION.						
Sodium (Na)	216	[a]38	66	1,409	23	[a]112
Potassium (K)						
Calcium (Ca)	92	98	33	630	56	138
Magnesium (Mg)	87	48	9	511	16	66
Iron oxide (Fe_2O_3)	....	22	....	....	....	1.9
Alumina (Al_2O_3)	....	....	....	....	....	
Sulphate (SO_4)	580	166	94	5,638	47	538
Chloride (Cl)	70	21	33	300	18	42
Nitrate (NO_3)	Trace.	....	....	Trace.	30	....
Carbonate (CO_3)	0	[b]193	[b]72	30	7.2	[b]144
Bicarbonate (HCO_3)	433	....	....	475	178	....
Silica (SiO_2)	87	1	2	38	29	12
	1,345	587	309	8,790	314.2	1,053.9
REACTING VALUES IN PER CENT.						
Alkalies:						
Sodium (rNa)	22.2	[a]7.8	27.3	22.7	9.8	[a]14.2
Potassium (rK)						
Alkaline earths:						
Calcium (rCa)	10.9	23.4	15.5	11.7	27.4	20.1
Magnesium (rMg)	16.9	18.8	7.2	15.6	12.8	15.7
Strong acids:						
Sulphate (rSO_4)	28.6	16.5	18.6	43.6	9.6	32.6
Chloride (rCl)	4.6	2.8	8.7	3.1	4.9	3.4
Nitrate (rNO_3)	....	....	....	....	4.7	....
Weak acids:						
Carbonate (rCO_3)	0	30.7	[b]22.7	.4	2.3	[b]14.0
Bicarbonate ($rHCO_3$)	16.8	....	....	2.9	28.5	....

[a] Reported and calculated as sodium but includes potassium.
[b] Reported and calculated as carbonate but probably in part bicarbonate.

20. Frazers Spring, sec. 2, T. 30 S., R. 21 E. Spring is probably in Maricopa shale, but source of water may be affected by near-by fault. Sampled by G. S. Rogers, September, 1915. Analyst, S. C. Dinsmore.
21. California Standard Spring near McKittrick. Analyst, Smith, Emery & Co.
22. Buena Vista lake water. Analyst, Kern Trading & Oil Co.
23. Bitterwater Creek, sec. 29, T. 11 N., R. 24 W. Sampled by G. S. Rogers, September, 1915. Analyst, S. C. Dinsmore.
24. Kern County Land Co. spring in west corner of San Emigdio land grant. Water issues close to a fault between granite and early Tertiary sedimentary rocks. Sampled from pipe line of Western Minerals Co. by G. S. Rogers, September, 1915. Analyst, S. C. Dinsmore.
25. San Emigdio Creek, San Emigdio land grant. Analyst, Standard Oil Co., June, 1910.

TABLE 19.—*Analyses of water from shallow wells in the Sunset-Midway field and the district to the north.*

[See also analysis 2, Table 14, and analyses 8 and 12, Table 16.]

	26	27	28	29	30	31	32
PROPERTIES OF REACTION IN PER CENT.							
Primary salinity	62.2	9.2	57.2	76	72.4	43.6	51.6
Secondary salinity	32.8	52.6	5.4	12.6	16.0	53.0	45.8
Primary alkalinity	0	0	0	0	0	0	0
Secondary alkalinity	5.0	38.2	37.4	11.4	11.6	3.4	2.6
Per cent of rSO_4 in rSO_4+rCl	48	89.3	75.7	26.6	25.3	74.5	62.8
Ratio of rCO_3+rHCO_3 to rSO_4	.11	.70	.79	.57	.52	.04	.04
CONSTITUENTS IN PARTS PER MILLION.							
Sodium (Na) Potassium (K)	869	[a] 18	[a] 207	254	273	[a] 697	[a] 672
Calcium (Ca)	280	89	47	61	77	647	431
Magnesium (Mg)	109	39	53	6	8	84	70
Iron oxide (Fe_2O_3) Alumina (Al_2O_3)	9	15	4	....	....	....	41
Sulphate (SO_4)	1,329	223	358	166	176	2,375	1,660
Chloride (Cl)	1,062	20	85	335	383	601	725
Nitrate (NO_3)	....	....	....	....	....	43	....
Carbonate (CO_3)[b]	92	97	176	51	57	72	43
Silica (SiO_2)	31	25	10	26	....	[c] 15	....
	3,781	526	940	899	974	4,534	3,642
REACTION VALUES IN PER CENT.							
Alkalies:							
Sodium (rNa) Potassium (rK)	31.1	[a] 4.6	[a] 28.6	38	36.2	[a] 21.8	[a] 25.8
Alkaline earths:							
Calcium (rCa)	11.5	26.3	7.5	10.3	11.8	23.3	19.1
Magnesium (rMg)	7.4	19.1	13.9	1.7	2.0	4.9	5.1
Strong acids:							
Sulphate (rSO_4)	22.8	27.6	23.7	11.8	11.2	35.6	30.6
Chloride (rCl)	24.7	3.3	7.6	32.5	33	12.2	18.1
Nitrate (rNO_3)	....	....	....	....	....	.5	....
Weak acids:							
Carbonate (rCO_3)[b]	2.5	19.1	18.7	5.7	5.8	1.7	1.3

[a] Reported and calculated as sodium but includes potassium.
[b] Reported and calculated as carbonate but probably in part bicarbonate.
[c] Includes $Fe_2O_3+Al_2O_3$.

26. Standard Oil Co. well Cahn No. 2, sec. 4, T. 27 S., R. 21 E.; depth 145 feet. Sample collected while drilling and analyzed by Standard Oil Co., October, 1911.

27. Chanslor-Canfield Midway Oil Co. water wells, Santa Maria Valley, about 3 miles southwest of McKittrick. Analyst, J. H. Parsons Chemical Co. Authority, Chanslor-Canfield Midway Oil Co.

28. Associated Oil Co. giant fresh-water well, sec. 11, T. 30 S., R. 21 E. Analysts, Smith, Emery & Co. Authority, Associated Oil Co.

29–30. Western Water Co. shallow wells on edge of Buena Vista Lake, sec. 5, T. 31 S., R. 25 E. Sample 29 was taken from the pipe line and represents water from several wells; sample 30 represents water produced by well 6. Sampled and analyzed by Kern Trading & Oil Co.

31–32. Kern Trading & Oil Co. water well in sec. 35, T. 31 S., R. 24 E.; depth 170 feet. Sample 31 was taken in August, 1910, and sample 32 eight months later.

MODIFIED WATERS.

Table 20 contains analyses of a few waters of the modified type encountered in wells drilled originally for oil. Most of these waters have primary alkalinity and show lower sulphate salinity than the normal ground waters. No. 34 is a remarkably dilute water, considering the depth from which it is supposed to have come (2,980 feet), and it is possible that the sample analyzed was mixed with drilling water. No. 35 is probably not a simple modified water but a mixture of normal and altered waters from strata above and below the oil zone. No. 36 is an almost completely altered water of the mixed type. Other analyses of modified waters are Nos. 3 and 4 (p. 63) and No. 10 (p. 65).

TABLE 20.—*Analyses of modified ground water from the Sunset-Midway field.*

[See also analyses 3 and 4, Table 14, and analysis 10, Table 15.]

	33	34	35	36
PROPERTIES OF REACTION IN PER CENT.				
Primary salinity	94.0	56.6	44.6	77.4
Secondary salinity	5.4	0	0	0
Primary alkalinity	0	11.0	39.0	15.6
Secondary alkalinity	.6	32.4	16.4	7.0
Per cent of rSO_4 in rSO_4+rCl	7.0	64	58.3	1.2
Ratio of rCO_3+rHCO_3 to rSO_4	.08	1.2	2.1	22.6
CONSTITUENTS IN PARTS PER MILLION.				
Sodium (Na)	[a] 8,794	[a] 93	618	4,969
Potassium (K)	....	....	33	102
Calcium (Ca)	397	26	31	109
Magnesium (Mg)	61	8	45	144
Iron (Fe)	[b] 2.4	[b] 4.8	Trace.	....
Aluminum (Al)	....	....	3.1	....
Sulphate (SO_4)	1,381	103	403	109
Chloride (Cl)	13,304	43	210	6,740
Carbonate (CO_3)	[c] 71	[c] 77	160	0
Bicarbonate (HCO_3)	....	....	693	2,623
Silica (SiO_2)	45	9.6	115	67
	24,055.4	364.4	1,959.1	14,025
Hydrogen sulphide (H_2S)	....	....	....	1.3
REACTING VALUES IN PER CENT.				
Alkalies:				
Sodium (rNa)	[a] 47.0	[a] 33.8	40.5	46.0
Potassium (rK)	....	....	1.3	.5
Alkaline earths:				
Calcium (rCa)	2.4	10.7	2.4	1.1
Magnesium (rMg)	.6	5.5	5.8	2.4
Strong acids:				
Sulphate (rSO_4)	3.5	18.1	13.0	.5
Chloride (rCl)	46.2	10.2	9.3	38.2
Weak acids:				
Carbonate (rCO_3)	[c] .3	[c] 21.7	8.3	0
Bicarbonate ($rHCO_3$)	....	....	19.4	11.3

[a] Reported and calculated as sodium but includes potassium.
[b] $Fe_2O_3+Al_2O_3$.
[c] Reported and calculated as carbonate but probably in part bicarbonate.

33. Standard Oil Co. well 6, sec. 12, T. 32 S., R. 23 E. Water from depth of 670 to 730 feet, or about 2,500 feet above top of zone C. Analyst, Standard Oil Co., January, 1912.

34. Midway Basin Oil Co. well in sec. 28, T. 31 S., R. 24 E. Water from depth of 2,980 feet. No oil encountered, and if oil is present it is probably more than 1,500 feet deeper. Analyst, Standard Oil Co., November, 1910.

35. Stratton Water Co. well 3, sec. 7, T. 32 S., R. 23 E. Water from depth of 600 to 615 feet; oil between 600 and 790 feet. Probably a mixture of water from beds just above the oil measures and water from Maricopa shale. Sampled by G. S. Rogers, August, 1914. Analyst, S. C. Dinsmore.

36. Union Oil Co. water well, Diamond No. 2, sec. 13, T. 11 N., R. 24 W. Sulphur water from depth of about 650 feet, or about 100 feet above the oil. Sampled by G. S. Rogers, September, 1915. Analyst, S. C. Dinsmore.

No. 33, which represents water encountered at a depth of 670 feet in Midway Valley, differs from the waters discussed above in its rather close resemblance to sea water. Its reactive properties are similar, its concentration is only slightly less, and it is clearly to be regarded as a slightly altered brine allied to those shown in Table 22. This is remarkable, for the water occurs in the upper part of the McKittrick group, or the Paso Robles ("Tulare") formation, which consists of deposits laid down in fresh water and which has probably never been submerged beneath the sea. This water, therefore, presumably represents sea water that was originally entrapped in the marine strata below and that has since migrated to the higher beds. Such an ascent would imply that the escape of the deeper waters by lateral migration through the beds is practically cut off and throws light on the completeness with which the connate water is trapped in the Midway syncline.

TABLE 21.—*Analyses of altered water (brine) from the northern part of Midway Valley and Buena Vista Hills.*

	37	38	39	40	41	42
PROPERTIES OF REACTION IN PER CENT.						
Primary salinity	91.4	75.9	83.2	88.6	83.6	91.8
Secondary salinity	5.4	22.5	15.8	9.4	14.4	6.6
Primary alkalinity	0	0	0	0	0	0
Secondary alkalinity	3.2	1.6	1.0	2.0	2.0	1.6
Per cent of rSO_4 in rSO_4+rCl	Trace.	.01	.4	Trace.	0	0
CONSTITUENTS IN PARTS PER MILLION.						
Sodium (Na)	13,470	[a] 10,522	[a] 10,559	11,120	13,513	10,704
Potassium (K)						
Calcium (Ca)	712	2,894	1,411	496	1,272	284
Magnesium (Mg)	239	7.2	281	457	643	326
Iron oxide (Fe_2O_3) and alumina (Al_2O_3)	....	35	51	....	....	....
Sulphate (SO_4)	.4	31	108	2.4	0	0
Chloride (Cl)	21,946	20,955	19,289	18,920	24,398	17,631
Carbonate (CO_3)	124	[b] 293	[b] 159	90	[b] 429	[b] 243
Bicarbonate (HCO_3)	1,021	....	....	506	....	....
Silica (SiO_2)	74	18	84	106	41	12
	37,075.4	34,755.2	31,942	31,440.4	40,296	29,200
REACTING VALUES IN PER CENT.						
Alkalies:						
Sodium (rNa)	45.7	[a] 37.95	[a] 41.6	44.3	41.8	[a] 45.9
Potassium (rK)						
Alkaline earths:						
Calcium (rCa)	2.8	12.00	6.4	2.3	4.5	1.4
Magnesium (rMg)	1.5	.05	2.0	3.4	3.7	2.7
Strong acids:						
Sulphate (rSO_4)	....	.05	.2	....	....	0
Chloride (rCl)	48.4	49.15	49.3	49.0	49.0	49.2
Weak acids:						
Carbonate (rCO_3)	.3	[b] .80	[b] .5	.3	[b] 1.0	[b] .8
Bicarbonate ($rHCO_3$)	1.3	....	....	.7	....	....

[a] Reported and calculated as sodium but includes potassium.
[b] Reported and calculated as carbonate but probably in part bicarbonate.

37. Caribou Oil Co. well 2, sec. 28, T. 31 S., R. 23 E. Water from depth of about 3,000 feet probably derived from water sand in upper part of zone C. Sampled by G. S. Rogers, September, 1915. Analyst, S. C. Dinsmore.

38. Standard Oil Co. well 6, sec. 22, T. 31 S., R. 23 E. Water from depth of 2,700 feet or near top of zone C. Analyst, Standard Oil Co., April, 1915.

39. Standard Oil Co. well 7, sec. 22, T. 31 S., R. 23 E. Water from depth of 2,740 to 2,855 feet, or about 150 feet below top of zone C. Analyst, Standard Oil Co., April, 1915.

40. Brookshire Oil Co. well 5, sec. 24, T. 31 S., R. 22 E. Probably water from above zone C (edge water of zone B). Sampled by G. S. Rogers, September, 1915. Analyst, C. S. Dinsmore.

41. Associated Oil Co. well, Pioneer Midway No. 3, sec. 30, T. 31 S., R. 23 E. Water is either the edge water of zone B and therefore above the main oil sand or is in zone C and below this sand. Analysts, Smith, Emery & Co. Authority, Associated Oil Co.

42. Associated Oil Co. well, Pioneer Midway No. 7, sec 30, T. 31 S., R. 23 E. Water from depth of 2,840 to 2,885 feet, or near base of zone C. Analysts, Smith, Emery & Co. Authority, Associated Oil Co.

WATERS ASSOCIATED WITH THE OIL.

BRINES IN THE CENTRAL AND EASTERN PARTS OF THE FIELD.

Analyses 37 to 52 (Tables 21, 22, and 23) represent the brine or altered fossil sea water associated with the oil in Midway Valley, the Buena Vista Hills, and Maricopa Flat. All these waters, like sea water, have secondary salinity, but none of them contain more than a few parts per million of sulphate, and many contain only a trace. All but two of the analyses represent waters closely associated with the oil, and there appears to be no general difference between the waters in oil zone B and those in zone C. In fact, analysis 45, which resembles the rest, represents water from a horizon nearly 1,000 feet above the top of zone B, but this appears to be an isolated and unusual occurrence, and in general modified water probably extends below this horizon. Analysis 52 represents a water similar in properties to the rest but very much more dilute, a feature which is probably connected with the fact that it occurs in the Vaqueros formation several thousand feet stratigraphically lower than the other waters and outside the productive field.

TABLE 22.—*Analyses of altered water (brine) from Midway Valley and Buena Vista Hills.*

	43	44	45	46	47	48
PROPERTIES OF REACTION IN PER CENT.						
Primary salinity	82. 6	83. 8	86. 8	84. 2	82. 0	73. 6
Secondary salinity	16. 2	13. 4	12. 8	14. 6	17. 0	21. 0
Primary alkalinity	0	0	0	0	0	0
Secondary alkalinity	1. 2	2. 8	. 4	1. 2	1. 0	. 4
Per cent of rSO_4 in rSO_4+rCl	. 6	. 06	. 2	. 01	. 01	. 02
CONSTITUENTS IN PARTS PER MILLION.						
Sodium (Na)	[a]8, 119	[a]13, 253	[a]10, 502	[a]15, 015	11, 011	[a]12, 734
Potassium (K)	....	....	....	....	156	....
Calcium (Ca)	787	1, 089	983	1, 895	1, 188	886
Magnesium (Mg)	417	685	241	342	510	1, 300
Iron oxide (Fe_2O_3) and alumina (Al_2O_3)	....	11	....	11	....	6
Sulphate (SO_4)	99	18	48	32	9	7
Chloride (Cl)	14, 846	23, 553	18, 473	27, 102	18, 750	24, 864
Carbonate (CO_3)	[b]151	[b]626	[b]75	[b]275	0	[b]92
Bicarbonate (HCO_3)	....	....	....	....	280	....
Silica (SiO_2)	24	65	15	60	123	112
	24, 443	39, 300	30, 337	44, 732	31, 885	40, 001
REACTING VALUES IN PER CENT.						
Alkalies:						
Sodium (rNa)	[a]41. 3	[a]41. 9	[a]43. 4	[a]42. 1	[a]40. 6	[a]39. 3
Potassium (rK)	....	....	....	....	. 4	....
Alkaline earths:						
Calcium (rCa)	4. 6	4. 0	4. 7	6. 1	5. 3	3. 1
Magnesium (rMg)	4. 1	4. 1	1. 9	1. 8	3. 7	7. 6
Strong acids:						
Sulphate (rSO_4)	. 3	....	. 1	....	Trace.	....
Chloride (rCl)	49. 1	48. 5	49. 7	49. 4	49. 5	49. 8
Weak acids:						
Carbonate (rCO_3)	[b]. 6	[b]1. 5	[b]. 2	[b]. 6	0	[b]. 2
Bicarbonate ($rHCO_3$)	....	....	....	....	. 5	....

[a] Reported and calculated as sodium but includes potassium.
[b] Reported and calculated as carbonate but probably in part bicarbonate.

43. Union Oil Co. well 1, sec. 34, T. 31 S., R. 23 E. Water from a short distance above the oil sand; probably edge water in zone B. Analysts, Smith, Emery & Co.

44. Associated Oil Co. well 2, sec. 32, T. 31 S., R. 23 E. Water from a short distance above 3,100 feet, or some 225 feet above top of zone C; probably edge water in zone B. Analysts, Smith, Emery & Co. Authority, Associated Oil Co.

45. Standard Oil Co. well 1, sec. 12, T. 32 S., R. 23 E. Water from depth of 2,055 to 2,075 feet. Top of zone C is at depth of about 3,500 feet, though well reached 3,827 feet without finding oil. Analyst, Standard Oil Co., May, 1913.

46. Standard Oil Co. well 7, sec. 12, T. 32 S., R. 23 E. Water from depth of 2,600 feet, or about 75 feet above top of zone C. Gas was encountered about 400 feet above the water. Analyst, Standard Oil Co., June, 1913.

47. Honolulu Oil Co. well 6, sec. 10, T. 32 S., R. 24 E. Water from depth of 2,755 feet, or 250 feet below top of zone B, about at top of zone C. Sampled by Paul Paine. Analyst, S. C. Dinsmore.

48. Kern Trading & Oil Co. well in NW. ¼ sec. 13, T. 32 S., R. 23 E. Water from depth of 3,455 feet, or bottom water about 300 feet below top of zone C. Analyst, Standard Oil Co., February, 1913.

TABLE 23.—*Analyses of altered water (brine) from the southern part of Midway Valley and from Maricopa Flat.*

	49	50	51	52
PROPERTIES OF REACTION IN PER CENT.				
Primary salinity	48.6	84.0	87.4	85.0
Secondary salinity	5.0	11.4	10.6	12.6
Primary alkalinity	0	0	0	0
Secondary alkalinity	46.4	4.6	2.0	2.4
Per cent of SO_4 in rSO_4+rCl	Trace.	0	.2	.48
CONSTITUENTS IN PARTS PER MILLION.				
Sodium (Na)	[a] 1,323	[a] 9,855	[a] 8,026	671
Potassium (K)				
Calcium (Ca)	1,223	1,064	222	69
Magnesium (Mg)		345	474	21
Iron oxide (Fe_2O_3) and alumina (Al_2O_3)	1.7	5		
Sulphate (SO_4)	3.6	0	54	7.8
Chloride (Cl)	2,254	17,231	13,800	1,170
Carbonate (CO_3)	[b] 1,645	[b] 692	[b] 238	0
Bicarbonate (HCO_3)				48
Silica (SiO_2)	4.1	10	15	5
	6,454.4	29,202	22,829	1,967.8
Carbon dioxide (CO_2)				Present.
REACTING VALUES IN PER CENT.				
Alkalies:				
Sodium (rNa)	[a] 24.3	[a] 42.0	43.7	42.5
Potassium (rK)				
Alkaline earths:				
Calcium (rCa)	25.7	5.2	1.4	5.0
Magnesium (rMg)		2.8	4.9	2.5
Strong acids:				
Sulphate (rSO_4)			.1	.2
Chloride (rCl)	26.8	47.7	48.9	48.6
Weak acids:				
Carbonate (rCO_3)	[b] 23.2	[b] 2.3	[b] 1.0	.0
Bicarbonate ($rHCO_3$)				1.2

[a] Reported and calculated as sodium, but includes potassium.
[b] Reported and calculated as carbonate but probably in part bicarbonate.

49. Standard Oil Co. well 3, sec. 20, T. 32 S., R. 24 E. Water from depth of 3,250 feet, or 125 feet below top of zone B. Probably edge water in zone B. Analyst, Standard Oil Co., February, 1911.
50. Standard Oil Co. well 1, sec. 28, T. 32 S., R. 24 E. Water from depth of 2,390 feet, or about 400 feet above top of zone B. Analyst, Standard Oil Co., August, 1909.
51. Standard Oil Co. well 5, sec. 28, T. 32 S., R. 24 E. Bottom water from depth of 3,704 feet, or about 700 feet below top of zone B. Analyst, Standard Oil Co., March, 1915.
52. Sunset Security Oil Co. well 1, sec. 29, T. 11 N., R. 23 W. Flowing water, probably from depth between 2,992 and 3,997 feet, or below several shows of oil, and in Vaqueros formation. Sampled by G. S. Rogers, September, 1915. Analyst, S. C. Dinsmore.

The concentration of the brines ranges in general between 25,000 and 40,000 parts per million and averages about 35,000 parts. Most of the brines containing less than 35,000 parts occur along the western edge of the brine area, or near the belt in which the more dilute meteoric waters have penetrated and have formed waters of the mixed type. These more dilute brines are also lower in secondary salinity because of the admixture with meteoric water and constitute a gradation toward waters of the mixed type, which are arbitrarily defined as waters of primary alkalinity instead of secondary salinity. The line separating the brine area from that in which waters of the mixed type occur is shown on Plate II, and the chemical gradation across this line is shown graphically in figures 5 and 6.

WATERS OF THE MIXED TYPE IN THE WESTERN PART OF THE FIELD.

Analyses 53 to 75 (Tables 24 to 27) represent altered waters of the mixed type associated with the oil in the western part of the field, or the shallower territory near the outcrop. All of these waters show primary alkalinity and contain practically no sulphate. As already stated, they are believed to have originated through the mixing of altered meteoric waters, entering at the outcrop, with the altered fossil sea water trapped in the Midway syncline. The water occurring nearest the outcrop are therefore in general predominantly meteoric, being more dilute and showing stronger primary alkalinity than those nearer the boundary of the brine area. (See figs. 5 and 6.) It is noteworthy, however, that the two waters which are most strongly meteoric and contain the smallest proportion of chloride occur in the extreme northern part of the field, or in the shallow territory in which several of the southward-pitching folds that dominate the structure of the main field originate. (See analyses 7, p. 63, and 53, p. 88.) It appears entirely probable that in such a locality meteoric waters would penetrate unusually far from the outcrop and drive down most of the salt water, though as both samples were taken near a fault, which may have disturbed the circulation within a limited area, it is impossible to say whether or not they are characteristic of the waters in the whole northern part of the field.

Oil zone A is productive in much of the area in which waters of the mixed type occur, and many of the analyses listed represent waters associated with this zone. Similar waters extend above zone A as far as the tar-sand zone, the waters of which are modified but generally not completely altered. (Compare analyses 10, p. 65, and 36, p. 83.) In much of the belt in which waters of the mixed type occur zones B and C are also recognized, and there appears to be no essential difference between the water of zone A and those of the deeper zones. In fact, as shown by several of the analyses, waters occurring in the Maricopa shale many hundred feet below the productive oil measures are entirely similar to those associated with zone A.

Invasion of the oil sands by water has proved troublesome in parts of the Twenty-five Hill district near Taft, and as there has been some difference in opinion concerning the original source of the water, the analyses given in Table 25 are of interest. Mr. Pack, on the basis of stratigraphic studies, regards the water as derived very largely from a bottom water sand occurring at the base of the oil measures, and the evidence afforded by analyses of the waters appears to be entirely concordant. Analysis 60 represents a sample of water from the bottom water sand, and No. 61 a sample from a well near by producing water from an unknown source; the two waters are evidently the same. Analyses 63 and 62, representing respectively the bottom water and water from an unknown source, offer similar testimony.

TABLE 24.—*Analyses of altered water (mixed type) from the western part of the Midway field north of Twenty-five Hill.*

	53	54	55	56	57	58	59
PROPERTIES OF REACTION IN PER CENT.							
Primary salinity	40.2	74.8	71.8	66.6	70.3	83.6	77.2
Secondary salinity	0	0	0	0	0	0	0
Primary alkalinity	57.8	24.4	24.4	30	26.3	11.8	21.6
Secondary alkalinity	2.0	.8	3.8	3.4	3.4	4.6	1.2
Ratio of rSO_4 to rSO_4+rCl	1.5	0	.02	.13	.08	.01	.01
CONSTITUENTS IN PARTS PER MILLION.							
Sodium (Na)	2,052	3,140	[a]4,110	[a]3,434	[a]3,955	[a]7,090	[a]5,933
Potassium (K)	9.7	24	....	....	....	....	....
Calcium (Ca)	19	9.3	55	50	50	73	29
Magnesium (Mg)	11	3.6	55	35	44	135	21
Iron oxide (Fe_2O_3) and alumina (Al_2O_3)	5.9	....	....	....	....	13	....
Sulphate (SO_4)	28	0	2	6.6	5.5	4.5	6
Chloride (Cl)	1,293	3,662	4,723	3,650	4,428	9,566	7,125
Carbonate (CO_3)	342	219	[b]1,569	[b]1,545	[b]1,590	[b]1,588	[b]1,784
Bicarbonate (HCO_3)	2,372	1,708	....	....	....	....	....
Silica (SiO_2)	72	40	77	55	72	44	117
	5,178.6	7,939.9	10,591	8,775.6	10,144.5	18,513.5	15,015
Carbon dioxide (CO_2)	....	....	None.	None.	None.	.0	....
REACTING VALUES IN PER CENT.							
Alkalies:							
Sodium (rNa)	48.9	49.4	[a] 48.1	[a]48.3	[a]48.3	[a]47.7	[a]49 4
Potassium (rK)	.1	.2	....	....	....	....	....
Alkaline earths:							
Calcium (rCa)	.5	.2	.7	.8	.7	.6	.3
Magnesium (rMg)	.5	.1	1.2	.9	1.0	1.7	.3
Strong acids:							
Sulphate (rSO_4)	.3	0	0	....	....	Trace.	Trace.
Chloride (rCl)	19.8	37.4	35.9	33.3	35.1	41.8	38 6
Weak acids:							
Carbonate (rCO_3)	6.2	2.6	[b]14.1	[b]16.7	[b]14.9	[b]8.2	[b]11.4
Bicarbonate ($rHCO_3$)	23.7	10.1	....	....	....	....	....

[a] Reported and calculated as sodium but includes potassium.
[b] Reported and calculated as carbonate but probably in part bicarbonate.

53. General Petroleum Co. Carnegie water well, sec. 9, T. 31 S., R. 22 E. Water from Maricopa shale at depth of 3,860 to 3,880 feet, or at least 3,000 feet below base of oil measures. Sampled by G. S. Rogers, July, 1914. Analyst, S. C. Dinsmore.

54. Associated Oil Co. well 1, sec. 35, T. 31 S., R. 22 E. Bottom water from depth of 1,495 to 1,727 feet, or about 50 feet below top of zone C. Sampled by G. S. Rogers, July, 1914. Analyst, Chase Palmer.

55–58. North American Oil Consolidated Co. wells in sec. 16, T. 32 S., R. 23 E. Analysts, Smith, Emery & Co. Authority, North American Oil Consolidated Co. 55, Well 1, bottom water from sands between 1,675 and 1,840 feet, or about 325 feet below top of zone A; 56, well 16, bottom water probably from 1,150 feet, or about 300 feet below top of zone A; 57, well 21, water apparently from sands between 1,151 and 1,345 feet, or in zone A; 58, well 71, bottom water probably from about 3,200 feet, or about 1,200 feet below top of zone B and presumably in Maricopa shale.

59. Standard Oil Co. well 2, sec. 14, T. 32 S., R. 23 E. Top water from depth of 2,000 feet, or above top of zone B. Analyst, Standard Oil Co., July, 1909.

TABLE 25.—*Analyses of altered water (mixed type) from Twenty-five Hill area (southwestern part of T. 32 S., R. 23 E.).*

	60	61	62	63	64	65	66
PROPERTIES OF REACTION IN PER CENT.							
Primary salinity	64.0	65.4	60.8	62.6	80.0	76.0	65.4
Secondary salinity	0	0	0	0	0	0	0
Primary alkalinity	33.2	32.8	37.0	35.4	14.8	20.2	31.2
Secondary alkalinity	2.8	1.8	2.2	2.0	5.2	3.8	3.4
Ratio of rSO_4 to rSO_4+rCl	Trace.	.01	.1	0.2	Trace.	.01	.02
CONSTITUENTS IN PARTS PER MILLION.							
Sodium (Na)	3,921	3,763	3,350	3,627	4,915	[a]3,595	[a]2,828
Potassium (K)		56	47	30	93	....	....
Calcium (Ca)	37	20	28	41	55	50	35
Magnesium (Mg)	41	24	24	17	107	48	30
Iron (Fe)	Trace.	.02	.02	0.3	....	[a]1.7	[b]8
Aluminum (Al)	....	4.7	4.2	6.6	....		
Sulphate (SO_4)	1	4	11	14	8.8	3.2	40
Chloride (Cl)	3,977	3,924	3,273	3,608	6,336	4,370	2,917
Carbonate (CO_3)	0	228	48	0	108	[c]1,172	[c]1,320
Bicarbonate (HCO_3)	3,855	3,184	3,684	3,793	2,281	....	....
Silica (SiO_2)	136	118	127	122	83	117	39
	10,011	9,706.72	8,724.22	9,333.9	12,827.8	15,015	7,217
REACTING VALUES IN PER CENT.							
Alkalies:							
Sodium (rNa)	48.6	48.7	48.5	48.8	46.9	[a]49.4	[a]48.3
Potassium (rK)		.4	.4	.2	.5	....	....
Alkaline earths:							
Calcium (rCa)	.5	.3	.5	.6	.6	.3	.7
Magnesium (rMg)	.9	.6	.6	.4	2.0	.3	1.0
Strong acids:							
Sulphate (rSO_4)	Trace.	....	.1	.1	Trace.	Trace.	.3
Chloride (rCl)	32	32.7	30.3	31.2	40.0	38.6	32.4
Weak acids:							
Carbonate (rCO_3)	0	2.2	.5	.0	.8	[c]11.4	[c]17.3
Bicarbonate ($rHCO_3$)	18.0	15.1	19.1	18.7	9.2	....	....

[a] Reported and calculated as sodium but includes potassium.

[b] $Fe_2O_3+Al_2O_3$.

[c] Reported and calculated as carbonate but probably in part bicarbonate.

60. General Petroleum Co. well 2, sec. 15. Bottom water from depth of 1,765 to 1,820 feet, or about 150 feet below top of zone B. (See Pl. XXXVIII of Part I, Prof. Paper 116.) Sampled by G. S. Rogers, July, 1914. Analyst, S. C. Dinsmore.

61. Traders Oil Co. well 71, sec. 23. Water produced with oil from sands of zone A, probably from depth between 1,200 and 1,300 feet. Note similarity to 60. Sampled by G. S. Rogers, July, 1914. Analyst, S. C. Dinsmore.

62. Mascot Oil Co. well 17, sec. 26. Thought to be bottom water produced from sand at depth of about 1,500 feet, or about 500 feet below top of zone A. (See Pl. XXXVIII of Part I, Prof. Paper 116.) Note similarity to 63. Sampled by G. S. Rogers, July, 1914. Analyst, S. C. Dinsmore.

63. Crescius Oil Co. well 6, sec. 25. Bottom water from depth of 1,460 feet, or about 475 feet below top of zone A. (See Pl. XXXVIII of Part I, Prof. Paper 116.) Sampled by G. S. Rogers, June, 1914. Analyst, S. C. Dinsmore.

64. Chanslor-Canfield Midway Oil Co. well 7, sec. 24. Water from depth of about 3,000 feet; apparently in zone C. Sampled by G. S. Rogers, September, 1915. Analyst, S. C. Dinsmore.

65. Standard Oil Co. well 3, sec. 24. Water from depth of 1,505 feet; edge water of zone A and about 75 feet above top of zone B. Analyst, Standard Oil Co., April, 1909.

66. B. H. & C. Oil Co., sec. 25. Water produced with oil from several wells. Probably derived chiefly from same sand as sample 63. Analysts, Smith, Emery & Co. Authority, Section Twenty-five Oil Co.

TABLE 26.—*Analyses of altered water (mixed type) from area southeast of Twenty-five Hill.*

	67	68	69	70
PROPERTIES OF REACTION IN PER CENT.				
Primary salinity	70. 4	70. 4	76	74. 0
Secondary salinity	0	0	0	0
Primary alkalinity	25. 9	27. 2	20. 8	23. 2
Secondary alkalinity	3. 7	2. 4	3. 2	2. 8
Per cent of rSO_4 in rSO_4+rCl	. 53	. 57	. 32	. 4
CONSTITUENTS IN PARTS PER MILLION.				
Sodium (Na)	[a]4, 442	[a]4, 413	[a]3, 971	5, 019
Potassium (K)				22
Calcium (Ca)	37	18	43	79
Magnesium (Mg)	67	45	43	26
Iron (Fe)	[b]12	[b]9		. 02
Aluminum (Al)				4. 2
Sulphate (SO_4)	37	4	87	35
Chloride (Cl)	4, 970	4, 872	4, 726	5, 913
Carbonate (CO_3)	[c]1, 784	[c]1, 748	[c]1, 284	0
Bicarbonate (HCO_3)				3, 721
Silica (SiO_2)	119	104		84
	11, 468	11, 250	10, 154	13, 012. 22
REACTING VALUES IN PER CENT.				
Alkalies:				
Sodium (rNa)	[a]48. 1	[a]48. 8	[a]48. 4	48. 5
Potassium (rK)				. 1
Alkaline earths:				
Calcium (rCa)	. 5	. 2	. 6	. 9
Magnesium (rMg)	1. 4	. 9	1. 0	. 5
Strong acids:				
Sulphate (rSO_4)	. 2	. 2	. 5	. 2
Chloride (rCl)	35. 0	35. 0	37. 5	36. 8
Weak acids:				
Carbonate (rCO_3)	[c]14. 8	[c]14. 9	[c]12. 0	0
Bicarbonate ($rHCO_3$)				13. 0

[a] Reported and calculated as sodium but includes potassium.
[b] $Fe_2O_3 + Al_2O_3$.
[c] Reported and calculated as carbonate but probably in part bicarbonate.

67. Section Twenty-five Oil Co. well 7, sec. 25, T. 32 S., R. 23 E. Water produced with oil; probably derived from bottom-water sand at base of zone A. Analysts, Smith, Emery & Co. Authority, Section Twenty-five Oil Co.

68. Section Twenty-five Oil Co. well 11, sec. 25, T. 32 S., R. 23 E. Water produced with oil; probably derived from bottom-water sand at base of zone A. Analysts, Smith, Emery & Co. Authority, Section Twenty-five Oil Co.

69. Standard Oil Co. well Monarch C, sec. 26, T. 12 N., R. 24 W. Water from depth of 2,156 to 2,182 feet, or about 600 feet below top of zone B and about 450 feet below top of Maricopa shale. Analyst, Bird-Archer Co., December, 1913.

70. Standard Oil Co. well M. & M. 7, sec. 36, T. 12 N., R. 24 W. Water from depth of 2,385 to 2,870 feet, or about 1,400 feet below top of zone B and about 1,250 feet below top of Maricopa shale. Sampled by G. S. Rogers, August, 1914. Analyst, S. C. Dinsmore.

TABLE 27.—*Analyses of altered water (mixed type) from the western part of the Sunset field.*

	71	72	73	74	75
PROPERTIES OF REACTION IN PER CENT.					
Primary salinity	70	82.6	62.8	74.2	66.8
Secondary salinity	0	0	0	0	0
Primary alkalinity	28.3	14.6	33.6	23.0	30.2
Secondary alkalinity	1.7	2.8	3.6	2.8	3.0
Per cent of rSO_4 in rSO_4+rCl	0	.04	.09	.4	.2
CONSTITUENTS IN PARTS PER MILLION.					
Sodium (Na)	[a]4,478	[a]6,440	[a]3,737	3,649	4,104
Potassium (K)	....	....	....	24	60
Calcium (Ca)	13	71	65	57	65
Magnesium (Mg)	33	59	38	23	28
Iron (Fe)	....	[b].34	....	.3	.14
Aluminum (Al)	....	....	....	4.5	4.6
Sulphate (SO_4)	....	5	5	27	27
Chloride (Cl)	4,903	8,418	3,754	4,364	4,435
Carbonate (CO_3)	[c]1,780	0	[c]1,880	0	0
Bicarbonate (HCO_3)	....	3,074	....	2,818	3,965
Silica (SiO_2)	....	89	123	98	125
	11,207	16,595.34	9,602	9,633.8	10,799.74
REACTING VALUES IN PER CENT.					
Alkalies:					
Sodium (rNa)	[a]49.1	[a]48.6	[a]48.2	48.4	48.1
Potassium (rK)	....	....	....	.2	.4
Alakline earths:					
Calcium (rCa)	.2	.6	.9	.8	.9
Magnesium (rMg)	.7	.8	.9	.6	.6
Strong acids:					
Sulphate (rSO_4)	....	....	....	.2	.1
Chloride (rCl)	35.0	41.3	31.4	36.9	33.3
Weak acids:					
Carbonate (rCO_3)	[c]15.0	0	[c]18.6	0	....
Bicarbonate ($rHCO_3$)	....	8.7	....	12.9	16.6

[a] Reported and calculated as sodium but includes potassium.
[b] $Fe_2O_3+Al_2O_3$.
[c] Reported and calculated as carbonate but probably in part bicarbonate.

71. Occidental Oil Co. well 4, sec. 2, T. 11 N., R. 24 W. Bottom water from depth of 1,505 to 1,556 feet, or 1,100 feet below top of zone A, in Maricopa shale. Analysts, Straus & Co. March, 1910. Authority, Sunset Monarch Oil Co.

72. Adeline Consolidated Oil Co. water well 31, sec. 2, T. 11 N., R. 24 W. Bottom water from depth of 1,828 to 1,875 feet, or 1,400 feet below top of zone A, in Maricopa shale. Sampled by G. S. Rogers, September, 1915. Analyst, S. C. Dinsmore.

73. Northern Oil Co. water well, sec. 12, T. 11 N., R. 24 W. Water from sand at depth of 1,423 feet, or about 150 feet below top of zone B. Analyst, Standard Oil Co., August, 1909.

74. Good Roads Oil Co. well 14, sec. 12, T. 11 N., R. 24 W. Flowing water from depth of 3,550 to 3,700 feet, or about 2,350 feet below top of zone B and 2,000 feet below top of Maricopa shale. Sampled by G. S. Rogers, July, 1914. Analyst, S. C. Dinsmore.

75. Maricopa Producers Oil Co. well 1, sec. 8, T. 11 N., R. 23 W. Flowing water from depth of 2,165 feet, or about 200 feet below top of zone B. Sampled by G. S. Rogers, July, 1914. Analyst, S. C. Dinsmore.

TABLE 28.—*Assays (partial analyses) of waters from the Sunset-Midway field.*

[Parts per million.]

Designation.	Lease.	Well No.	Location.			Insoluble solids.	Soluble solids.	Calcium (Ca).	Magnesium (Mg).	Chlorine (Cl).	Interpretation of type of water.
			Sec.	T.	R.						
A	Toronto Midway	1	18	31 S.	23 E.	......	33,040	......	......	17,800	Brine (altered).
B	American Oilfields	76	36	31 S.	22 E.	......	8,010	......	......	3,420	Mixed type (altered).
C	.....do	92	36	31 S.	22 E.	......	6,630	......	......	400	Mixed type (modified?)
D	.....do	73	36	31 S.	22 E.	200	8,660	......	......	2,840	Mixed type (altered).
E	Chanslor-Canfield Midway Oil.	12	36	31 S.	22 E.	150	7,140	......	......	3,280	Do.
F	American Oilfields	57	36	31 S.	22 E.	......	20,720	......	......	7,720	Do.
G	.....do	23	36	31 S.	22 E.	......	26,484	......	......	14,840	Brine (altered).
H	General Petroleum	14	32	32 S.	24 E.	......	27,618	......	......	16,440	Do.
I	American Oilfields	6	32	12 N.	23 W.	......	72,930	......	......	30,800	Do.
J	Ethel D	21	36	12 N.	24 W.	......	......	236	180	17,800	Do.
K	Jewett & Blodgett	3	28	11 N.	23 W.	36,678		1,709	188	22,159	Do.
L	.....do	2	28	11 N.	23 W.	10,769		111	465	10,769	Brine (modified), probably mixed with surface water.
M	"Flowing brine well"	....	13	11 N.	24 W.	......	18,945	......	......	8,774	Mixed type?
N	Well at Salt Marsh	....	11	11 N.	24 W.	......	11,440	......	......	5,995	Do.
O	Spring	....	13	11 N.	24 W.	......	5,883	......	......	1,693	Normal ground water.

A–J. Assays made and furnished by American Oilfields Co.

K–O. Partial analyses cited by Watts, W. L., The gas and petroleum yielding formations of California: California State Min. Bur. Bull. 3, pp. 91–92, 1894.

INVASION OF OIL SANDS BY WATER.

GENERAL STATEMENT.

The problem of preventing the invasion of oil sands by water is recognized by California operators as one of the most important problems confronting the industry to-day. The disastrous results of such invasion have been only too well shown in parts of all the California fields, and during the past few years a considerable amount of study has been devoted not only to methods for the exclusion of the water while a well is being drilled, but also to methods of tracing the source of water that may appear in the well some time after its completion. The actual exclusion of water from the well is largely a technologic problem which falls outside the scope of this report, but the problem of tracing the migration of the water and of determining its source is largely geologic and will be briefly considered in the following pages.

The removal of oil and gas from an inclosed sand naturally results in a disturbance of the pressure equilibria that had previously existed, lowering the pressure in the sand and thus creating a tendency on the part of the fluids in neighboring beds to migrate toward the sand and into it. Water is, of course, the most abundant fluid in the surrounding beds, and its movement is facilitated by its low viscosity. The bore hole itself affords an artificial line of communication between the beds, and this channel, even when blocked and obstructed by every means at the driller's command, is probably still more open than any natural crack or fissure would be. If there is water under high head in a neighboring sand, the tendency of this water to force its way past the barriers increases as more and more oil is removed from the oil sand and as the pressure in the oil sand becomes correspondingly lower. It is chiefly for this reason that water troubles become more prevalent as the field grows older and also that the largest wells (those which have lowered the pressure most and have established drainage lines in the oil sand for a considerable distance around them) are especially liable to such troubles.

As the original gas pressure in many sands is somewhat greater than the hydrostatic pressure there is usually a brief early period during which invasion of the sand by water is impossible; and as more or less effective measures are taken to exclude the water, considerable time may elapse before the gas pressure is reduced sufficiently to enable the water to force its way past the barriers and enter the sands. Accordingly, in the early history of the field, when the gas pressure was high, little attention was paid to the exclusion of water, and when the pressure began to decrease and water began to appear in the wells it was generally thought that the water and oil existed in the same sand and that the appearance of the water was therefore inevitable. When the damage became serious enough in several parts of the field to demand investigation and study, however, it was found that the water was extraneous and that with proper precautions it might be excluded. It is interesting to note that not only the Sunset-Midway field, but practically all other fields in California and the geologically similar fields in Russia, Rumania, and other countries, have had a similar history—an early period in which water was ignored, a second period in which its appearance was regarded as inevitable, and a third period characterized by an investigation of the causes of water troubles and an energetic campaign for their mitigation or removal. In the Sunset-Midway field much of the damage wrought by the older wells has been repaired, and new wells are being finished in such a way as to exclude water almost perfectly. Nevertheless, the problem is by no means disposed of, for as time passes and the gas pressure becomes lower the tendency of water to enter the sands will become correspondingly greater.

On the assumption that it will continue to be possible to exclude water from the oil sands or to pump out such water as may enter them, it is evident that the time will eventually come when the pressure in the inclosed sands will be reduced practically to atmospheric pressure. Further extraction of the oil could perhaps be accomplished for a short time by vacuum pumps, but nothing like complete extraction could be attained without admitting another fluid to take the place of the oil and gas removed. At this stage in the life of the field admission of compressed air or of water to the oil sands would be beneficial instead of disastrous, but this stage will evidently not be reached for many years. Moreover, many or most of the oil sands themselves are not inclosed but become water-bearing down the dip, and as the oil is removed this water will naturally follow the oil up the slope and replace it, thus maintaining a portion of the pressure. Proposals to deliberately permit water to enter the oil sands have already been made, but for many years, at least, they should not be considered.

MANNER OF INVASION.

Extraneous water gains access to the oil sand either because the mechanical barriers placed to exclude it are inadequate or faulty, or because they are placed without proper regard for geologic conditions. The simplest example of invasion is the seepage of top water down the outside of the casing. This difficulty was common in the earlier days of the field but is now effectively overcome by forcing cement up around the end of the casing and into the space between it and the walls of the hole. Various mechanical conditions may of course impair or destroy the effectiveness of this shut-off; the cement may be improperly placed or may fail to set, or the casing may later collapse or may be corroded through by the chemical action of the water itself. Invasion by bottom water is also common and is caused by drilling the well either into a bottom-water sand or so close to it that when the gas pressure in the overlying oil sand is reduced and the fluid level in the well falls the bottom water bursts through, or the well "drills itself in." Bottom water is commonly under high head and may therefore be difficult to exclude.

Less obvious and less easily traceable difficulties are likely to be brought about by disregard of geologic conditions, for when water once gains access to a partly exhausted oil sand it may travel rapidly for considerable distances. One defective well may let enough water into the sand to flood it over many acres, thus causing a number of neighboring and properly finished wells to "go to water." Moreover, in a group of wells, each in itself properly finished, water troubles may arise through the location of the shut-off at different horizons. In well A, for example, the uppermost oil sands may be cased off with the overlying water sands, whereas in the neighboring well B the shut-off may be placed above the uppermost oil sand. As this sand in well A is in free communication with the water sands it soon becomes flooded, and the water migrating through it will appear in well B. If more water enters well B in this manner than can be pumped out the excess will pass into the lower or main producing oil sands and so may appear in well A and other neighboring wells. This condition has existed in several localities in the field, and when once permanently established it practically compels the abandonment of the upper sand in all the wells. As stated on page 51, this condition has been brought about especially in the "transition belts" (the belts in which the oil sands become water bearing) of oil zones A and B, for in these belts some of the operators are likely to case off the upper oil sands, whereas others attempt to obtain oil from them.

Wells drilled and abandoned in the early days of the field, before the geologic conditions were known, have proved a source of trouble in many localities, for it was formerly customary to pull the casing and abandon the hole without plugging it or otherwise destroying communication between the water and oil sands. So long as no oil was extracted from the oil sands no water could enter them, but when other wells were drilled and began to remove the oil, extensive invasion took place. One abandoned hole tapping a strong water sand may turn many hundred barrels of water a day into the oil measures, or more than a dozen neighboring wells can pump out.

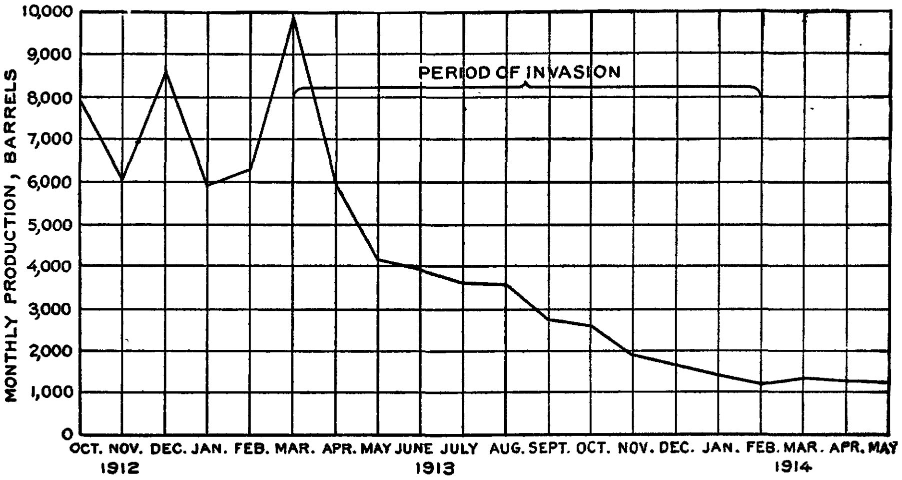


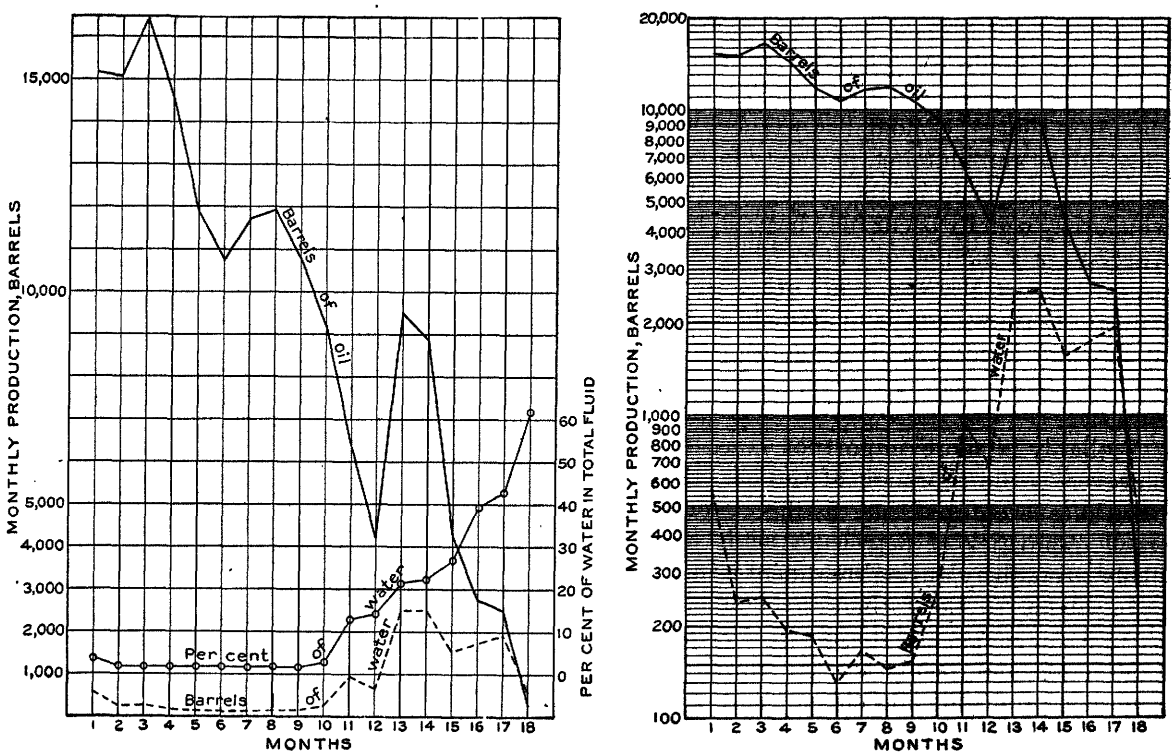
FIGURE 7.—Diagram showing decrease in the production of an oil well in the northern part of the Midway field caused by the invasion of the oil sand by water.

EFFECTS OF INVASION.

The extent of the damage caused by the entrance of water into an oil sand depends on many factors, chief among which are the thickness, character, and stage of exhaustion of the oil sand, the volume and head of the water, and the chemical character of the water and oil. The importance of the last-named factor is conjectural, but there is reason to believe that water containing sulphate or sulphide reacts with oil of the Sunset-Midway type, and that even a comparatively short period of association is likely to injure the quality of the oil. (See pp. 26–31.)

The chief result of water invasion is of course decrease in production. If the sand invaded is thin and carries light oil the gas pressure may be "killed" and a great decrease in production may immediately ensue. The effect on the production of such sands is too well known to operators to need description, but to those unfamiliar with the field figures 7 and 8, which represent typical instances of decrease in production through water invasion, may be of interest. In a thick oil sand carrying heavy oil with little gas the effects of invasion are less noticeable, probably in part because the water collects at the bottom of the sand and does not interfere greatly with the removal of the oil above it, unless the well is pumped too rapidly. When a large amount of water enters the oil sand, however, it is likely to drive the oil back and away from the well, and once the water has entered the sand it tends to cling in the interstices and prevent the flow of oil toward the well. When the amount of water entering the sand is so small that it may be pumped out with the oil, little or no permanent damage is done, though the process of raising the water to the surface and separating it from the oil of course involves considerable expense. The use of compressed-air lifts, capable of handling large volumes of fluid, may permit the removal of the water as fast as it enters the sand, though this process also is an expensive one.

A result of water invasion common in most of the California fields is the formation of a thick brown viscous liquid called emulsion, consisting of an intimate mixture of oil and water. Emulsion is especially likely to form when water gains access to a flowing well or floods a sand containing light oil under considerable pressure, though it may also form in heavy oil sands in which the pressure is comparatively low. Some emulsions separate out on standing a few days, but others remain stable for an indefinite period. The famous Lakeview No. 1 gusher, which ceased flowing September 9, 1911, produced considerable emulsion, some of which remained without separating in the bottom of a sump exposed to the air until July, 1914. Emulsions are common in the Galician and Rumanian oil fields, and a thick viscous variety, known as marais, is so enduring that it is used to spread on roads, where it remains without change for as long as two years.[1]



A. *B.*

FIGURE 8.—Diagram showing in three ways the decrease in the production of oil caused by the invasion of the oil sand by water. *A*, barrels of oil, barrels of water, and percentage of water in total fluid plotted on natural scale; *B*, barrels of oil and barrels of water plotted on logarithmic scale in order to magnify small variations in quantity of water and thus develop two easily comparable curves.

In order to remove marketable oil from such refractory emulsions special treatment is required. Emulsions can be broken up by the addition of ether, which dissolves out the oil, or of salt, which is taken up by the water, but such methods are too expensive for commercial use. An old method consisted of heating the emulsion in open ditches lined with steam coils, but the heat attained was not high enough to break down a refractory emulsion and, on the other hand, the more volatile fractions of the oil were lost. Better results are obtained by "cooking" the emulsion in a boiler over a direct flame. At a temperature slightly above the boiling point the water globules are converted into steam and condensed as free water, while the volatile fractions of the oil are condensed and saved.[2] Several electrical processes have also been devised whereby the emulsion is subjected to the action of a high-tension current which punctures and agglomerates the globules of water and allows them to settle out.[3]

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[1] Legrand, P., Sur les mouvements du pétrole et de l'eau: 2d Cong. internat. pétrole, Liège, Compt. rend., 1905.

[2] Hardison, S. J., The dehydrating oil plant of the Nevada Petroleum Co., California: Am. Inst. Min. Eng. Trans., vol. 51, p. 627, 1915.

[3] Beazley, A. T., Dehydration of crude petroleum: Oil Age, vol. 3, p. 2, Apr. 21, 1911. Harris, F. W., The Raney-Laird dehydrating system: Oil Age, vol. 11, p. 6, January, 1915.

analyses is a matter of simple comparison and depends only remotely on the principles involved in the variation in the water as it approaches the oil zone. In the Sunset-Midway field, where variations in the character of the water are not as marked as in other areas and where a slight difference in sulphate content may indicate a difference in position of several hundred feet, this method will probably be essential in the accumulation of an adequate amount of data regarding the character of the water in the 1,000 feet or so above the oil measures.

In comparing the analyses of two different waters all the mineral constituents must be taken into account and the presence or absence of petroleum acids should also be noted. The practice of attempting to estimate the horizon of a water on the basis of a partial analysis is to be condemned. Some oil men have attempted to compare waters simply by tasting them, but it is evident that only the roughest distinctions can be made in this way, and the analyses given in this report suffice to show that the amount of salt a water contains is no indication of its horizon, except perhaps very locally. Others have used hydrogen sulphide as a means of identification, chiefly because it can readily be detected by its odor, but as this constituent is found only in the modified waters its value as a criterion for comparison is limited. A complete analysis is always the most satisfactory, and several dozen such analyses cost less than the operation of bridging the well or attempting to determine the source of the water by other mechanical methods.

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