CHEMICAL RELATIONS OF THE OIL-FIELD WATERS IN SAN JOAQUIN VALLEY, CALIFORNIA

PRELIMINARY REPORT

BY

G. SHERBURNE ROGERS

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INTRODUCTION.

CONCLUSIONS AND RECOMMENDATIONS.

During the rapid rise of the petroleum industry in the last 50 years the geologic occurrence of petroleum has received a great amount of study, and the interesting problems involved in its origin and migration have engaged the attention of many geologists. It has long been known that oil and gas are commonly associated with water, and the great importance of the water as a physical agent in the migration of the oil has been recognized in all geologic theories of the accumulation of oil. Of the chemical relations between the water and the oil, however, we know little, and scientific literature contains only a few references even to the chemical character of the waters themselves. Apparently many of the current ideas on this subject either are erroneous or can be accepted only with important modifications.

In the oil fields of San Joaquin Valley, Cal., the oil and water are found in practically unconsolidated rocks. At most localities several water-bearing sands are intercalated in the shales above the oil measures, and there is also a water sand a short distance beneath them. In some places a water sand occurs in the shale that separates the oil sands, and less commonly oil and water have been found in the same stratum. In sinking a well through this complex it is difficult to prevent the water, which in places is under high head, from entering the oil sand, in which event it may drive the oil some distance back and so ruin a considerable tract of land. The writer studied the physical and chemical relations of the water and oil in these fields during the summers of 1914 and 1915. The chief conclusions concerning the chemistry of the waters, deduced by him from a study of several hundred analyses of water from different depths, are as follows:

1. Oil-field water is not necessarily salty, as is generally believed, and may not be even slightly salty to the taste. The degree of concentration of chloride in such water is governed primarily by local conditions and is not affected by the position of the water in relation to oil.

2. Sulphate, which predominates in most of the shallow ground waters on the west side of San Joaquin Valley, diminishes in amount as the oil zone is approached and finally disappears.

3. The concentration of carbonate increases as the oil zone is approached but depends largely on the concentration of chloride.

4. The horizon, with respect to the oil zone, at which these alterations take place, is different in each field.

On the basis of these conclusions, which appear to be well grounded, at least for the area studied, the following practical suggestions may be made:

In drilling a well in untested territory it may be possible to obtain an indication of the presence or absence of oil and gas below by ascertaining by analysis whether the sulphate is diminishing and the carbonate increasing in the waters successively encountered. In some areas a significant change may be detected as much as 1,000 feet above the oil; in others the upper limit of alteration may be within a few hundred feet of the oil.

The source of the water in a well that produces a mixture of water and oil may be determined, at least in a general way, by studying its chemical composition. In the Westside Coalinga field, for example, the source of the water may thus be determined rather definitely; in the Midway-Sunset field, where the distinctions are less sharp, the success of this method will depend largely on the number of authentic analyses that are available for comparison.

In this report the writer aims first to present the evidence on which the foregoing conclusions are based and to discuss the interpretation of water analyses and their value from the operator's standpoint, and second, to discuss the chemical relations of water and oil in so far as present information permits. It is hoped that this preliminary presentation will indicate the importance of experimental geochemical work on the interaction of the organic constituents of oils and the inorganic substances found in the oil-field waters. Enough is known already to warrant the belief that systematic experimental work in petroleum hydrology will yield results of practical as well as scientific value.

ACKNOWLEDGMENTS.

the system of interpretation of water analyses adopted in this report, have been freely consulted, and Dr. Palmer in particular has been a constant source of help in the study of the chemical relations of water and oil. The writer is indebted also to Mr. R. B. Dole for generous consultation on some of the problems touching the chemistry of natural waters. Dr. Chase Palmer and Mr. S. C. Dinsmore made many of the water analyses included in the report.

Special mention should be made of the unpublished work of Mr. E. A. Starke, of the Standard Oil Co., on the chemistry of the waters of the California oil fields. Mr. Starke has collected and studied a large number of water analyses and reached several years ago many of the conclusions that the writer has recently arrived at independently. Mr. Starke noted the absence of sulphate in waters associated with oil and ascribed it to chemical reaction between the two, and so has guided his prospecting to a considerable extent by studying the composition of the waters encountered in prospect wells. The special thanks of the writer are due Mr. Starke for his free discussion of the subject and for the use of some of the analyses included in this report.

The success of any study of underground conditions in an oil field depends on the good will and courtesy of the operators, and the writer desires gratefully to acknowledge the support and cooperation of all the companies visited. A complete list of those who have cheerfully and generously furnished information would include practically all the operators in the Coalinga, Midway, and Sunset fields, many of whom spent considerable time in assisting in the collection of samples of water for analysis. The following gentlemen rendered the writer especially valuable aid: Messrs. B. H. van der Linden, M. E. Lombardi, E. G. Gaylord, Paul Paine, M. J. Kirwan, W. W. Orcutt, M. L. Requa, T. A. O'Donnell, E. O. Faulkner, W. M. Wallace, J. E. Elliot, W. A. Ambrose, F. B. Tough, J. J. Hern, R. D. Bush, T. J. Crumpton, W. A. Greer, W. E. Brown, and J. H. Dearin.

NEED FOR MORE ANALYSES.

In the course of this investigation more than 50 samples of water have been specially analyzed and about 250 analyses, most of them made for industrial purposes, have been furnished by the oil companies. These have been sufficient, it is believed, to form a fair basis for the principles set forth in this paper, but they are inadequate to give more than a general idea as to the character of the waters in any particular locality. In the Westside Coalinga field all the evidence leads to the conclusion that conditions are fairly constant, and that even with the data at hand it is possible to determine the general horizon of a water from its analysis. In the Midway-Sunset field, however, the zone of water altered by the oil may in some localities extend 600 feet above the oil measures, and it is at present impossible to deter-

mine whether or not this zone of altered water may be satisfactorily subdivided. Even if this differentiation could not be made analyses will be of great value in locally correlating the various waters, as, for example, in determining whether or not the water produced by two neighboring wells is the same.

It is generally recognized to-day that the problem of preventing water from invading the oil sands is one of the gravest problems confronting the oil industry in California. By following the methods suggested in this report a clue can probably be obtained to the source of the water that floods a well, a knowledge of which is essential to its proper exclusion. These methods are being successfully used by the Standard Oil Co. and should prove equally valuable to other operators.

It may be borne in mind, however, that the work of gathering the data must fall on the operators themselves, for it is impossible for anyone not constantly on the ground to collect an adequate set of samples. An analysis is of little value as a standard for comparison unless the position of the water is known, and properly located samples can usually be taken only while the well is being drilled or repaired. The samples need not necessarily be analyzed immediately but may be sealed and stored away until their analysis becomes desirable. Several of the larger companies have begun to realize the value of analyses and are taking samples wherever good ones can be obtained. It is well to bear in mind that the trouble and cost of collecting a sample and having it analyzed are negligible in comparison with the value that the information thus made available may later acquire.

LOCATION OF THE OIL FIELDS.

The oil fields of San Joaquin Valley are in Fresno and Kern counties. The most important fields are on the west side of the valley, along the flanks of the Coast Ranges, and extend, with intervening unproductive areas, for a distance of 110 miles. The Coalinga field, in Fresno County, is the northernmost of the developed fields, and the Midway-Sunset field, in Kern County, is the southernmost. The Lost Hills and Devils Den districts are roughly halfway between the two, and the Belridge and McKittrick fields are between the Devils Den and the Midway. The only field on the east side of San Joaquin Valley is the Kern River field, which is on the lowest foothills of the Sierra Nevada near Bakersfield, about 30 miles northeast of the Midway-Sunset field. By far the most important of these fields, named in order of age of exploitation, are the Kern River, Coalinga, and Midway-Sunset fields. At present, however, the Midway-Sunset field is the largest in the State in annual production, and it is followed by the Coalinga and the Kern River, in the order named.

SAN JOAQUIN VALLEY.

GEOGRAPHY AND DRAINAGE.

San Joaquin Valley, a part of the great and nearly level-floored depression which traverses the central part of California, is bounded on the east by the Sierra Nevada and on the west by the Coast Ranges. San Joaquin River, which directly drains the northern two-thirds of this great valley, discharges through Carquinez Strait into San Francisco Bay and thence through the Golden Gate into the Pacific Ocean. The southern, more arid third of the valley has no surface outlet under normal conditions, and the surface waters accumulate in the Buena Vista reservoir, near the Midway-Sunset field, and in the depression occupied by Tulare Lake, southeast of Coalinga. The streams that drain into the valley from the Sierra Nevada carry practically 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. On this account the valley floor is unsymmetric, the axis or line of lowest depression lying nearer the western than the eastern foothills.

A considerable portion of the drainage from the mountains sinks into the sand and silt of the valley floor and joins the underground circulation. As all the drainage from the valley must pass through the narrow outlet at Carquinez Strait the underground circulation is probably extremely slow. Mendenhall has aptly referred to the great central depression of California, of which San Joaquin Valley is the southern part, as "canoe-shaped, with only a notch in the rim at the straits through which the waters spill." [1]

GEOLOGY.[2]

It is not the purpose of this report to describe in any detail the geology of San Joaquin Valley or of its oil fields, but a brief outline is necessary to a proper understanding of the conditions governing the chemical character and the flow of the underground water.

Although San Joaquin Valley is essentially a great structural trough filled with valley wash, the geologic conditions on its east and west sides present many points of contrast. The east boundary of the valley is the Sierra Nevada, which is composed of granites and metamorphosed sedimentary and igneous masses of pre-Cretaceous

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[1] Mendenhall, W. C., Preliminary report on the ground waters of San Joaquin Valley, Cal.: U. S. Geol. Survey Water-Supply Paper 222, p. 25, 1908.

[2] The geology of the oil fields of San Joaquin Valley is more completely described in the following reports: Arnold, Ralph, and Anderson, Robert, Geology and oil resources of the Coalinga district, Cal.: U. S. Geol. Survey Bull. 398, 1910. Arnold, Ralph, and Johnson, H. R., Preliminary report on the McKittrick-Sunset oil region, Kern and San Luis Obispo counties, Cal.: U. S. Geol. Survey Bull. 406, 1910. Anderson, Robert, Preliminary report on the geology and possible oil resources of the south end of the San Joaquin Valley, Cal.: U. S. Geol. Survey Bull. 471, pp. 106–136, 1912. Anderson, Robert, and Pack, R. W., Geology and oil resources of the west border of the San Joaquin Valley north of Coalinga, Cal.: U. S. Geol. Survey Bull. 603, 1915.

age. At the foot of the Sierra these rocks are overlain by practically unaltered Tertiary sediments, which dip gently to the west and disappear beneath the sand and gravel of the valley proper. These Tertiary formations are not everywhere present, but are well developed in the neighborhood of the Kern River field. The lower of the Tertiary formations is made up in part of diatomaceous shale, which is probably the source of the oil; the upper division consists of coarse sand, gravel, and clay, into which the oil has probably migrated, and in which it is now obtained.

The oldest rocks on the west side of the valley are probably of Jurassic age and comprise a series of altered igneous and sedimentary rocks. This formation forms the backbone of the Diablo Range north of Coalinga and probably extends beneath the surface for some distance to the south. It is overlain on the valley side by a thick series of Cretaceous shale and sandstone, from the upper part of which oil in commercial quantities is produced in the Oil City district of the Coalinga field. The Cretaceous is overlain by rocks of Eocene and Oligocene (?) (earlier Tertiary) age, above which is a mass of sandstone and diatomaceous shale belonging to the middle Tertiary. Shale, sandstone, and conglomerate of later Tertiary age (upper Miocene and Pliocene) overlie these formations, in most places unconformably, and these are in turn overlain by similar Quaternary sediments. The later Tertiary deposits, which are practically unconsolidated, were probably laid down under alternating marine, brackish, and fresh-water conditions; the series as a whole is characterized by many minor unconformities and by the lenticularity of its individual beds.

In the Coalinga district the oil is believed to have formed in the Oligocene (?) shale and to have migrated up into overlying beds, which are partly middle Tertiary and partly younger. In the Temblor Range fields to the south most of the oil probably originated in the thick beds of diatomaceous shale of middle Tertiary age; it is now found in the irregularly stratified rocks of the later Tertiary. As the lower part of these lenticular masses constitutes the main oil measures everywhere except in part of the Coalinga field, the correlation of individual oil and water sands by a study of the well logs is very difficult.

This whole sedimentary series, resting in what may be considered broadly as a great eroded anticline, constitutes the Diablo and Temblor ranges. The older rocks, closely folded, form the main mountain mass; the younger rocks, more gently folded but dipping in general away from the axis, form the lower flanks and foothills. The oil-bearing strata outcrop well down at the foot of the range, where the prevailing dips are toward the north or northeast at a comparatively low angle. In many places, however, these strata

are affected by one or more minor flexures which run obliquely out from the main ranges, and it has been pointed out by Anderson and Pack [1] that all of the oil fields on the west side are associated with folds of this kind. In other words, all of these fields lie either on such an anticline or in the syncline back of it, or extend over both anticline and syncline. The Midway-Sunset field extends over several minor folds. The reason for the accumulation of oil only under these structural conditions need not be considered here, but it is important to note that all of the fields on the west side are characterized by this type of structure, for it undoubtedly influences the circulation of the oil-field waters.

UNDERGROUND WATER. [2]

A large proportion of the surface water entering San Joaquin Valley sinks below the surface and joins the underground 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 generally fine, and the outlet at Carquinez Straits is narrow. As a result of these conditions the ground water is under artesian head in a wide belt along the center of the valley. Near the north end of the valley the waters are practically ponded and the deeper waters are highly mineralized, and even in the southern part the main valley circulation probably is abnormally sluggish.

Owing to the sharp contrast in meteorologic and geologic conditions between the east and west sides of the valley the ground waters present some interesting chemical variations. As the Sierra is a region of moderate rainfall, and as the Temblor and Diablo ranges are semiarid, practically all the surface water entering the valley is brought down by streams on the east side. As this water is the drainage of a region underlain by granites and other relatively insoluble silicate rocks, it is low in mineral content and carries chiefly carbonates. The west side of the valley, on the other hand, is a region of very scanty rainfall, nearly all of which sinks beneath the surface before reaching the valley proper and circulates through a great series of sedimentary formations. These strata contain a large amount of disseminated gypsum and other sulphates, which

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[1] Anderson, Robert, and Pack, R. W., Geology and oil resources of the west border of the San Joaquin Valley north of Coalinga, Cal.: U. S. Geol. Survey Bull. 603, pp. 116-121, 1915.

[2] 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, Cal.: U. S. Geol. Survey Water-Supply Paper 398, 1916.

are readily dissolved by the waters leaching through them. The waters of the west side are therefore high in mineral matter and predominantly sulphate in character. Dole[1] has shown that an intermediate or axial zone may be distinguished near the center of the valley, where the waters are characterized principally by their high content of alkalies (sodium and potassium).

The character of ground waters in San Joaquin Valley is, therefore, controlled primarily by geologic conditions, and it will be shown that in the oil fields local chemical influences have led to the development of still other types of water. Broadly speaking, the ground water of the valley enters it chiefly from the east side and flows slowly and against considerable resistance toward the north. It has been suggested that because of these conditions the meteoric water entering from the Sierra side has produced sufficient hydrostatic head to force the oil to the west side of the valley and to trap it under the peculiar structural features locally existing there. In other words, a flow or pressure across the valley rather than in a longitudinal direction is postulated. That underground waters have had much to do with the accumulation of the oil can not be doubted, and some support is lent this view by the fact that the water certainly encounters considerable resistance in its normal northerly course. The possibility of lateral pressure must be borne in mind in considering the accumulation of the oil, but it may be pointed out that the chemistry of the oil-field waters offers little support to this view; that if the theory is correct the anomalous position of the Kern River field on the east side of the valley must be explained; and that a theory involving the transmission of hydrostatic head through 20 to 40 miles of lenticular materials, and with only a slight initial difference in head, involves grave difficulties.

OCCURRENCE OF WATER IN THE OIL FIELDS.

GENERAL DISTRIBUTION.

In considering the ground-water system of the valley as a whole it has been tacitly assumed that the water exists as a continuous body saturating all the rocks to an indefinite depth. This conception is well founded and is valuable in a broad study, although the fact that the circulation of the water is confined largely to certain strata is of course of great practical importance. The question in which layers the water will circulate depends on a variety of factors, most of which are well understood. There is no intrinsic difference between a water sand and any other sand.

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[1] Mendenhall, W. C., Dole, R. B., and Stabler, Herman, op. cit., p. 117.

WATER SANDS.

Texture.—Water flows most readily through rocks of uniformly coarse grain, and hence tends to circulate chiefly in the sandy layers.[1] The amount and pressure of the water in a sand depends 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. In other words, the character of the rock has much to do with its content of available water, which in a thick sandy stratum is usually concentrated in one or more "pay streaks" just as oil is concentrated in certain parts of an oil sand.

The rapidity of circulation of the water through a stratum is not, however, an index of the amount of water that the rock contains. 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, of 38 to 42 per cent; and clay, of 44 to 47 per cent.[2] The important consideration for practical purposes is, however, that the sand yields its water readily because more fluid can easily take its place, whereas movement is slower in the clay and much of the water is probably held by capillary attraction. A sandy shale or a tight sand may also contain considerable water which will not be apparent in drilling because it escapes too slowly from the bed. If all the strata penetrated by an ordinary oil well could be carefully examined, those below the ground-water level probably would be found to contain more or less water, although the water content of certain strata might be far less than the absorptive capacity of the rock. Most of the beds, however, are too fine grained to permit perceptible movement of the water in them, and consequently most of the drainage passes through a few layers.

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 governing the movement of water and oil.

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[1] Slichter, C. S., The motions of underground waters: U. S. Geol. Survey Water-Supply Paper 67, 1902; Field measurements of the rate of movement of underground water: U. S. Geol. Survey Water-Supply Paper 140, 1905.

[2] 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.

Freedom of circulation.—Although the grain of the rocks is an important factor in determining which beds the drainage follows, as the term "water sand" implies, an equally great 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 that entering at the outcrop can escape at the lower end of the lens, either into another lens or through some practicable channel. (See fig. 1.) 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
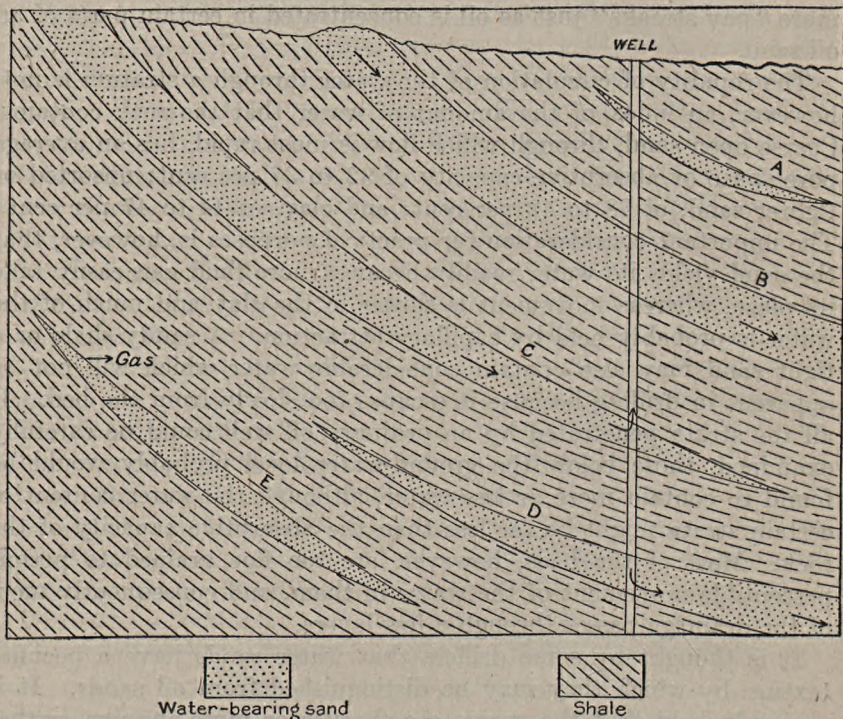
FIGURE 1.—Diagram showing circulation or stagnation of the water in open and closed sand lenses before and after the lenses are penetrated by wells.

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 which circumstances the expansion of the gases may displace some of the water. It is probable that most of the so-called water sands in the valley fields fall in one of these three classes, which are shown diagrammatically in figure 1.

DRY SANDS.

In most well logs an attempt is made to differentiate water sands and "dry" sands, the "dry" sands being typically those which absorb water instead of yielding it. Under ordinary conditions of drilling it is generally necessary to maintain a certain depth of water in the drill hole, ranging from a few hundred feet when drilling shallow wells by the standard method to the total depth of the hole when the rotary method is used. The driller's characterization of a stratum as water sand or dry sand must then depend largely on the fluctuation of the water level in the hole. If the water in the sand is under high artesian head the water will rise in the drill hole and may flow at the surface (fig. 1, C). However, a column of drilling water a thousand feet high exerts a pressure of 434 pounds per square inch at the bottom of the hole, and this pressure must be counter-balanced by the hydrostatic pressure in the sand before the water level in the drill hole will rise. If the hydrostatic pressure is equal to the weight of the column of drilling water no change in level will occur, but if the pressure is lower the water level will sink and most of the drilling water may be absorbed. Thus sands which rapidly absorb most of the drilling water might instead yield a short column of water if the drill hole were dry, and if they were pumped might prove steady producers. Many such sands have doubtless been reported to be dry. This distinction is by no means an academic one. Water under low hydrostatic head may be unimportant in the early history of an oil field, 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 convenient reservoir, and such water on entering them is capable of doing considerable damage.

The factors causing artesian flows are well known and need not be discussed here, but some of the causes of unusually low hydrostatic head, leading to the conditions described above, may be mentioned. If the sand is a sealed lens completely filled with water it can neither receive nor yield water when it is penetrated by the drill. If, on the other hand, it is open at both ends so that there is free circulation the head may be either moderate or low, depending chiefly on the inclination or dip of the bed and the amount of resistance encountered by the water in its passage between the sand grains (fig. 1, B). If the resistance is extremely low the head will be very low, for the water will follow the path of least resistance. In many wells of this kind the head is probably less than that of the water in the drill hole, and as circulation is comparatively free, part of this water will be absorbed.

However, in some drill holes, in which the drilling water has disappeared into a sand with great rapidity, the conditions just described

do not offer adequate explanation.   For these drill holes, figure 1, D, which shows a water-filled sand lens with free outlet at the lower end but sealed at the upper, is suggestive.   Under these conditions a negative head or partial vacuum would be created, and if such a sand were penetrated by the drill the drilling water might be taken up as fast as it could be poured into the well.   These conditions do not depend on the complete sealing of the upper end of the lens, for the same principle would operate to a lesser degree providing only that the outlet is larger and accommodates more water than the intake.   As the freedom of circulation normally decreases with depth, the outlet might have to be considerably greater than the intake, but this relation is probably no less common than the reverse, by which a high positive head would be developed.

It may be mentioned in passing that many geologists believe that meteoric and connate waters are confined to a relatively shallow zone near the earth's surface, below which the rocks are normally dry. The literature of ore deposits contains many references to this belief [1] and strong evidence in favor of it is also found in the Appalachian oil fields.   In the fields of San Joaquin Valley, however, large amounts of water have been found at the greatest depths reached, more than 4,000 feet, in the fields of the west side, and 5,000 feet in the Kern River field.

RELATION TO THE OIL.

The lenticular rocks overlying the oil in the San Joaquin Valley fields include a number of well-recognized water sands.   These sands may be traced within small areas, though wide correlations are impossible.   Numerous factors influence the distribution of the water and the course of its circulation and therefore where irregular and lenticular rocks are concerned it is impossible to predict in advance of drilling where the greatest flows will be found.

The ground-water level, or the plane below which most of the strata are saturated, varies from place to place but is generally within 300 feet of the surface.   Between this level and the horizon of the oil from one to a dozen or more water sands are found, the number depending on the locality and on the depth of the oil.   In some localities no flows are encountered in the 300 feet or more of strata directly above the oil, but in others there is a water sand less than 50 feet above it.   Sands yielding large quantities of water are generally encountered below the oil, the distance depending somewhat on the thickness and character of the oil zone itself.   Where the oil is confined to sands in one zone 300 feet or more thick, there is generally a water sand between 10 and 100 feet below the base of the oil zone.

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[1] One of the earliest papers is that of Kemp, J. F., The rôle of the igneous rocks in the formation of veins: Am. Inst. Min. Eng. Trans., vol. 31, pp. 169-198, 1902.

Where the oil occurs in several more widely separated sands water is usually encountered between them.

In addition to the sands that are wholly filled with either oil or water there are sands that contain both, the oil occupying the up-slope and the water the down-slope portion. The topmost sand in the oil zone in the Westside Coalinga field, for example, contains water down the dip, and analogous conditions exist in several localities in the Midway and Sunset fields. It is generally recognized that if any persistent oil sand in any of the fields could be followed far enough down the dip the oil would finally be found to be replaced by water.

The terms locally applied to waters in the three positions described are respectively "top water," "bottom water," and "edge water." 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, and edge water may be either top water or bottom water or both. These terms are perhaps too commonly used and too convenient to discard, but the term top water should be restricted to water above the highest oil sand, and the other terms should be used only when their meaning is perfectly clear. The terminology suggested by the writer (see p. 51), which is also based ultimately on the position of the water in relation to the oil, is believed to offer a basis for more rational distinctions.

PHYSICAL CHARACTERISTICS.

HEAD, OR PRESSURE.

In several fields of the San Joaquin Valley the water in many sands is under great pressure, and it has been necessary to devise special methods of shutting off this water in order to prevent its entering the oil sands. In the McKittrick field, for example, several wells near McKittrick encountered water which is said to have flowed for a while over the derrick, and in the Midway-Sunset field many flowing waters have been struck at different depths, the greatest more than 3,500 feet. As a general rule, to which there are many exceptions, the pressure increases with the depth, and the waters below the oil zone are generally confined under considerable pressure. The head in most of the sands reported as water sands by drillers is more than 200 feet, and it has already been pointed out that many sands reported as dry probably carry water under a head of more than 50 feet.

The pressure of the water in most sands, however, is not constant, but 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 given sand depends on local factors and may differ widely among neighboring wells, but the general decrease in any area as a whole is striking.

In water wells outside of oil fields the pressure is generally either hydrostatic or artesian in character, or is due to rock pressure. Hydrostatic pressure is caused by the weight of the downward-bearing column of water, and its amount at any point is controlled chiefly by the difference in elevation of that point and the point at which the water enters the bed, and in practice by the fineness of the material through which the pressure is transmitted. The factors controlling hydrostatic head are fairly well understood and may be determined with considerable accuracy. Rock pressure is commonly believed to be the weight of the overlying column of rock, which exerts a compressive effect on the beds beneath it. During the deposition of the sediments this undoubtedly leads to closer packing of the grains, but after a state of equilibrium has been reached the effect of further compression is a matter of speculation, unless the rocks concerned are deeply buried. A factor often overlooked in this connection is the tensile strength of the overlying rocks, which may conceivably be great enough to relieve a part of the pressure from a given point. As the weight of the strata is thus somewhat irregularly distributed, the rock pressure on a body of ground water must be irregular. Rock pressure is doubtless an important factor under some conditions, but its effect is generally an unknown quantity.

Gas pressure must also be taken into account in regions in which gas is contained in the rocks. In general the gas pressure in any sand is less than the weight of an overlying column of water, but there are many sands in which it is considerably 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. (See fig. 1, E.) When the gas has expanded somewhat, the apparent head of the water decreases, and some, though not all, of the decrease in the head of oil-field waters is doubtless due to diminishing gas pressure. Some puzzling differences in the head of these waters may also be ascribed to gas pressure, the effect of which can not be overlooked, although its ultimate cause has never been satisfactorily determined.

Aside from 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 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 as 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 quite reach the surface.

In the oil fields of the west side of the valley much of the water is under high initial head or pressure, but in the main Kern River field on the east side of the valley the pressure is notably lower. Its present pressures are not comparable with those in the more recently developed fields of the west side, but even in the early period of its development fewer flowing waters were found. Most of the important factors influencing head or pressure have probably entered into this difference; the geologic structure in the Kern River field is more gentle, and the sands are thicker and more persistent, the underground circulation is freer, and the initial gas pressures were considerably lower.

<div align="center">TEMPERATURE.</div>

The temperature of the oil-field waters generally increases with depth at about the rate that is normal in most regions, or possibly at a slightly higher rate. The temperature of the shallow waters is generally between 80° and 90° F., and that of the waters near the oil sands between 95° and 110° F. The waters from depths of 3,000 to 4,000 feet in several wells have a temperature of 120° to 130° F., though that from similar depths in other wells is cooler. The geothermic gradient is fairly regular, so that the source of the water is indicated in a general way by its temperature, and a sand receiving much surface drainage is generally abnormally cool. The temperatures of some of the waters discussed in this report are given in the tables of analyses on pages 63, 66, 70, 73, 74, 76, and 77. The cooling effect of expanding gas, as well as several minor factors, may injure the value of temperature measurements made at the mouth of a well, so that some variation would be expected, and in addition it seems certain that the waters undergo chemical changes, probably exothermic in character, which may locally disturb the normal gradient still more.

Measurements of the geothermic gradient have been made in several localities in North America and Europe, and it is interesting to note that Koenigsberger and Mühlberg [1] after studying and correcting these measurements conclude that the gradient is abnormally high 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 available are deemed inadequate and that there are apparent exceptions. Although the average of the gradients measured by Koenigsberger and Mühlberg in oil fields is slightly higher than that of gradients in other regions,

[1] 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; also Über Messungen der geothermischen Tiefenstufe: Neues Jahrb., Beilage Band 31, pp. 107–157, 1911.

the wide variation between individual gradients in oil fields suggests that more data might reverse their results. Irregular variations, as stated above, also characterize the temperatures of the waters in the oil fields of the San Joaquin Valley.

GEOLOGIC CONDITIONS THAT INFLUENCE THE COMPOSITION OF WATER.

GENERAL FEATURES.

Owing to the fact that underground waters in a region of sedimentary rocks tend to follow the bedding planes, the structure or attitude of the rocks has an important 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. Whether the water so trapped was originally salt or fresh, it is evident that during its long period of association with the rocks it will dissolve certain of their constituents and become more highly mineralized. The waters of the oil fields of the valley differ widely from one another in both their content of chloride and their total load of dissolved mineral matter, and it is thought that these variations are caused by such physical factors as the geologic structure, the lenticularity of the beds, and the amount of rainfall. The solution of rock constituents by underground waters is a somewhat complicated problem that may best be discussed in connection with the chemistry of the waters, but the distribution of chloride is so largely a physical problem that it will be considered here.

ORIGIN OF SALT WATER IN 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 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, only slightly altered by its contact with the rocks, 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 the water will accu-

mulate in its deepest portion and remain there, somewhat as the surface waters of Great Salt Lake are held in their basin. Where the outlet is not entirely closed but is merely restricted, other factors enter into the problem, 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 such subordinate factors as 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. The deeper of two deep wells in the same locality would ordinarily be expected to yield a more salty water, owing to the smaller volume of circulation in the deeper rocks as compared with those nearer the surface. In a region of lenticular beds irregularities are to be expected, for the freedom of circulation differs from bed to bed and some sands will therefore retain their salt water much longer than others.

After marine sediments have been elevated to form land and the underground circulation thus set up has leached out part or all of the connate water the rocks may again subside beneath sea level. In this event the fresh water contained in the beds will be partly replaced by sea water, and sediments that are laid down over these beds will be saturated with sea water. After the second period of elevation has occurred and circulation has again been established the process of freshening will be repeated. Under these conditions it is evident that the older or deeper formations, having undergone longer continued leaching, may contain less salt water than those nearer the surface, where the replacement by fresh water may be incomplete. Examples of salt water underlain by fresh water are not uncommon on the Atlantic Coastal Plain,[1] and it is possible that similar conditions exist in several places along the borders of San Joaquin Valley.

In the foregoing paragraphs the burial and retention of sea water only has been considered, but it is evident that strata laid down in a fresh-water lake may contain entrapped fresh water, which is just as truly connate as entrapped salt water. In other words, the term connate water as originally employed[2] means simply water occluded in the sediments when they were deposited and is not restricted to any particular chemical type of water. On the other hand, if used in this strict sense, the term should be restricted to water laid down with the formation in which it is now found; it therefore should not be applied to water that has migrated from one formation to another,

[1] Sanford, Samuel, Saline artesian waters of the Atlantic Coastal Plain: U. S. Geol. Survey Water-Supply Paper 258, pp. 75-86, 1911.

Stephenson, L. W., and Palmer, Chase, A deep well at Charleston, S. C.: U. S. Geol. Survey Prof. Paper 90, pp. 69-94, 1915.

[2] Lane, A. C., Mine waters and their field assay: Geol. Soc. America Bull., vol. 19, p. 501, 1909.

or to water that has entered the rocks during a second period of immersion.

The general concept of connate water is a valuable one, but the practical application of the term in its strict sense is attended by so many difficulties that it seems advisable to redefine it in conformity to current usage. A sample of salt water may reasonably be called connate if it approximates ocean water in chemical composition and if it occurs in rocks of marine origin in which the circulation of the water is very slight. The water in beds of fresh-water origin may be thought to be connate, but as the composition of the body of fresh water in which the beds were deposited is unknown, the application of the term can not be supported by chemical evidence and must rest wholly on geologic considerations of a more or less conjectural nature. In actual practice, the term can not be applied to a specific sample of water unless chemical evidence can be adduced, that is, unless the composition of the original body of water is available for comparison, and usually this is possible only when the water is of marine origin. Practically, therefore, the term connate must be restricted to connate waters of the marine type, and so far as the writer can learn this accords with the common use of the term at the present time. On the other hand, it is generally impossible to ascertain how far a water has migrated or whether it is actually connate to the rocks in which it is now found. (See discussion of analysis 25, p. 61.) If it has migrated from one formation to another or if it entered the rocks during a later period of immersion, it is not strictly connate, but neither is it pluvial or meteoric. If it were ordinarily possible to determine these facts it might be advisable to introduce a new term, but as it is not the writer believes that the term connate may be extended to include such extraneous waters. Although Lane,[1] in introducing the term connate, notes that connate water may be either salt or fresh, neither he nor any other investigator, so far as the writer knows, has ever attempted to apply the term to specific samples of fresh water. If, however, this application should become desirable a qualifying adjective may be used to distinguish connate fresh water from connate marine water. Similarly, if it is desired to use the term in its strict etymologic sense—as water that was buried with the bed at the time of deposition—a phrase such as "connate to the bed in which it is found" may be used. For practical purposes, therefore, connate water may be defined simply as fossil sea water. The term is so used in this report, and although it is recognized that connate fresh waters are thereby included with the meteoric or pluvial types there seems to be no practicable way of distinguishing them.

The definition here adopted is thus based principally on chemical rather than geologic evidence, though as water in contact with rock

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[1] Lane, A. C., op. cit.

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, like the Paleozoic, may have changed so materially that its origin, so far as chemical evidence goes, may be in doubt, but some of the salt water in the rocks of San Joaquin Valley is so similar to sea water that there can be little doubt that it is fossil sea water. (See Table 8, p. 73.) This view is strengthened by the fact that the differences in composition between it and normal sea water may be adequately explained by fairly definite chemical reactions and is corroborated by the fact that geologic conditions in the areas in which it occurs are such as to prevent free circulation, which explains why it has not been leached out. Some geologists hold that connate water can not be retained long in rocks that have been elevated above sea level and that salt ground waters are due to the leaching of salt deposits. However, waters that have leached salt deposits would ordinarily differ in composition from ocean water in several respects and would probably be unlike any waters in the San Joaquin Valley oil fields that are known to the writer. Moreover, as geologic conditions in that region seem to be locally favorable to the retention of connate water, the view ascribing salt waters to the leaching of hypothetic saline deposits need not be considered further.

RELATION OF GEOLOGIC STRUCTURE TO DISTRIBUTION OF SALT WATER IN THE OIL FIELDS.

Though much of the deeper water in the oil fields of San Joaquin Valley is very salty, in some localities it is practically fresh. This difference is believed to be due largely to difference in structural conditions. All the fields of the west side are characterized by similar structure, being associated with the minor anticlines that border the edge of Temblor and Diablo ranges. The anticlines and the synclines behind them in all these fields have a general southward plunge. In considering hydrologic conditions each field may be regarded as occupying one or more of the following positions: The eastern flank of the anticline near its north end, where erosion has uncovered and truncated the oil-bearing strata; the summit and flanks of the anticline, where the oil-bearing rocks are deeply buried and do not outcrop; the trough between the anticline and the main slope of the valley; and the western limb of this trough near the outcrop of the oil-bearing beds. If San Joaquin Valley itself be thought of as a great open trough with these structural features perched high on its western rim it becomes evident that the synclines constitute traps in which the ground water may be effectually ponded. In the first position mentioned, however, drainage down into the main valley should be relatively free, and in the second and fourth positions the freedom of drainage would depend on the completeness with which the waters are

ponded in the trough. It is perhaps noteworthy that the accumulation of oil in the first position seems to be unusual and is illustrated only in the northern part of the Eastside Coalinga field.

These ideas seem to be supported by the character of the water in the four structural provinces distinguished. So far as data are available, all the synclines are characterized by more or less salty water, and the proportion of chloride at any point in the trough is apparently governed by its depth and distance from the outcrop. The water near the axis of the Midway syncline, for example, is very salty, whereas, nearer the outcrop to the west, where fresh water may enter the beds, it is much less so, and every gradation between the two extremes may apparently be found. (See figs. 6 and 7 and discussion, pp. 86–91.) On the other hand, in the northern part of the Eastside Coalinga field, which is on the eastern slope of the southward-pitching anticline, the waters contain only a small proportion of chloride, many of them far less than is perceptible to the taste. (See analyses 35 and 36, Table 6, p. 69.) The pitch of the anticline has caused the oil-bearing strata in this locality to outcrop a short distance west of the field, and as there is apparently no structural barrier to the east to prevent circulation down into the main valley, practically all the connate water has been driven from the beds. The removal of chloride has been even more complete north of the limits of the productive field, where the structure becomes truly monoclinal and the dip somewhat steeper. Chloride is much more abundant toward the southern end of the field, however, or down the pitch of the fold where the strata are deeply buried.

A similar contrast is apparent if the Kern River field on the east side of the San Joaquin Valley is compared with the Midway field. The structure in the Kern River field is very much more gentle than that typical of the fields of the west side, and apparently no structural barrier exists to pond the water. Furthermore, owing to the much greater abundance of water on the east side of the valley, the chlorides have been in large part removed, and such other salts as are derived from the rocks usually form only a dilute solution. The writer knows of only two waters whose analyses show a concentration greater than 2,000 parts per million, and most of the waters contain less than 1,000 parts of dissolved mineral matter. (See p. 85.)

The period of subsidence during which the salt water now present in the oil fields became entrapped in the rocks can not be determined. The Cretaceous and older Tertiary deposits were laid down beneath the sea and were once saturated with salt water, and some of the later Tertiary formations are also to a large extent of marine origin. However, much of the water originally entrapped in the Cretaceous sediments was probably leached out during later periods of elevation, and some of the salt water now found in these rocks doubtless

entered them during the Tertiary periods of subsidence. Furthermore, the stresses incident to the folding of the strata may have caused migration from one formation to another; this appears to be the most plausible explanation for the local occurrence of salt water in the fresh-water beds of late Tertiary age. (See p. 61.) In one locality or another salt water is now found in all the Cretaceous and older Tertiary formations and in most of the later Tertiary deposits as well, but there is usually no way of telling whether or not it is connate to the beds in which it occurs, and doubtless much of it was entrapped during the most recent periods of immersion.

GENERAL ASSOCIATION OF SALT WATER AND PETROLEUM.

It has long been known that in most oil fields petroleum is rather closely associated with salt water, and many attempts have been made to explain this widespread association. Few analyses of oil-field waters have been made, however, and the presence of salt in many waters has probably been detected by the taste. Although presumably the water in most oil fields is salty, and in some is extremely salty, it may be borne in mind that the degree of saltiness is known to be variable and must therefore be influenced to some extent by local conditions.

Presumably on the assumption that all oil-field waters are strongly salty Ochsenius,[1] Zaloziecki,[2] Beeby Thompson,[3] and others have suggested that the chloride was concerned in the formation of the oil itself, either by acting chemically on the organic matter or by retarding premature decomposition. Although there is as yet little chemical evidence to support these views it is possible that the chloride has exercised some such effect, or has influenced the polymerization of the oil during a later period in its history. The fact that the present distribution of chloride in the oil fields of San Joaquin Valley is apparently controlled by local structural conditions would not necessarily refute this theory. Such influence as the salt water might have would be exercised during the earlier stages of formation of the petroleum; and as the diatomaceous shales which are the · probable source of the California oil are known to have been laid down beneath the sea they must have been originally saturated with sea water.

On the other hand, there is a possibility that the occurrence of salt water in oil fields may be everywhere explained by the simple principles that seem to be effective in the San Joaquin Valley fields, namely, that the water is more or less completely trapped in closed

[1] Ochsenius, C., Zur Entstehung des Erdöles: Chem. Zeitung, Band 15, pp. 935 and 1735, 1891; Erdölbildung: Deutsche geol. Gesell. Zeitschr., Band 48, pp. 239, 685, 1896; Erdöl und Salz: Chem. Zeitung, Band 21, p. 57, 1897.

[2] Zaloziecki, R., Zur Entstehung des Erdöles: Chem. Zeitung, Band 15, p. 1203, 1891.

[3] Thompson, A. B., Petroleum mining, p. 113, 1910.

sand lenses or by structural barriers. The very fact that the oil itself can accumulate and remain within a small area under high pressure for long periods of time implies that the underground circulation is decidedly restricted. Hence if salt water originally saturated the beds it is reasonable to expect that under most conditions some of it would be retained also. No very positive proofs of this simple explanation can be offered until more is known of the chemical character of oil-field waters in relation to physical conditions, but in the absence of evidence to substantiate the theory that chlorides are concerned in the formation of the oil, this suggestion may be worthy of consideration.

Another view that may be mentioned in passing is that salt water in oil fields has certain peculiarities of composition which indicate that it is, in part at least, of deep-seated origin.[1] It has been shown that the distribution of salt water in the San Joaquin Valley oil fields may be explained on simple physical principles, and it will be shown below that this water has nearly the composition of sea water with certain modifications due to definite chemical reactions. There is nothing to show that it has emanated from the interior of the earth, and an appeal to recondite agencies is unnecessary.

DISTRIBUTION OF WATER IN THE OIL FIELDS.

The following notes on the occurrence of water in the several oil fields are included in order to enable one unfamiliar with the fields to understand more clearly certain features of the chemical relations of the waters. No attempt is made to describe local conditions in detail or the damage wrought by the intrusion of water into the oil sand. Most of the analyses on which this paper is based represent waters from the Coalinga, Midway, and Sunset fields, and reference to the physical conditions in these fields will again be made in discussing the chemical relations of the waters.

COALINGA FIELD.

The Coalinga oil field is divided into two fairly distinct districts, the Westside and the Eastside fields. The Westside field is situated on the western limb of a syncline and the Eastside field is practically confined to the summit and eastern limb of the anticline to the east. The deeper portion of the syncline has not been explored. The ground-water level in the whole area is generally within 200 feet of the surface, and most of the water needed for industrial use is obtained from comparatively shallow water wells. Throughout the area the shallower waters are highly mineralized and are notable for their very high proportion of sulphate.

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[1] Washburne, C. W., Chlorides in oil-field waters: Am. Inst. Min. Eng. Trans., vol. 48, pp. 687-694, 1915.

In the Westside field many of the waters above the oil sands are under considerable head, and water flowed at the surface from some wells for several years. Some of these top waters are very corrosive and have caused considerable damage by attacking and destroying the casing used to prevent their entrance into the oil sands. Strong water sands are generally encountered near the tar sand zone, and many of these waters contain hydrogen sulphide and are known as sulphur waters. In the deeper or eastern part of the Westside field there is a water sand a short distance above the oil zone but farther up the rise to the west this same sand carries oil. In most localities a similar condition apparently exists in a sand near the base of the oil zone; to the east this sand carries the "bottom water," but up the rise it is oil bearing and the first water below the oil is in the upper part of the Oligocene (?) shale. In general the water below the oil zone is confined under considerable pressure, and even now rises within a few hundred feet of the surface.

Owing to the southerly pitch of the anticline on which the Eastside field is situated the strata outcrop a short distance west of the northern end of the field but at the southern end are deeply buried. As the beds dip rather steeply to the east in the northern part of the field, and as there is apparently no structural barrier to the east to restrict circulation, a relatively free passage is afforded such water as seeps in at the outcrop. In most sands the water is therefore not under very high head. It is not so highly mineralized as in the Westside field and is characterized by a low proportion of chloride. However, toward the southern end of the Eastside field the circulation is more restricted, and the average head is therefore higher and the percentage of dissolved matter, especially chloride, is greater. The occurrence and distribution of the water in the Eastside field is not yet thoroughly understood and presents many puzzling irregularities.

LOST HILLS FIELD.

The Lost Hills field extends in a narrow belt along the axis of a well-defined anticline, the continuation of that which dominates the structure in the Coalinga field. Most of the strata penetrated by the wells probably do not outcrop, and conditions are therefore not favorable for free circulation. On the west or inclosed slope of the anticline very salty water is obtained at relatively shallow depths, in some places within a few hundred feet of the surface, but farther east the shallow water contains a high proportion of sulphates. From the scanty information available it appears that the water near the oil zone is very salty and is confined under considerable pressure.

McKITTRICK FIELD.

The McKittrick field is characterized by more complex structural features than any other field in San Joaquin Valley. In a general

way, the productive district lies on the flanks of three folds, but the structure is complicated by overturned folds and thrust faults.

The circulation of the shallower waters is apparently controlled chiefly by the topography, these waters being more abundant and more highly mineralized in the McKittrick Valley than in the foothills to the west. The deeper circulation, however, is undoubtedly affected by the complex geologic structure, and little can be said of its course or nature until more complete information is available. The oil-bearing zone is generally underlain by a sand carrying warm water under considerable pressure. In part of the field the oil sands have been flooded, and it is generally believed that the damage had been done by this water. Whatever its original source, the water that has flooded the oil zone is very uniform in chemical composition and is probably the yield of a single water sand. Little variation is shown by about 30 analyses of this water at the writer's disposal, and analysis 89 (Table 14, p. 85) is entirely representative.

MIDWAY-SUNSET FIELD.

The Midway and Sunset fields are arbitrary divisions of a great oil-producing area, and as the geology of both fields is similar they may best be described together. The developed area extends west from the east slope of the Buena Vista anticline across the Midway syncline and up on its western limb, where the oil-bearing strata outcrop. The western limb of the trough is not a regular slope as in the Westside Coalinga field but is broken by several minor anticlines, all pitching to the southeast.

The ground-water level in the Midway-Sunset field is lower than in the Coalinga field and is generally 250 to 500 feet below the surface. Along the hilly western part of the field the shallower water is almost lacking and in some localities is not abundant even to the depth of the oil zone. Generally, however, some water is found near the tar sands and also between them and the oil. At a variable depth below the oil zone, usually less than a hundred feet, abundant supplies of warm water under considerable pressure are found. Owing to the scarcity of shallow water this "bottom water" is widely used for industrial purposes in this part of the field.

In the Midway Valley and the Buena Vista Hills, which are the surface reflections of a syncline and an anticline, respectively, the water conditions are somewhat different. In the valley moderate supplies of water may generally be obtained at a depth of 200 to 500 feet, but in many localities even the shallower water contains a remarkably high percentage of sodium chloride. In the Buena Vista Hills the water level is generally lower, but the water is similarly salty. The percentage of salt increases with depth, but at a variable rate; in some localities water from 700 feet is almost fresh

enough to be potable, whereas in others it is nearly as salty as sea water. Many of the deeper top waters are confined under high pressure and flow at the surface. In most localities there is a rising or flowing water a short distance below the top oil sand, and in the deeper part of the syncline this oil sand is itself water bearing. Where second and third oil sands have been found, strong water sands are generally present between them. Although the water pressure as a rule is high, it is decidedly variable, and "dry" sands have been reported in many places. The deeper waters in this part of the field are fairly uniform in chemical character but differ from those at the same horizon in the shallower western part of the field. (See figs. 6, p. 88, and 7, p. 91.) Their average temperature is also different, being ordinarily some 10° higher.

KERN RIVER FIELD.

The Kern River field, lying on the lowest foothills of the Sierra Nevada on the east side of San Joaquin Valley, differs in many respects from those just described. The geologic structure is relatively simple; the strata lie in a gentle monocline, which is modified in places by minor wrinkles. The oil sands are very thick and are highly productive, but the gas pressure has never been very high.

Kern River, which has a large drainage basin in the Sierra Nevada flows along the edge of the field. The waters draining from the Sierra are very different in chemical character from the waters on the west side of the valley and contain only a very small amount of dissolved salts, which are chiefly carbonates. The ground-water level in the Kern River field is high, and in most localities abundant supplies of potable water are obtained relatively close to the surface, and thence at short intervals down to a depth of many hundred feet. In general the percentage of dissolved salts increases with depth, but even in the deepest waters reached is usually less than in the average shallow water in the fields of the west side. Owing to the sandy character of the strata and to the fact that no pronounced structural barrier separates the field from the valley proper, the underground circulation is less restricted than in most of the fields of the west side, and the general water pressure is therefore comparatively low. Flowing waters have been encountered, but they are not common.

ANALYSIS OF WATER AND INTERPRETATION OF RESULTS.

MINERAL CONSTITUENTS IN WATER.

Natural waters are essentially solutions of mineral substances which have been derived from the rocks or other material with which the waters have come in contact. All solutions may be regarded as homogeneous bodies, through which the mineral substances are

uniformly distributed, and all solutions have definite properties, which depend on the nature and proportional amounts of the substances of which they are composed. By chemical analysis of water only the proportional amounts of the constituents are determined. The nature of each constituent, that is, its conduct toward other substances whose natures are known, has been learned by other methods, and as the properties of a solution are an assemblage of the properties of all its constituents, the properties of a water may be deduced from the statement of its analysis.

The amount and character of the mineral substances dissolved in different waters vary greatly and depend on many factors. Chief among these 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. Water under a given temperature and pressure can dissolve only a definite amount of any substance; and if the heat and pressure are lowered, as, for example, when an underground water emerges at the surface, the excess of dissolved matter may go out of solution as a precipitate. It is through this readjustment to changed conditions that mineral matter is deposited around some springs or wells. Similarly, if two waters carrying different salts in solution come into contact, a chemical reaction may take place and some of the dissolved material may be precipitated. Although many of the reactions that take place are obscure and can not be completely explained, the properties of natural solutions, which are the net results of these reactions, furnish a rational basis for general classification.

In addition to dissolved mineral solids or gases, which chiefly determine the chemical properties of a water, two other classes of substances are generally present—material in suspension, which can be removed by filtering, and material in colloidal solution, a state intermediate between suspension and true solution. In the present study consideration has been given chiefly to the commoner dissolved mineral substances. Small amounts of several elements, such as lithium, barium, phosphorus, and boron, are probably present in some of the oil-field waters, but they do not materially affect the quality of the water and their determination is not essential to a study of the relations of water to petroleum.

COLLECTION OF SAMPLES.

In most districts the collection of representative water samples for analysis is a simple matter, but in the oil fields, where the universal aim is to shut the water out of the wells, it is often very difficult. In wells that supply water for industrial uses the depth of the water sands is generally known, and samples can, of course, be easily taken,

but the waters that can be obtained 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 oil fields, 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. When a sufficient number of authentic samples of typical waters in any area has been collected and analyzed it will then be possible, by comparison with these standards, to form an estimate of the probable source of any water.

Authentic samples can usually be taken only while drilling the well or while repairing it later. Flowing waters may, 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. When the well is being drilled by the standard method the collection of samples is not especially difficult, and samples uncontaminated by water from upper sands may 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 rotary systems are 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 slight 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.

DETERMINATION OF CONSTITUENTS

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 former 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 con-

stituents 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 or equilibrium 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.

The number of constituents to be determined and the accuracy with which the work is done differs 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), a nonvolatile negative constituent, and the volatile substances hydrogen sulphide (H_2S), and carbon dioxide (CO_2). The quantity of suspended matter and the quantity of organic matter also are usually determined.

Iron and aluminum are usually precipitated and weighed together and reported as the oxides ($Fe_2O_3 + Al_2O_3$) in industrial analyses, and carbonate and bicarbonate are often not distinguished from each other. The laborious determination and separation of sodium (Na) and potassium (K) 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 implies, of course, that the determination of all the other radicles is absolutely correct, which is practically never the case; whatever errors are made in the determination of all the other radicles are repeated and thrown together in the calculation of the alkalies. This practice thus conceals all error of analysis and makes it impossible to ascertain the accuracy of the analysis from the reported figures. If, on the other hand, all the radicles are actually determined the bases can be balanced against the acids and the discrepancy discovered. Even with reasonably careful work the unavoidable errors in determination usually amount to 1 per cent and may be 4 or 5 per cent.

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 roots or portions of compounds that are known as radicles. In fact, present chemical knowledge indicates that a salt dissolved in water largely ceases to exist as an actual compound; according to the ionic theory it becomes partly dissociated into its component radicles, which become electrically charged or ionized, and it participates in chemical reactions only in so far as it is ionized. Even if it were held that the radicles of dissolved salts are actually combined it is a chemical and mathematical impossibility to ascertain by analysis to what extent a given base is combined with a given acid.[1] Despite this condition it is common practice to report hypothetical combinations by several methods of calculation, founded on different theories or devised from different points of view, in accordance with which the radicles are apportioned to one another. 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. It has been shown that the character of a water for industrial purposes, its fitness for domestic use, and its relation to its environment can be defined without recourse to hypothetical combinations.[2]

As there appears to be 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 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.

For the convenience of those who may desire to transform results into parts per million it may be stated that 1 grain per United States gallon is equivalent to 17.1 parts per million, 1 grain per imperial gallon to 14.3 parts per million, 1 part per hundred thousand to 10 parts per million, 1 gram per kilogram to 1,000 parts per million by weight, and 1 gram per liter to 1,000 parts (weight) per million (volume). All the analyses in this report made by the Geological Survey are stated in parts by weight per million volume, and the remaining analyses are believed to be also stated in this way.

[1] Dole, R. B., Hypothetical combinations in water analysis: Jour. Ind. and Eng. Chemistry, vol. 6, pp. 710-721, 1914.

[2] Stabler, Herman, The mineral analysis of water for industrial purposes and its interpretation by the engineer: Eng. News, vol. 60, p. 355, 1908; Some stream waters of the western United States, with chapters on sediment carried by the Rio Grande and the industrial application of water analyses: U. S. Geol. Survey Water-Supply Paper 274, pp. 165-181, 1911. Clarke, F. W., The data of geochemistry, 3d ed.: U. S. Geol. Survey Bull. 616, pp. 59-61, 1916. See also U. S. Geol. Survey Water-Supply Paper 254, pp. 233-258, 1910, and Water-Supply Paper 259, pp. 173-197, 1912.

The factors in the accompanying table may be used for converting statements in hypothetic combinations into ionic form. The product obtained by multiplying the reported content of each salt by the appropriate factor is the content of the positive radicle or base, and the difference between this product and the reported content of the salt is the content of the negative or acid radicle in the compound. The aggregate for each radicle in the various salts is the total quantity of that radicle in the water. Silica, iron oxide, and alumina may generally be considered colloids and so retained in the restated analysis.

Factors for calculating the amount of the base or positive radicle in various salts.

Given—	To find—	Factor.
Calcium sulphate ($CaSO_4$)	Calcium (Ca)	0.294
Calcium chloride ($CaCl_2$)	....do....	.361
Calcium carbonate ($CaCO_3$)	....do....	.400
Calcium bicarbonate ($CaH_2(CO_3)_2$)	....do....	.247
Magnesium sulphate ($MgSO_4$)	Magnesium (Mg)	.202
Magnesium chloride ($MgCl_2$)	....do....	.255
Magnesium carbonate ($MgCO_3$)	....do....	.288
Magnesium bicarbonate ($MgH_2(CO_3)_2$)	....do....	.165
Sodium sulphate (Na_2SO_4)	Sodium (Na)	.324
Sodium chloride (NaCl)	....do....	.394
Sodium carbonate (Na_2CO_3)	....do....	.434
Sodium bicarbonate ($NaHCO_3$)	....do....	.274
Sodium sulphide (Na_2S)	....do....	.590
Sodium acid sulphide (NaHS)	....do....	.411
Potassium sulphate (K_2SO_4)	Potassium (K)	.449
Potassium chloride (KCl)	....do....	.524
Potassium carbonate (K_2CO_3)	....do....	.569
Potassium bicarbonate ($KHCO_3$)	....do....	.391
Hydrogen sulphide (H_2S)	Hydrogen (H)	.059

For illustration the details of converting an analysis into ionic form in parts per million are given. The labor involved is considerably lessened if a slide rule or similar calculating machine is used.

Analysis as reported:

	Grains per U. S. gallon.
Calcium sulphate ($CaSO_4$)	3.79
Calcium carbonate ($CaCO_3$)	7.90
Sodium chloride (NaCl)	40.60
Sodium carbonate (Na_2CO_3)	21.70
	73.99

Recalculation:

3.79 grains $CaSO_4$ × .294	1.11 Ca
3.79 − 1.11	2.68 SO_4
7.90 grains $CaCO_3$ × .400	3.16 Ca
7.90 − 3.16	4.74 CO_3
40.60 grains NaCl × .394	16.00 Na
40.60 − 16.00	24.60 Cl
21.70 grains Na_2CO_3 × .434	9.43 Na
21.70 − 9.43	12.27 CO_3

Recalculation—Continued.

	Grains per U. S. gallon.
Total Ca $=1.11 +3.16$	4. 27
Total Na $=16.00+9.43$	25. 43
Total SO_4	2. 68
Total Cl	24. 60
Total $CO_3=4.74 +12.27$	17. 01
	73. 99

	Grains per U. S. gallon.			Parts per million.
Ca	= 4. 27	$\times$	17. 1=	73. 1
Na	=25. 43	$\times$	17. 1=	435. 2
SO_4=	2. 68	$\times$	17. 1=	45. 9
Cl	=24. 60	$\times$	17. 1=	421. 1
CO_3=	17. 01	$\times$	17. 1=	291. 2
	73. 99			1, 266. 5

Proof: $73.99 \times 17.1 = 1,266.5$.

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 of reacting values, which shows numerically the relative proportions of the radicles by chemical weight, in terms of capacity for reaction. 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 capacity for chemical reaction, though the ratios for the several radicles are different and the relation between the two forms of statement is therefore complex. The reacting value per unit weight of magnesium, for example, is much higher than that of sulphate, 10 parts of magnesium being chemically equivalent to 39.5 parts of sulphate. In order to understand the possibilities of reaction of the radicles in a water they should be considered as individuals acting together under the law of equivalent combining weights, each contributing its proportional share to the balance of the system.

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 is the ratio of the reaction capacity of one part of that radicle to the reaction capacity of eight parts of oxygen; in numerical value it is the valence of the radicle divided by its weight on the

[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.

atomic scale.   The following table shows the reaction coefficients of
the positive and negative radicles most commonly found in waters:

Reaction coefficients of positive and negative radicles most commonly found in waters.

Positive radicles.	Reaction coefficients.	Negative radicles.	Reaction coefficients.
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 reacting values of silica, iron, and alumina 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 of 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.   This principle is utilized by the chemist
in making a partial analysis wherein the alkalies are calculated by
difference.   If the analysis under consideration is of this type the
sum of the reacting values of the bases and acids should therefore be
the same, but if all the constituents have been directly determined
unavoidable errors usually cause the totals of basic and acidic reacting
values to differ slightly and this difference is an index of the accuracy
of the analysis.

The conversion of the following analysis from the ionic form into
reacting values is included in order to make this explanation clearer:

Conversion of analysis from ionic form into reacting values.

	Parts per million.		Reaction coefficients.		Reacting values.	Reacting values in per cent.
Na	435.2	×	0.0434	=	18.88	41.9
Ca	73.1	×	.0499	=	3.64	8.1
	508.3				22.52	50.0
SO_4	45.9	×	.0208	=	.95	2.1
Cl	421.1	×	.0282	=	11.87	26.4
CO_3	291.2	×	.0333	=	9.70	21.5
	758.2				22.52	50.0

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 [1] 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 the one followed in this report. The writer has found this system very valuable, for it emphasizes certain differences between waters that are fundamental from the standpoint of the geologist and the industrial chemist, and is very convenient in the comparison of analyses.

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 soft, but 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 and determinable properties. For example, if 90 parts of sodium chloride and 10 parts of sodium carbonate are dissolved in water, the properties of the composite solution will be a summation of those of the solutions of the separate salts; in other words, the composite solution is characterized by 90 per cent salinity and 10 per cent alkalinity. If to this solution calcium chloride is added, the percentage of these properties is altered, and a third property, hardness, is introduced. In a mixed solution of this kind it is no longer possible to state how much of each salt is present; reactions have taken place and it is impossible to learn by analytical methods the order of the combinations that have resulted. Chemical analysis can determine only the amounts of the different radicles present.

Although for the sake of simplicity the properties or qualities of the solution have in the preceding paragraph been ascribed to various salts, they are in reality due to the radicles themselves, uniformly distributed and held in balance; and inasmuch as the salts can not be determined they need not be considered further. The general reactive properties of the solution may be readily deduced from the amounts of the radicles present, and in order to do this without undue complication those radicles which are similar chemically or associated geologically may conveniently be grouped together. Thus, the common bases may be grouped as alkalies (Na and K) and alka-

[1] Palmer, Chase, Geochemical interpretation of water analyses: U. S. Geol. Survey Bull. 479, 1911.

line earths (Ca and Mg), and the common acids as strong acids (Cl, SO_4, and NO_3) and weak acids (CO_3, HCO_3, and S). The reactive properties of a water are governed by the respective proportions of these groups. Thus, if the value of the alkalies exceeds that of the strong acids, the hardness of the water may be removed simply by boiling, but if the strong acids exceed the alkalies, the water is permanently hard. Similarly, if the value of the strong acids is less than that of the alkalies plus the earths, the water is characterized by alkalinity, but if it is greater the water is acid.

In order to define more exactly the properties of a water, Palmer considers in detail the balances that may exist between the two basic and two acid groups of radicles and assigns to each a name. Salinity is defined as the property induced by the strong acids and alkalinity as that measured by the weak acids. The properties due to the presence of alkalies are called primary, and those due to the presence of the alkaline earths secondary properties. Hence the balance between the alkalies and the strong acids is called primary salinity and that between the alkaline earths and the weak acids secondary alkalinity, which is more commonly known as temporary hardness. If the strong acids exceed the alkalies, the excess must be held in equilibrium by the alkaline earths, and this balance is accordingly called secondary salinity, which is permanent hardness. If, on the other hand, the alkalies exceed the strong acids, the excess is balanced against the weak acids, and this balance is known as primary alkalinity. The two last-named properties are obviously incompatible; nearly all waters are characterized by either one or the other, but a water can not exhibit both. All the oil-field waters are characterized by primary salinity and secondary alkalinity and by either primary alkalinity or secondary salinity. The three properties furnish a rational basis for classification and preliminary study, and are evidently far more convenient for general comparison than the detailed analyses.

The manner in which these properties are deduced from the analysis is shown graphically in figure 2, which represents analysis 31 (Table 5, p. 66). It is assumed that the analysis has already been converted into the ionic form and that the reacting values of the radicles have been determined and reduced to a percentage basis as previously described. In this form the values of the basic radicles constitute 50 per cent of the total and those of the acid radicles 50 per cent. In the figure the bases and acids have been plotted to scale in two columns of equal length, the alkalies and strong acids being placed at the bottom and the earths and weak acids above. In the central column are shown the properties of reaction that result from the proportions of these groups shown. As primary salinity is due to the balance between equal values of the alkalies and strong acids

its amount is determined by the smaller of its two components.   In
other words, the 22.3 per cent of strong acids present, in connection
with an equal amount of alkalies, forms 44.6 per cent of primary
salinity.   This leaves an excess (19.5 per cent) of the alkalies which
balances with an equal value of the weak acids and induces the prop-
erty primary alkalinity to the extent of 39 per cent.   Of the 27.7
per cent of weak acids 8.2 per cent are then left
in balance with the total (8.2 per cent) alkaline
earths, which gives rise to 16.4 per cent of sec-
ondary alkalinity.   This water is therefore char-
acterized by 44.6 per cent primary salinity, 39
per cent primary alkalinity, and 16.4 per cent
secondary alkalinity.   On the basis of these prop-
erties, or relations of reacting values, it may be
rationally classified or compared with any other
water.

In the analysis selected the alkalies exceed the
strong acids and therefore induce primary alka-
linity.   If the reverse were true, and the strong
acids exceeded the alkalies, it is evident that a
different property would result.   In such a water
some of the strong acids would be balanced by
the alkaline earths and secondary salinity would
result instead of primary alkalinity; in other
words, the water would be permanently hard.
The writer has found this distinction one of the
most valuable features of Palmer's classification,
for by it all waters are separated into two impor-
tant groups.   The distinction is valuable indus-
trially, for it separates permanently hard waters
from those whose hardness is mostly lost on boil-
ing.   The distinction is of equal importance geo-
logically.   Thus, the surface waters on the west
side of San Joaquin Valley are characterized by
high sulphate and low carbonate and by roughly
equal amounts of the alkalies and alkaline earths;
some of the strong acids are balanced by alkaline
earths and the waters have, therefore, the prop-

FIGURE 2.—Graphic repre-
sentation of analysis 31
(Table 5, p. 66), showing
method of deducing the
properties of a water from
its composition.

erty of secondary salinity.   On the other hand, in most of the waters
associated with the oil the alkalies are very high and sulphate is
lacking; in these waters some of the alkali group are in equilibrium
with weak acids and the waters therefore have the property of pri-
mary alkalinity.   By a study of the properties of the waters all the
stages in the transition from the extreme secondary saline type to the
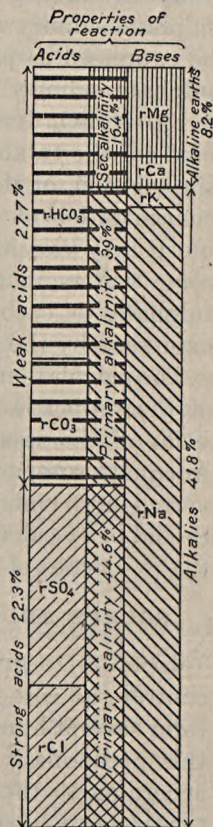extreme primary alkaline type may be definitely traced, and distinc-

tions become apparent that do not suggest themselves in a study of the original analysis.

In addition to the three properties of reaction two other factors may be taken into account as criteria for comparison. One of these factors is the ratio of the chloride to the sulphate radicles, for in Palmer's system these radicles are classed together as strong acids. Since the strong acids give rise to salinity, chloride salinity and sulphate salinity may be distinguished, and these may conveniently be expressed as percentages of the total salinity. For example, the sulphate salinity ratio in analysis 31 (shown graphically in fig. 2, p. 39) is rSO_4 divided by $rSO_4 + rCl$, or 13 divided by $22.3 = 58.3$ per cent (of the total salinity). The other factor 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. In 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.

The calculations involved in the stages leading up to the deduction of the properties of reaction may seem long and tedious, but the value of the results should more than pay for the necessary labor. Adequate comparison is impossible until the analyses have been converted into ionic form; and when this step has been accomplished the labor of calculating the reacting values and deducing from them the properties of reaction is inconsiderable.

SOURCE AND STATEMENT OF ANALYSES IN THIS REPORT.

In order to give an adequate idea of the principles that seem to control the composition of the oil-field waters, 88 analyses selected from several hundred available for the writer's study are included in this preliminary report. These analyses have been selected, first, according to their representation of the chemical variation encountered; second, according to their position with regard to the oil; third, according to the probable accuracy of the analytical work; and, fourth, according to their geographic distribution.

Of the 88 analyses given 30 were made by the Geological Survey, 17 by the Standard Oil Co., 12 by the Kern Trading & Oil Co., and 29 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 pretty close limits. The remaining analyses are believed to be reliable, but they were made only for

industrial purposes and doubtless 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.

In the tables of analyses the properties of reaction are stated first, as they are believed to be the most suggestive as well as the most convenient basis for general comparison. The sulphate salinity ratio, or the percentage of rSO_4 in $rSO_4 + rCl$, is included under the properties of reaction, and in certain types of water the ratio of the values of carbonate and bicarbonate to the sulphate value is also given. Below the reaction properties is given the analysis itself, stated in radicles in parts per million; this is a summary of the basic data on which any form of interpretation must rest. The analysis is also stated in reacting values in percentages, a form that admits direct comparison of the chemical values of the radicles but does not express the actual amounts present or the concentration of the solution. Finally, those analyses which were not made by the Geological Survey and which were originally stated in hypothetical combinations in grains per United States gallon are given in the tables in their original form also. To some readers this form of statement may be the most familiar, but for rational scientific study one of the other forms is strongly recommended.

CLASSIFICATION OF THE OIL-FIELD WATERS.

DISTRIBUTION AND SIGNIFICANCE OF THE CONSTITUENTS.

Alkalies (sodium and potassium).—In most of the analyses in this report the alkalies, sodium and potassium, have not been separated, and as their chemical properties and distribution are similar they will be considered together. The alkalies are by far the most abundant bases in the oil-field waters, and in many of the deeper waters they and their equivalent acid radicles constitute over 95 per cent of the total mineral content. In surface waters the alkalies are less prominent, but in waters from depths of more than 250 or 300 feet they usually predominate over the other bases. The waters associated with the oil in the western parts of the Coalinga, Midway, and Sunset fields contain the alkalies almost to the exclusion of the other bases.

The great predominance of alkalies over the other bases is a notable feature of the composition of the waters of the oil fields of the west side of San Joaquin Valley, for in most regions of sedimentary rocks the waters are characterized by a moderate to low proportion of alkalies. The salts of the alkalies are highly soluble and therefore are never deposited from saturated solution, except in arid regions, where they tend to accumulate at the surface as deposits of "alkali,"

which is usually the sulphate. As the oil fields on the west side of the valley are located in a very arid region the relative prominence of the alkalies in the shallower waters is to be expected. Furthermore, in connate water (fossil sea water) the alkalies greatly predominate over the other bases, and as the deeper oil-field waters are partly or wholly of connate origin, two sets of conditions have combined to cause the high concentration of alkalies in the waters of the fields of the west side. In the Kern River field, on the east side of the valley, water is more plentiful, and the first condition is therefore less pronounced, but as the deeper waters are partly of connate origin their content of alkalies is fairly high.

In sixteen of the analyses given below sodium and potassium have been determined separately. The potassium is generally present in very small proportion, the average ratio of sodium to potassium by weight being about 125 to 1. The average surface water in most regions contains by weight about one-fourth as much potassium as sodium, and ocean water only about one-thirtieth as much.[1] This discrepancy is due to the fact that when mixed solutions containing sodium and potassium are passed through soil or clay the potassium is almost wholly extracted and held, whereas the sodium is comparatively unaffected;[2] hence the potassium in ordinary surface waters is largely lost during their passage to the sea. Similarly, if sea water is then entrapped in the sediments, the separation will continue still further and nearly all the potassium will be removed. This principle has thus operated to remove nearly all of the potassium in the connate and partly connate water of the oil fields. (See p. 93.)

Alkaline earths (calcium and magnesium).—In a few of the surface waters and shallow ground waters in the oil fields of the west side of the valley the alkaline earths exceed the alkalies, but in practically all the deeper waters their relative proportion is very low. This is due not only to the high concentration of the alkalies, as already explained, but also to the fact that the alkaline earths themselves are generally present in small actual amount. Large amounts of the earths can not be retained in waters in which more than a certain value of carbonate or bicarbonate is present, and if this value 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 important constituents, but in the waters near the oil zone in the western parts of the Coalinga, Midway, and Sunset fields carbonate is high and the earths are accordingly low. In the connate waters in the central part of the Midway and Sunset fields chloride is very high and carbonate low,

[1] Clarke, F. W., The data of geochemistry, 3d ed.: U. S. Geol. Survey Bull. 616, p. 138, 1916.
[2] Van Bemmelen, J. M., Das Absorptionsvermögen der Ackererde: Landw. Versuchs-Stationen (Berlin), vol. 21, pp. 135–191, 1878.

and in this type of water the earths constitute as much as 10 per cent of the total mineral content.

In sea water the ratio of magnesium to calcium by weight is about 3, or if expressed in terms of reacting values, about 5. It is therefore interesting to note that in that type of oil-field water which the writer considers connate, and which closely resembles sea water in all other respects, the average ratio of the reacting values of magnesium to calcium is only 0.71. In some of the surface waters and shallower ground waters, especially those in the Coalinga field, the ratio is almost as high as in sea water, but this is accounted for by the fact that these waters are a part of the drainage of areas in which ferromagnesian (Jurassic) rocks outcrop. The deficiency of magnesium in the deeper waters can not be so easily explained. At high temperatures magnesium is deposited from solution as basic carbonate or hydrate,[1] and it is possible that the temperatures of 100° to 125° F., which prevail in the oil fields at depths of 1,000 to 3,000 feet, have had some effect in lowering the concentration of magnesium. It is also possible that the magnesium is removed as magnesium silicate, though no evidence was obtained in the field to support this view.

In the table on page 92 are given the average ratios of magnesium to calcium in the several types of water in the Coalinga, Midway, and Sunset fields, only the analyses included in this report being represented. The variations in these ratios are discussed in more detail below, but it may be pointed out here that the average ratio in the Coalinga field is considerably higher than in the Midway and Sunset fields, and that the ratio in the brine is only about half as great as in the other types of water.

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 Coalinga field sulphate and its equivalent basic radicles constitute over 85 per cent of the total mineral content. Outside of the oil fields most of the deeper ground waters are also characterized by a high concentration of sulphate, but this figure bears no constant relation to depth. Within the oil fields, 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 1 per cent, although in the Eastside Coalinga field sulphate is usually higher and some of the waters may contain as much as 5 per cent. The tables of analyses below show the ratio of sulphate to sulphate plus chloride by reacting value in all the waters discussed, and in many of these waters the ratio of sulphate to carbonate as well.

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

The decrease of sulphate in the waters as the oil measures are approached, 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 93–99.

A great predominance of sulphate in the shallower waters is characteristic of most arid regions. Gypsum (calcium sulphate) is disseminated through the rocks and furnishes an abundant supply to the scanty volume of water percolating through them. In addition, much of the "alkali" that occurs as an incrustation or efflorescence in arid regions is sodium and magnesium sulphate. Ocean water contains about 2,700 parts per million of sulphate, or 7.7 per cent of the total mineral content.

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.

As already explained, the chloride in the oil-field waters is undoubtedly 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. Where the geologic structure is such as to prevent circulation the water is very salty, and in some localities the concentration of chloride in it is as great as in ocean water. Near the surface and 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 rever-

sion 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 formed, most of the normal carbonate is thrown out as a precipitate or "scale." The solubility of the alkaline earth radicle in the presence of the carbonate radicle therefore depends largely on the concentration or "partial pressure" of carbon dioxide in the solution. 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 the San Joaquin Valley, and in the normal ground water are generally present in minor amount. In the waters associated with the oil, however, they are generally present in larger amounts, and when chloride is absent carbonate and bicarbonate constitute the only acid radicles. As chloride increases, however, these weak acid radicles decrease, and in the strong brines they are present only in very small amounts.

Carbonate and bicarbonate have been differentiated in 30 of the analyses in this report. In 19 of these waters there is no carbonate, and in the remaining 11 the average carbonate value is only one-fifth of the bicarbonate value. Three of these 11 waters may be disregarded, for the carbonate reported probably formed during the time the samples had stood before being analyzed. It is perhaps noteworthy that of the remaining 8, in which carbonate and bicarbonate exist together, 3 are surface waters and shallow ground water, and 5 are deep waters, either from or below the oil measures. Apparently in the zone directly above the oil, in which the carbonate waters are believed to have formed there is a sufficient excess of carbon dioxide to prevent the formation of normal carbonate.

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.

Many waters from the Eastside Coalinga field carry considerable amounts of sulphide, which is reported in the industrial analyses as "sodium sulphide." In these analyses, however, the alkalies are calculated by difference, and as the amount of alkalies present is not definitely known, the assumption that a sufficient amount is present to balance all of the sulphide is unwarranted. Although some of it may be balanced by alkalies, it is probable that much of it is actually present as the acid sulphide, which implies only half as much alkali as the normal sulphide, and that at least some of it is merely hydrogen sulphide.

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 an important product. 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 water percolates into the brown shale below the oil measures, as along the western edge of the Midway field, and there 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. Some of the most pronounced sulphur waters in the oil fields are obtained from wells located near the outcrop of the oil sands, which draw their water from the strata below the oil.

Iron and aluminum.—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.

In a great many natural waters much the larger part of the "iron oxide and alumina" reported is iron oxide, and the amount of alumina is very small. In a few of the analyses given in this report the two have been separately determined, and in these oil-field waters the reverse seems to be more generally true. The iron is usually very low, although it varies widely. It seems probable that the low content of iron is due to the fact that in the presence of hydrogen sulphide it has reverted from the colloidal state and formed iron sulphide, which being only slightly soluble has been mostly precipitated. On the other hand, the unusually large amounts of iron sometimes found are probably derived through the corrosion of the iron casing of wells, and some of this iron may be present not as colloid but in true solution.

Silica.—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 primary alkaline waters 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 primary alkaline waters than in brine.

Other constituents.—Several mineral constituents in addition to those already mentioned are probably present in the oil-field waters. Nitrate has been sought in 27 of the samples here discussed and has been found in only 5, of which 4 are surface waters. A small quantity of boron was found in the one sample tested for it. Bromine and iodine have been detected in some of the oil-field brines, and the iodine was determined quantitatively in one sample. (See analysis 58, Table 9, p. 74.)* Iodine in unusually large amounts in several samples of brine from the Midway and Sunset fields was also reported many years ago by Watts.[1]

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 oil-field waters. In the surface water and shallow ground water of the Kern River field the content of dissolved mineral matter is lowest and is generally less than 200 parts per million. All the shallower waters examined in the fields of the west side of the valley contain more than 300 parts, and most of them contain between 1,000 and 4,000 parts. The concentration in general increases with depth; most of the deeper waters of the Kern River field contain between 1,500 and 4,000 parts, and those of the fields on the west side of the valley between 8,000 and 40,000 parts. Although the concentration of the various types of water is fairly regular, individual samples may show considerable variation.

In the tables of analyses given below the concentration is represented simply by the totals of the constituents reported except when 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.

Organic and volatile matter.—The figure given in most industrial analyses under the heading "organic and volatile" represents the loss in weight when the solid matter obtained on evaporation is heated to redness. It consists chiefly of carbon dioxide and whatever organic or hydrocarbon matter was present in the water. Many of the primary alkaline waters that have been closely associated with the oil contain dissolved organic matter in the form of petroleum acids, which would be included in this determination. However, most

[1] Watts, W. L., The gas and petroleum yielding formations of the Central Valley of California: California State Min. Bur. Bull. 3, pp. 90–91, 1874.

samples of oil-field water as submitted for analysis contain a small amount of oil floating on the surface, and as this oil is also included in the determination it is evident that the figure has no exact value. It has therefore been omitted from the tables of analyses published in this report.

CRITERIA FOR COMPARISON.

Natural waters differ widely in the chemical character of the substances dissolved in them, and several different types of water may be found in nearly every region. However, the different varieties tend to mingle and react through constant circulation, until the pure types may be less common than the gradations between them. Moreover, if the rocks differ irregularly in composition, the waters, whose character reflects that of the rocks with which they come in contact, must be similarly different. In many areas, therefore, the natural waters present such infinite variation in chemical composition that even though it is recognized that a certain type is normally characteristic of a certain locality or formation it is impossible to draw a definite line of demarcation.

In the oil fields of San Joaquin Valley, however, special conditions have led to the formation of very distinct types of water. As the transitions from one type to another occur within relatively short distances fairly definite zones or localities that are characterized by the same type of water can be established. The development of these distinct types has been due partly to the influence of the oil and gas, and the oil-field waters therefore present contrasts that are lacking in the waters of most areas.

The three groups of salts most commonly dissolved in natural waters are chlorides, sulphates, and carbonates, and in the oil fields there are waters which contain any one of the three almost to the exclusion of the others. The concentration of chloride has already been shown to be governed by physical conditions, such as freedom of circulation; and since these conditions are more or less local and irregular the content of chloride furnishes the least satisfactory basis for the comparison of waters. The relative proportion of sulphate and carbonate, on the other hand, is influenced by fairly definite chemical reactions that take place only near accumulations of oil and gas; hence the carbonate-sulphate ratio may serve as an indication of the position of the water with respect to hydrocarbons. Study of the carbonate-sulphate ratio in waters in a developed field, in which the relations of oil, gas, and water have been discovered, forms an excellent criterion for differentiation and a tangible basis for a system of classification; in an undeveloped field, on the other hand, it may be used as an indication of the presence or absence of hydrocarbons near by.

It is often difficult, owing to the wide variations in the chemical character of natural waters, to distinguish without careful study the significant differences from the 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. The carbonate-sulphate ratio is a significant criterion, for it is apparently governed chiefly by the position of the water with regard to the oil; but the ratio of sodium to potassium, for example, is controlled by factors that are indeterminable or not well understood. These ratios are interesting and are valuable for some purposes, but they involve too much speculation to be of basic importance in a study of oil-field waters. Unfortunately, several investigators who have already undertaken the study of the California oil-field waters have deemed it unnecessary to make complete analyses, and have based their estimates of the position of a water upon such isolated criteria as the concentration of chloride, the ratio of magnesium to calcium, or the presence or absence of such rare constituents as lithium or iodide. Some of the conclusions based on these incomplete studies have proved erroneous, and the writer encountered considerable skepticism among the oil operators as to the practical value of chemical studies of the oil-field waters. The more complete information now available furnishes a better basis for conclusions, both as to the influence of hydrocarbon material on the composition of a water and also as to the genetic relations of the waters themselves.

PROPOSED CLASSIFICATION.

Since 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. For practical convenience it is evident that oil-field waters should be classified as far as possible according to their position in relation to the oil. As waters near the oil measures differ in composition from those nearer the surface, a classification based directly on the chemical character of the waters and indirectly on their position in relation to the oil may be made.

The sulphate-carbonate ratio furnishes a convenient basis for classifying waters that contain only minor amounts of chloride, but in most localities chloride must be taken into account. Thus, in the Midway field chloride may be far more prominent than sulphate in the shallow waters, and in the deeper waters may be present almost to the exclusion of carbonate. Under these circumstances the replacement of sulphate by carbonate is less striking.

The relation of the various types becomes clearer when their origin is considered. The sulphate water, being the normal ground water

of the region, is typically of meteoric origin; that is, it is rain water that has entered the ground and dissolved some of the more soluble constituents of the rocks. The salt water, however, is typically of connate origin and represents sea water that has been entrapped and retained in the sediments, dissolving some of their constituents and losing some of its own, but in the main retaining its original composition. The connate water is relatively stationary or stagnant, but the meteoric water is to some extent continually descending from the surface and mixing with the connate water. Both types are similarly affected by constituents of the oil or gas, sulphate being removed and carbonate introduced, but whereas the composition of the meteoric water is entirely reversed by this process, the pure connate water, which contains at the start only a small proportion of sulphate, is much less conspicuously altered. Most waters are mixtures of connate and meteoric types, and the extent of their alteration therefore depends on the proportions of the mixture. Two sets of forces are at work; the one leads to the mixing of two opposing types of water in various proportions, and the other induces in both types chemical changes which are similar in kind but different in degree.

This distinction between meteoric and connate waters is valuable in forming a conception of the genetic relations of the oil-field waters, but it may be well to reiterate that it can not be strictly applied in the field. (See p. 22.) Connate marine water is readily identified by its high content of chloride, but the connate fresh water which the rocks may contain can not be distinguished from meteoric water. Although the terms strictly represent origin, in actual practice they are necessarily reduced to a chemical basis and are so used in this report. As the reactions of a water with hydrocarbon material depend on its chemical character rather than on its origin, the precise genetic classification is chiefly of theoretic value.

An attempt has been made to present graphically the chemical relations of the oil-field waters in figure 3. In this diagram the meteoric water is shown as entering the rocks and percolating down toward the oil, undergoing a modification and finally a reversal of its chemical character; the connate water is shown as already existing in the rocks but undergoing a similar alteration as the oil is approached; and the two classes are shown as converging and mixing in various proportions. The three broad divisions of both types and their mixtures, according to their relation to the oil, may be called normal, modified, and altered. Normal ground water is that which contains a normal percentage of sulphate; this percentage is generally high, for this type is either pure meteoric water or a mixture in which meteoric water predominates. Strictly normal or unaltered connate water has not been encountered. The modified group, characterized by a percentage of sulphate lower than normal, may be either meteoric

or connate but is generally a mixture in which meteoric water predominates. The waters of the altered group contain practically no sulphate; they may be either meteoric or connate, or a mixture of the two. Many analyses of altered waters are available, and since the two extremes, meteoric and connate, are well represented, three types of altered water may be distinguished. Altered water of meteoric origin may be called the reversed type; altered connate water may
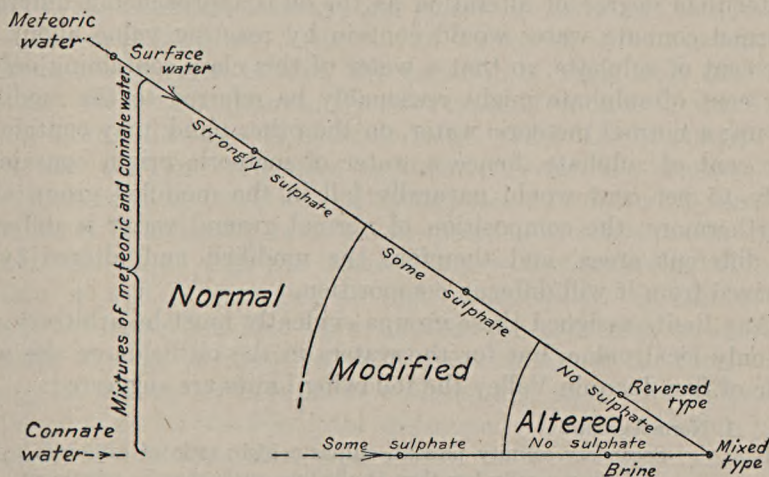
FIGURE 3.—Diagram illustrating relation of oil-field waters of the meteoric and connate types, and their alteration as the oil zone is approached.

be called simply brine, and altered mixtures of the two may be called the mixed type. This classification may be summarized as follows:

Group 1.—Normal, strongly sulphate water (typically of meteoric origin).
Group 2.—Modified, less strongly sulphate water (may be either meteoric or connate but is commonly a mixture in which meteoric water predominates).
Group 3.—Altered, practically sulphate-free water (meteoric and connate waters and mixtures of the two).
        Reversed (carbonate water, originally meteoric).
        Brine (chloride water, originally connate).
        Mixed (chloride-carbonate water).

This is primarily a classification of the ground waters, but for convenience surface waters may be included in the normal group. The normal group includes most shallow ground water, but the depth to which normal waters descend depends principally on the depth of the oil zone. Modified waters occupy the zone below the normal zone and include the sulphur waters often found some distance above the oil. The thickness of the modified zone is generally several hundred feet, but it is variable and no definite limits can be assigned. In the Westside Coalinga field the oil measures occur at the base of the modified zone, and the normal and modified groups are therefore

coincident with the "top water," but in the Midway-Sunset fields several hundred feet of strata containing altered water intervene between the base of the modified zone and the top of the oil measures. All the "bottom water" or "edge water" examined is of the altered type, and in general this type extends for several thousand feet below the oil measures.

As most of these waters are mixtures of meteoric and connate water their degree of alteration as the oil is approached is different. Normal connate water would contain by reacting value about 9.2 per cent of sulphate, so that a water of this class containing only 3 per cent of sulphate might reasonably be referred to the modified group; a normal meteoric water, on the other hand, may contain 45 per cent of sulphate, hence a water of meteoric origin containing only 15 per cent would naturally fall in the modified group also. Furthermore, the composition of normal ground water is different in different areas, and therefore the modified and altered types derived from it will differ in composition.

Any limits assigned these groups evidently must be arbitrary and of only local value, but for the waters in the oil fields on the west side of San Joaquin Valley the following limits are suggested:

1. Normal group:
   Secondary salinity present, sulphate high; ratio of carbonate to sulphate generally less than 1; alkaline earths may be prominent.
2. Modified group:
   Chiefly of meteoric origin. Primary alkalinity present; sulphate salinity greater than 15 per cent of the total salinity; ratio of carbonate to sulphate generally between 1 and 15; alkaline earths generally subordinate to alkalies.
   Chiefly of connate origin. Secondary salinity present; sulphate salinity greater than 1 per cent of the total salinity; alkaline earths generally less than 10 per cent of total reacting value.
3. Altered group:
   Reversed type. Primary alkalinity greater than 50 per cent; sulphate salinity less than 15 per cent of the total salinity; ratio of carbonate to sulphate generally greater than 15; alkaline earths generally less than 8 per cent of total reacting value.
   Brine. Secondary salinity present; sulphate salinity less than 0.5 per cent of total salinity; alkaline earths generally between 2 and 10 per cent.
   Mixed type. Primary alkalinity less than 50 per cent; sulphate salinity less than 1 per cent of total salinity; alkaline earths generally about 1 or 2 per cent.

These limits have been observed as far as possible in grouping the analyses. The groups are not mutually exclusive, however, and when a water falls in two groups its classification has been decided by comparison with the waters above and below it.

COMPOSITION OF THE OIL-FIELD WATERS.

DESCRIPTION OF THE TYPES.

GENERAL COMPARISON.

The analyses of the oil-field waters are discussed and the general characteristics of each type are pointed out in the following sections. Seventy-three of the analyses given represent the types of water found in the Coalinga, Midway, and Sunset oil fields, and these have been classified in Tables 1 to 11. In Tables 12 and 13 groups of analyses are arranged to show the variation in water from different depths. Table 14 contains analyses of types of water from the Kern River, Lost Hills, and McKittrick fields, which are introduced to show that the same principles apparently govern the character of the waters in those localities. Although the classification is directly chemical it is indirectly based on the position of the water in relation to the oil, so that the tables group waters according to their horizon as well as according to their composition. A number of waters have been included that differ in one particular or another from the average for the type, or, if they conform to the type, they occupy an apparently anomalous position, and these exceptions are explained as far as possible in the discussion. Undue stress has perhaps been laid on these rarer occurrences, but it has seemed desirable to point out at this time such variations from the normal as are most likely to be encountered.

In order to sum up the more important variations in the chemical character of the waters and to show graphically their genetic relations, all the analyses given in this paper have been plotted in figure 4. In this diagram the two incompatible properties of waters—secondary salinity or permanent hardness and primary alkalinity—expressed in per cent, represent the horizontal axis to the left and right respectively of a common line. All the secondary saline waters therefore fall in the left section of the chart and all of the primary alkaline in the right. On the vertical axis has been plotted the sulphate salinity ratio (per cent of rSO_4 in $rSO_4 + rCl$), and accordingly all of the sulphate-free waters associated with the oil appear along the base line of the chart. The approximate concentration (total mineral solids) in parts per million of each water is shown by symbols.

It is believed that the properties selected to represent the axes of this diagram furnish the most satisfactory criteria for a broad comparison of oil-field waters. It will be noted that most of the surface waters, high in sulphate and in alkaline earths, fall in the upper left-hand corner of the chart. The normal ground waters of meteoric
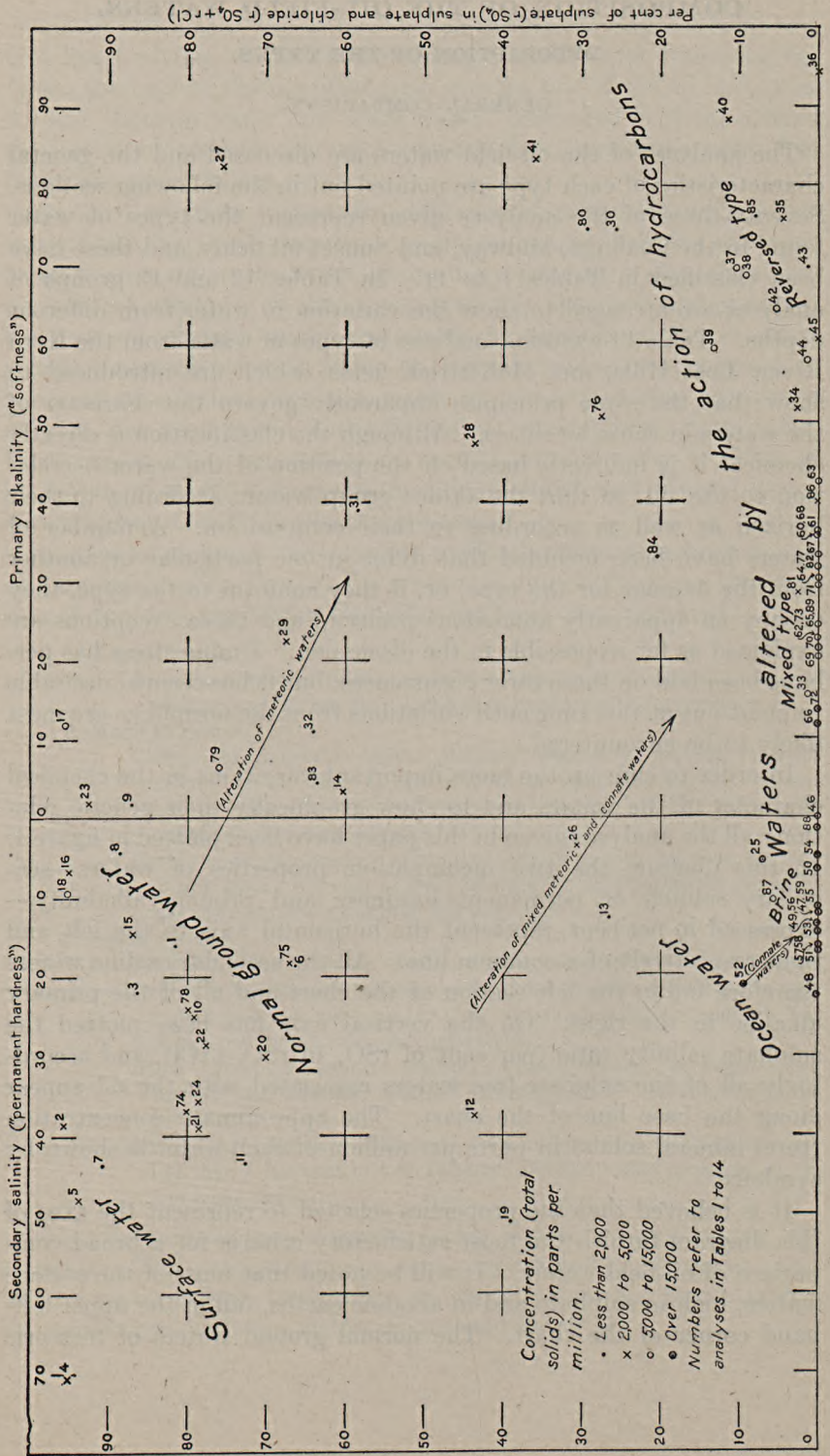
FIGURE 4.—Chart showing chemical relations of the oil-field waters.

origin show a somewhat lower percentage of secondary salinity but a fairly high proportion of sulphate, and therefore fall to the right of and somewhat below the surface waters. The waters closer to the oil measures, being lower in sulphate and higher in carbonate, fall still farther in the same direction, which is indicated by an arrow. In the lower right-hand corner of the chart are the altered waters of meteoric origin, forming the reversed type. In the course of their progressive alteration from the surface downward these meteoric waters therefore fall along a line extending diagonally across the whole chart. Their concentration is never high, although the deeper waters naturally contain more dissolved mineral matter than those near the surface.

The alteration of the connate waters proceeds in the same direction but along another course. For purposes of comparison an analysis of ocean water (analysis 52) has been plotted, and it will be noted that all of the oil-field brines fall below it and somewhat to the right, indicating a loss of sulphate and a decrease in secondary salinity. Analyses 25 and 87 may be regarded as intermediate and as representing modified connate waters. The concentration of all these brines is fairly uniform, being close to that of sea water. As suggested by the length of the arrows, the amount of alteration undergone by the connate waters in their transition to the brine type is very small as compared with the almost complete reversal of composition undergone by the meteoric waters.

Between the chiefly meteoric waters and the chiefly connate fall the various mixtures. Only four analyses of normal and modified waters of distinctly mixed origin are available, but in the group of altered waters variously proportioned mixtures are common. Nearly every gradation from typical brine to the practically pure carbonate water represented by analysis 36 is shown. The concentration shows a similar gradation from more than 15,000 parts per million in the brines to less than 5,000 parts in waters of the reversed type.

SURFACE WATER.

Representative analyses of surface water from the Coalinga, Midway, and Sunset fields are shown in Table 1. Although these waters differ widely in some respects, all of them except No. 6 have certain fundamental properties in common. It will be noted that in all of them, except No. 6, the sulphate salinity ratio is over 80 per cent and that all of them are characterized by secondary salinity. In all of them the primary salinity is 50 per cent or less, the secondary salinity between 15 and 70 per cent, and the secondary alkalinity between 11 and 62 per cent. In other words the alkaline earths exceed the alkalies and sulphate is generally the predominating acid

radicle.   The concentration ranges between 314 parts per million and 8,790 parts.

The water of Los Gatos and Diaz creeks in the Coalinga field (analyses 1 and 2) is the drainage of a district in which igneous and metamorphic as well as sedimentary rocks outcrop.   These waters differ from the other surface types in their higher content of alkalies and in the marked predominance of the magnesium value over that of calcium.   Crocker Spring (analysis 4) in the Midway field is interesting as the most extreme secondary saline type encountered, the predominating dissolved salt being gypsum.   (See fig. 4.)   Bitterwater Creek (No. 5) is characterized by high sulphate and by an extremely large amount of dissolved solids, greater than that carried by many of the deeper waters.   The Kern County Land Co. Spring (analysis 6), on the other hand, is characterized by a lower proportion of dissolved solids than any of the other waters of the west side, which may be due to the fact that it issues near a fault between granite and sedimentary rocks.   Chiefly because of its low concentration it is characterized by a much higher proportion of secondary alkalinity than any of the others.

Analysis 83 (Table 14, p. 85) shows the average composition of Kern River on the east side of San Joaquin Valley.   As this water is the drainage of a region underlain by granites and other resistant rocks it is characterized by primary alkalinity rather than secondary salinity, and contains a relatively low proportion of sulphate.   It is a very dilute solution dominantly secondary alkaline in character.

TABLE 1.—*Analyses of surface water from the Coalinga, Midway, and Sunset oil fields, Cal.*

	1	2	3	4	5	6	7
PROPERTIES OF REACTION IN PER CENT.							
Primary salinity	40.8	50.0	44.4	14.4	45.4	19.6	28.4
Secondary salinity	16.0	38.4	22	70.4	48	18.8	43.6
Primary alkalinity	0	0	0	0	0	0	0
Secondary alkalinity	43.2	11.6	33.6	15.2	6.6	61.6	28.0
Per cent of rSO_4 in $rSO_4 + rCl$	81.4	95.7	86.1	94.9	93.4	66.1	90.5
CONSTITUENTS IN PARTS PER MILLION.							
Sodium (Na)	a 185	a 668	216	117	1,409	23	a 112
Potassium (K)							
Calcium (Ca)	40	248	92	444	630	56	138
Magnesium (Mg)	117	203	87	107	511	16	66
Iron oxide (Fe_2O_3) and alumina (Al_2O_3)	4.5						1.9
Sulphate (SO_4)	436	2,361	580	1,393	5,638	47	538
Nitrate (NO_3)			Trace.	5	Trace.	30	
Chloride (Cl)	75	78	70	53	300	18	42
Carbonate (CO_3)	b 255	b 203	0	0	30	7.2	b 144
Bicarbonate (HCO_3)			433	335	475	178	
Silica (SiO_2)	4.4	13	87	50	38	29	12
	1,116.9	3,774	1,345	2,334	8,790	314.2	1,053.9
REACTING VALUES IN PER CENT.							
Alkalies:							
Sodium (rNa)	a 20.4	a 25.0	22.2	7.2	22.7	9.8	a 14.2
Potassium (rK)							
Alkaline earths:							
Calcium (rCa)	5.1	10.6	10.9	30.7	11.7	27.4	20.1
Magnesium (rMg)	24.5	14.4	16.9	12.1	15.6	12.8	15.7
Strong acids:							
Sulphate (rSO_4)	23.1	42.3	28.6	40.2	43.6	9.6	32.6
Nitrate (rNO_3)				.1		4.7	
Chloride (rCl)	5.3	1.9	4.6	2.1	3.1	4.9	3.4
Weak acids:							
Carbonate (rCO_3)	b 21.6	b 5.8	.0	.0	.4	2.3	b 14.0
Bicarbonate (rHCO_3)			16.8	7.6	2.9	28.5	
ANALYSIS AS REPORTED. c							
Sodium sulphate	24.53	111.30					15.30
Sodium chloride	7.21	7.51					4.06
Calcium sulphate		27.28					8.36
Calcium carbonate	5.85	16.10					14.04
Magnesium sulphate	11.17	54.49					19.04
Magnesium carbonate	15.99	3.06					
Iron oxide and alumina	.26						.11
Silica	.26	.76					.69
	65.27	220.50					61.60

a Reported and calculated as sodium but includes potassium.
b Reported and calculated as carbonate but probably in part bicarbonate.
c In hypothetic combinations, in grains per U. S. gallon.

Coalinga field:
1. Los Gatos Creek, T. 20 S., R. 14 E. Analyst, Kern Trading & Oil Co.
2. Diaz Creek, T. 19 S., R. 14 E., sampled above junction with Los Gatos Creek. Analyst, Kern Trading & Oil Co.
Midway field:
3. Frazers Spring, sec. 2, T. 30 S., R. 21 E. Spring is in Santa Margarita (?) formation, but source of water may be affected by near-by fault. Sampled by G. S. Rogers, September, 1915. Analyst, S. C. Dinsmore.
4. Crocker Spring, sec. 18, T. 31 S., R. 22 E. Spring is in shale of Monterey group. Sampled by G. S. Rogers, September, 1915. Analyst, S. C. Dinsmore.
Sunset field:
5. Bitterwater Creek, sec. 29, T. 11 N., R. 24 W. Sampled by G. S. Rogers, September, 1915. Analyst, S. C. Dinsmore.
6. Kern County Land Co. Spring in west corner of San Emigdio land grant. Sampled from pipe line of Western Minerals Co. by G. S. Rogers, September, 1915. Analyst, S. C. Dinsmore.
7. San Emigdio Creek, San Emigdio land grant. Analyst, Standard Oil Co., June, 1910.

NORMAL GROUND WATER.

Shallow water wells.—Analyses of normal ground water from shallow water wells in the Coalinga, Midway, and Sunset fields are given in Table 2. These waters, like the surface waters, show a rather wide range in composition. All of them except Nos. 9 and 14 are secondary saline waters, but the secondary salinity is generally lower than in the surface waters and the primary salinity higher. Chloride and the alkalies are somewhat higher, especially in the waters from the Midway field.

Analyses 8 and 9 represent shallow well waters from the Eastside Coalinga field. They are very similar in composition, though on opposite sides of the dividing line, No. 8 being slightly secondary saline and No. 9 showing 1.8 per cent of primary alkalinity. Analysis 10 shows the general composition of the water in many of the shallow wells in the northern part of the Westside Coalinga field. Nos. 11 and 12 are very similar to surface waters, although in No. 12 chloride is high. Analyses 13 and 14 represent waters from the Midway-Sunset field, both of which are characterized by high chloride. No. 14 represents a mixed water derived from two sands, 450 feet apart, the deeper of which has probably contributed the small percentage of primary alkalinity present.

Analyses 84 and 87 (Table 14, p. 85) represent shallow ground waters of very different types from the Kern River and Lost Hills fields. No. 84 is similar to the water of Kern River, already discussed, differing from it only as the shallow ground waters of the west side of the valley differ from the surface waters of that region. No. 87 is water from a well 180 feet deep, located somewhat west of the axis of the Lost Hills anticline. Its properties are very close to those of sea water (see fig. 4, p. 54), the chief differences being a slight reduction in sulphate and a very small increase in carbonate. The concentration is exceptionally high for a shallow water, being over a third of that of sea water. This water is distinctly a connate type, and the slight alteration that it has undergone is remarkable in view of its proximity to the surface.

Oil wells (top water).—Tables 3 and 4 contain twelve analyses of normal ground water or top water from oil wells in the Coalinga and Midway-Sunset fields. There is, of course, no essential difference between these waters and those from shallow water wells, the separation being merely one of convenience. However, most of these waters are deeper than those shown in Table 2, and consequently the primary salinity is generally higher and the secondary salinity and secondary alkalinity lower. The concentration is generally higher, and in several waters is very high.

TABLE 2.—*Analyses of normal ground water from shallow-water wells in the Coalinga, Midway, and Sunset oil fields, Cal.*

	8	9	10	11	12	13	14
PROPERTIES OF REACTION IN PER CENT.							
Primary salinity	78.0	80.2	72	37.2	58.2	76.0	87.4
Secondary salinity	4.2	.0	25	43.4	37.6	12.6	0
Primary alkalinity	.0	1.8	0	.0	0	0	3.4
Secondary alkalinity	17.8	18.0	3	19.4	4.2	11.4	9.2
Per cent of rSO₄ in rSO₄+rCl	88.5	87.0	79	72.7	43.6	26.6	60.2
CONSTITUENTS IN PARTS PER MILLION.							
Sodium (Na)	a 470	a 457	a 981	a 198	a 980	a 254	719
Potassium (K)							9.5
Calcium (Ca)	59	45	297	166	257	61	39
Magnesium (Mg)	34	26	21	75	217	6	22
Iron oxide (Fe₂O₃) and alumina (Al₂O₃)	Trace.	7	48	....	3.3	....	....
Sulphate (SO₄)	914	814	2,177	649	1,473	166	879
Chloride (Cl)	88	88	423	180	1,399	335	429
Carbonate (CO₃)	b 140	b 143	b 54	b 134	b 91	b 51	32
Bicarbonate (HCO₃)							170
Silica (SiO₂)	44	61	21	....	45	26	44
	1,749	1,641	4,022	1,402	4,465.3	899	2,257.5
REACTING VALUES IN PER CENT.							
Alkalies:							
Sodium (rNa)	a 39.0	a 41.0	a 36.0	a 18.6	a 29.1	38.0	45.0
Potassium (rK)							.4
Alkaline earths:							
Calcium (rCa)	5.6	4.6	12.5	18.0	8.7	10.3	2.8
Magnesium (rMg)	5.4	4.4	1.5	13.4	12.2	1.7	2.6
Strong acids:							
Sulphate (rSO₄)	36.4	35.0	38.4	29.3	20.9	11.8	26.3
Chloride (rCl)	4.7	5.1	10.1	11.0	27.0	32.5	17.4
Weak acids:							
Carbonate (rCO₃)	b 8.9	b 9.9	b 1.5	b 9.7	b 2.1	5.7	1.5
Bicarbonate (rHCO₃)							4.0
ANALYSIS AS REPORTED.c							
Sodium sulphate	74.30	70.35	126.49	14.56	11.03		
Sodium chloride	8.48	8.50	40.82	17.40	134.91		
Sodium carbonate		1.27	.58		1.20		
Calcium sulphate			55.96	15.20	45.78		
Calcium carbonate	8.56	6.60	2.19	13.10	3.79		
Magnesium sulphate	4.01		2.96	21.70	57.95		
Magnesium carbonate	4.22	5.20	2.17		3.36		
Iron oxide and alumina	Trace.	.41	1.25		.19		
Silica	2.56	3.57	2.82		2.62		
	102.13	95.90	235.24	81.96	260.83		

a Reported and calculated as sodium but includes potassium.
b Reported and calculated as carbonate but probably in part bicarbonate.
c In hypothetic combinations, in grains per U. S. gallon.

Coalinga field:
  8. Standard Oil Co. water well 3, sec. 28, T. 19 S., R. 15 E. Analyst, Standard Oil Co., September, 1910.
  9. Standard Oil Co. water well 2, sec. 36, T. 19 S., R. 15 E. Depth, 444 feet. Analyst, Standard Oil Co., February, 1913.
  10. Associated Pipeline Co., shallow water well at station 1, sec. 18, T. 20 S., R. 15 E. Analyst, Smith, Emery & Co. Authority, Associated Oil Co.
  11. Traders Oil Co. water well, sec. 24, T. 20 S., R. 14 E. Depth, 85 feet. Analyst, L. J. Stabler, May, 1909. Authority, Traders Oil Co.
  12. California Oil & Gas Co., water well 1, sec. 6, T. 21 S., R. 15 E. Analyst, Smith Emery & Co.
Midway and Sunset fields:
  13. Western Water Co. wells in sec. 5, T. 31 S., R. 25 E. Analyst, Kern Trading & Oil Co., Jan. 1, 1913.
  14. Midway Northern Oil Co. water well, sec. 32, T. 12 N., R. 23 W. Water from sands at 350 and 790 feet. Sampled by G. S. Rogers, August, 1914. Analyst, Chase Palmer.

Most of these waters may be readily distinguished from surface waters, but their distinction from the modified waters beneath them is less easy. As shown by figure 4, the shallower waters are

secondary saline in character and high in sulphate, whereas those near the oil are primary alkaline and free from sulphate. However, there are many intermediate types which show primary alkalinity and still retain a fairly high proportion of sulphate. For convenience in discussing the waters of the fields of the west side the secondary saline waters high in sulphate have been referred to the normal group and those of primary alkaline character containing considerable sulphate to the modified group. The line of demarcation is therefore assumed to be the point at which secondary salinity disappears and primary alkalinity appears. As a rule this division is justified, for the decrease of secondary salinity is probably due as much to the normal increase of alkalies with depth as to actual decrease of sulphate. However, when sulphate is very high and the alkalies are proportionately less abundant than usual, the property of secondary salinity may be retained after some of the sulphate has been removed. Analyses 21 and 26, for example, represent sulphur waters, the hydrogen sulphide being presumably due to the reduction of some of the sulphate, yet both of these waters are secondary saline and are therefore grouped with normal types. As an additional criterion of the alteration of the waters the ratio of carbonate to sulphate is shown in Tables 3 to 7. It will be noted that in all of the analyses in Tables 3 and 4 except Nos. 19 and 21 this ratio is less than 0.25, and that No. 21 is a sulphur water which has doubtless been somewhat modified. This ratio explains another apparent inconsistency in Table 3, namely, the inclusion of No. 17, a primary alkaline water, with the normal secondary saline waters. In this water the sulphate is extremely high in comparison with both chloride and carbonate and the appearance of primary alkalinity is due rather to the abnormally low proportion of alkaline earths than to any loss of sulphate. As already stated, no single property or constituent of a natural water can be a universal criterion of its relation to the oil.

Analyses 15 and 16 represent the ordinary top water in the northern part of the Eastside Coalinga field. The exact position of these waters is not known, but from the higher primary salinity and concentration of No. 16 it is thought to be somewhat the deeper of the two. No. 18, from the Westside Coalinga field, is a water very similar in composition to the last but of exceptionally high concentration. It is a sulphur water and therefore has probably been slightly influenced by the hydrocarbons, though the proportion of sulphate as compared with both carbonate and chloride is still very high. No. 19 represents an unusual top water whose exact horizon is unknown. Its concentration is very much lower than that of most waters of the west side and therefore the sparingly soluble bicarbonates of calcium and magnesium, though present in small actual

amount, constitute an unusually high percentage of the total solids. The alkalies are exceptionally low, though chloride predominates over sulphate. No. 21 is somewhat similar in character to the last. In the locality from which this water was obtained the oil measures are only 650 feet below the surface and the water 304 feet. The water is essentially a shallow type and yet has undergone some alteration, as evidenced by the higher ratio of carbonate to sulphate and by the presence of hydrogen sulphide. No. 20 is somewhat similar to No. 21 but more nearly resembles the types represented by the preceding analyses. Analyses 22 and 24 represent very similar top waters, both being pronounced secondary saline types. No. 23 is a water characterized by a small percentage of primary alkalinity, but it is included here because of its very low carbonate-sulphate ratio and its very high sulphate salinity ratio.

Analysis 25 represents a water encountered at a depth of 670 feet in Midway Valley. This water is very similar in composition to No. 87, discussed above, and represents as near an approach to normal connate water as can be expected. Its reactive properties resemble those of sea water (see analysis 52, Table 8, p. 73), though the secondary salinity is rather low. The sulphate salinity ratio is about that of sea water and therefore much lower than in the shallow meteoric types. The carbonate-sulphate ratio is about normal for either the meteoric or the connate type. The concentration is almost three-fourths that of sea water. It is noteworthy that this water occurs in that part of the McKittrick formation correlated with the Tulare formation, which consists of deposits laid down in fresh water and which probably has never been submerged beneath the sea. Assuming that the sample was correctly taken, 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 indicate considerable artesian pressure and would imply that the escape of the deeper waters by migration along the lines of stratification is practically cut off. If this explanation is correct it throws light on the completeness with which the connate water is trapped in the Midway syncline.

Analysis 26 represents sulphur water from a well drilled near the outcrop of the oil measures which probably penetrates the shale of the Monterey group. The presence of hydrogen sulphide and also the somewhat high carbonate-sulphate ratio indicate that this water has been slightly modified, but it is included here because of its secondary salinity. Owing to the proximity of the outcrop of the sand there has been a considerable admixture of meteoric (sulphate) water, and chloride is not so high as in the waters farther east. Several other wells drilled in the brown shale just west of the western edge of the Midway field have obtained similar sulphur water, but,

as already explained (p. 46), the presence of small amounts of oil or gas in this formation may lead to the development of a modified type of water some distance stratigraphically below the oil measures.

TABLE 3.—*Analyses of normal ground water ("top water") from oil wells in the Coalinga oil field, Cal.*

	15	16	17	18	19	20	21
PROPERTIES OF REACTION IN PER CENT.							
Primary salinity	74.2	85.4	82.4	82.4	11	66	35.6
Secondary salinity	14.6	6.6	0	9.4	51	30	39.0
Primary alkalinity	0	0	12.0	0	0	0	0
Secondary alkalinity	11.2	8.0	5.6	8.2	38	4	25.4
Per cent of rSO_4 in rSO_4+rCl	86.9	95.0	95.4	95.0	38.7	70	78.5
Ratio of rCO_3+rHCO_3 to rSO_4	.15	.09	.22	.09	1.58	.06	.43
CONSTITUENTS IN PARTS PER MILLION.							
Sodium (Na)[a] and potassium (K)	596	1,111	1,760	3,285	40	641	521
Calcium (Ca)	163	83	22	385	105	209	265
Magnesium (Mg)	9	51	42	142	107	47	336
Iron oxide (Fe_2O_3) and alumina (Al_2O_3)	102	27	62	1	....	6	0
Sulphate (SO_4)	1,276	2,376	3,058	7,264	185	1,365	1,789
Chloride (Cl)	140	91	109	296	212	427	360
Carbonate (CO_3)	b 117	b 135	b 427	b 419	0	b 49	b 484
Bicarbonate (HCO_3)	....	....	....	....	364	....	....
Silica (SiO_2)	3	441	6.7	49	29	7	40
	2,406	4,315	5,486.7	11,841	857	2,751	3,795
Hydrogen sulphide (H_2S)	14	....	.0	Present.	....	.0	Present.
REACTING VALUES, IN PER CENT.							
Alkalies:							
Sodium (rNa)[a]	37.1	42.7	47.2	41.2	} 5.5	{ 33.0	17.8
Potassium (rK)						....	....
Alkaline earths:							
Calcium (rCa)	11.8	3.6	.7	5.5	16.5	12.4	10.5
Magnesium (rMg)	1.1	3.7	2.1	3.3	28	4.6	21.7
Strong acids:							
Sulphate (rSO₄)	38.6	43.7	39.3	43.5	12	33.7	29.3
Chloride (rCl)	5.8	2.3	1.9	2.4	19	14.3	8.0
Weak acids:							
Carbonate (rCO₃)	b 5.6	b 4.0	b 8.8	b 4.1	0	b 2.0	b 12.'
Bicarbonate (rHCO₃)					19		
ANALYSIS AS REPORTED.[c]							
Sodium sulphate	88.82	187.46	258.46	557.32	....	65.54	42.05
Sodium chloride	13.47	8.75	10.49	28.57	....	41.18	34.72
Sodium carbonate	.46	1.55	34.33	....	....		7.16
Calcium sulphate	20.19	7.42	....	28.33	....	41.41	10.40
Calcium carbonate	8.96	6.63	3.23	35.39	....		31.09
Magnesium sulphate	.35	8.64	4.98	34.66	....	7.83	86.12
Magnesium carbonate	1.65	4.29	5.05	4.56	....	4.06	7.82
Iron oxide and alumina	5.97	1.59	3.64	.06	....	.35	.00
Silica	.19	25.78	.39	2.86	....	.38	2.34
	140.06	252.11	320.57	691.75	....	160.75	221.70
Hydrogen sulphide	.82	....	.00	Present.	....	.00	Present.

a Reported and calculated as sodium but includes potassium.
b Reported and calculated as carbonate but probably in part bicarbonate.
c In hypothetic combinations, in grains per U. S. gallon.

15. California Oilfields (Ltd.) well 2, sec. 10, T. 19 S., R. 15 E. Analyst, Smith, Emery & Co., October, 1915. Authority, California Oilfields (Ltd.).
16. California Oilfields (Ltd.) well 16, sec. 14, T. 19 S., R. 15 E. Analyst, Smith, Emery & Co., September, 1915. Authority, California Oilfields (Ltd.).
17. Record Oil Co. well 5, sec. 22, T. 19 S., R. 15 E. Water from above oil zone. Analyst, Smith Emery & Co., October, 1915.
18. Premier Oil Co. well 3, sec. 24, T. 20 S., R. 14 E. Black sulphur water from about 700 feet, or about 400 feet above the oil. Analyst, Schalk Chemical Co. Authority, Premier Oil Co.
19. Kern Trading & Oil Co. well in sec. 13, T. 20 S., R. 14 E. Sampled by G. S. Rogers, October, 1915. Analyst, S. C. Dinsmore.
20. Nevada Petroleum Co. well 3, sec. 30, T. 20 S., R. 15 E. Flowing water from about 2,100 feet, or about 500 feet above the oil. Analyst, Dodge Manfacturing Co., March, 1911. Authority, Nevada Petroleum Co.
21. Ozark Oil Co. well 3, sec. 26, T. 20 S., R. 14 E. Sulphur water from 304 feet, or about 350 feet above oil. Analyst, Smith, Emery & Co., January, 1912. Authority, Ozark Oil Co.

TABLE 4.—*Analyses of normal ground water ("top water") from wells in the Coalinga and Midway oil fields, Cal.*

	22	23	24	25	26
PROPERTIES OF REACTION IN PER CENT.					
Primary salinity	59.2	92.4	53.8	94.0	90.2
Secondary salinity	28.4	0	35.6	5.4	3.4
Primary alkalinity	0	2.0	0	0	0
Secondary alkalinity	12.4	5.6	10.6	.6	6.4
Per cent of rSO_4 in rSO_4+rCl	77.7	92.4	78.3	7.0	39.6
Ratio of rCO_3+rHCO_3 to rSO_4	.18	.09	.15	.08	.22
CONSTITUENTS IN PARTS PER MILLION.					
Sodium (Na)	a 442	a1,335	a 661	a8,794	911
Potassium (K)					8.4
Calcium (Ca)	140	34	249	397	23
Magnesium (Mg)	76	22	148	61	39
Iron oxide (Fe_2O_3) and alumina (Al_2O_3)	b 39		b 105	b 2.4	
Sulphate (SO_4)	1,062	2,518	1,793	1,381	605
Chloride (Cl)	226	154	368	13,304	1,013
Carbonate (CO_3)	b 121	b 141	b 169	b 71	0
Bicarbonate (HCO_3)					175
Silica (SiO_2)		17		45	32
	2,106	4,221	3,493	24,055.4	2,717.4
Hydrogen sulphide (H_2S)					Present.
REACTING VALUES IN PER CENT.					
Alkalies:					
Sodium (rNa)	a 29.6	a 47.2	a 26.9	a 47.0	44.7
Potassium (rK)					.4
Alkaline earths:					
Calcium (rCa)	10.7	1.4	11.6	2.4	1.3
Magnesium (rMg)	9.7	1.4	11.5	.6	3.6
Strong acids:					
Sulphate (rSO4)	34.0	42.7	35.0	3.5	14
Chloride (rCl)	9.8	3.5	9.7	46.2	32
Weak acids:					
Carbonate (rCO3)	b 6.2	b 3.8	b 5.3	b .3	.0
Bicarbonate (rHCO3)					3.2
ANALYSIS AS REPORTED.c					
Sodium sulphate	53.33	217.70	76.10	25.95	
Sodium chloride	21.74	14.83	35.46	1,282.50	
Sodium carbonate		3.59			
Calcium sulphate	14.84		33.01	69.42	
Calcium carbonate	9.47	5.00	12.07	6.92	
Magnesium sulphate	19.44		37.62	17.75	
Magnesium carbonate	1.92	4.48	3.67		
Iron oxide and alumina	2.27		6.12	.14	
Silica		.98		2.65	
	123.01	246.58	204.05	1,405.33	

a Reported and calculated as sodium but includes potassium.
b Reported and calculated as carbonate but probably in part bicarbonate.
c In hypothetic combinations, in grains per U. S. gallon.

Coalinga field:
   22, 23, and 24. Kern Trading & Oil Co. wells in sec. 25, T. 20 S., R. 14 E. Nos. 22 and 23 represent water which corroded the casing and temporarily flooded the wells. The water certainly occurs above the oil and probably more than 500 feet above it. No. 24 represents water from a depth of 648 feet, or just above the zone of tar sands and 480 feet above the oil. Analyst, Kern Trading & Oil Co.
Midway field:
   25. Standard Oil Co. well 6, sec. 12, T. 32 S., R. 23 E. Water is from 670 to 730 feet, or about 2,000 feet above the horizon of the oil. Analyst, Standard Oil Co. January, 1912.
   26. August Water Co., California Amalgamated well 2, sec. 35, T. 32 S., R. 23 E. Sulphur water from 1,090 feet, probably in shale of Monterey group. Temperature, 84° F. (See p. 19.) Sampled by G. S. Rogers, July, 1914. Analyst, Chase Palmer.

MODIFIED GROUND WATER.

Table 5 contains analyses of water, modified presumably by the action of the hydrocarbons, from the Coalinga, Midway, and Sunset fields. As already explained, the modified group is arbitrarily assumed to include only those waters that are primary alkaline in character and that contain a moderate to high proportion of sulphate. In all the analyses included in Table 5 the ratio of carbonate to sulphate is greater than 1, and in several it is much higher. Most of these waters are characterized by a high percentage of primary alkalinity, but this figure is largely governed by the concentration of the chloride.

Analysis 27 represents the type of water that occurs in the Eastside Coalinga field some distance above the oil. It will be noted that the primary salinity is very low and primary alkalinity very high. The sulphate salinity ratio is fairly high, but this is due chiefly to the very small proportion of chloride present. When chloride is as low as it is in most of the waters from this district the relative proportions of sulphate and chloride are of less value than the comparison of sulphate and carbonate. Analysis 28 shows a somewhat saltier water from the north end of the Coalinga syncline. The primary alkalinity is fairly high though the water still contains a large amount of sulphate. No. 29 is a good analysis of the distinctly modified water that occurs just above the tar sand zone in the Westside Coalinga field. Despite the high sulphate salinity ratio and the low carbonate-sulphate ratio the fact that some of the sulphate has already been reduced is indicated by the presence of a considerable amount of sulphide, part of which is combined as hydrogen sulphide. Analysis 30 represents the water used at the Coalinga Sulphur Baths, which is interesting because, although distinctly a modified type, it occurs 600 feet below the oil. This water, however, is probably obtained from the Chico strata (Upper Cretaceous[1]) and is very different from that obtained in or just below the oil zone (upper Miocene), which is represented by analysis 64 (Table 10, p. 76).

Analysis 31 probably represents a mixture of waters above and below the oil from a well on the extreme western edge of the Midway field. The sulphate is high in proportion to both chloride and carbonate, indicating a considerable admixture of upper water. It is also possible, because of the proximity of the outcrop of the sands and the fact that large quantities of water are being removed from them, that sulphate water is entering at the outcrop of the lower water sand faster than it is being altered. Analysis 32 represents an unusual type of water from Buena Vista Valley. Although occurring

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[1] Arnold, Ralph, and Anderson, Robert, Geology and oil resources of the Coalinga district, Cal.: U. S. Geol. Survey Bull. 398, p. 223, 1910.

at a depth of about 3,000 feet its concentration is only 364 parts, which is less than that of even the shallowest ground water in most localities in the fields of the west side. No oil had been encountered at this depth, and if present is probably some distance below. The low carbonate-sulphate ratio shown by the analysis indicates a water only slightly modified, if at all, though as no shallower water from this locality is available for comparison a definite estimate of its relations can not be made. No. 33 is a much saltier and more concentrated water than any of the foregoing and is included here for purposes of comparison. This water has been greatly modified and closely approaches the altered water associated with the oil along the western edge of the Midway and Sunset fields. (See Table 11, p. 77.) The presence of hydrogen sulphide and the appreciable amount of sulphate still retained prevent its classification as an altered water, especially as it occurs at least a hundred feet above the oil. A similar type is shown by analysis 81 (Table 13, p. 83).

Analysis 80 (Table 12, p. 81) represents a meteoric water of the modified type similar in every way to those discussed above but formed under very different conditions. This water is the mine water at the old coal mine in sec. 26, T. 30 S., R. 14 E. It probably has not been affected by oil or gas and its modification must therefore be due to the coal.

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TABLE 5.—*Analyses of ground water modified by action of oil, from wells in the Coalinga, Midway, and Sunset oil fields, Cal.*

	27	28	29	30	31	32	33
PROPERTIES OF REACTION IN PER CENT.							
Primary salinity	14.0	49.0	45.4	20.2	44.6	56.6	77.4
Secondary salinity	0	0	0	0	0	0	0
Primary alkalinity	82.6	47.4	22.4	74.2	39.0	11.0	15.6
Secondary alkalinity	3.4	3.6	32.2	5.6	16.4	32.4	7.0
Ratio of rSO₄ to rSO₄+rCl	75.7	43.7	67.4	25.7	58.3	64.0	1.2
Ratio of rCO₃+rHCO₃ to rSO₄	7.5	2.4	1.6	15.3	2.1	1.2	22.6
CONSTITUENTS IN PARTS PER MILLION.							
Sodium (Na)	*a*1,003	*a* 807	705	460	618	*a* 93	4,969
Potassium (K)			21	10	33		102
Calcium (Ca)	17	26	124	19	31	26	109
Magnesium (Mg)	9		104	2.6	45	8	144
Iron (Fe)	} *b* 4.8		{ Trace.	Trace.	Trace.	} *b* 4.8	
Aluminum (Al)					3.1		
Sulphate (SO₄)	231	377	679	53	403	103	109
Chloride (Cl)	54	354	241	113	210	43	6,740
Carbonate (CO₃)	*c*1,067	*c* 555	0	0	160	*c* 77	0
Bicarbonate (HCO₃)			1,366	1,037	693		3,623
Sulphide (S)	52		45				
Silica (SiO₂)	60		97	34	115	9.6	67
	2,497.8	2,119	2,690	1,202.6	1,959.1	364.4	14,025
Hydrogen sulphide (H₂S)			27	2			1.3
REACTING VALUES IN PER CENT.							
Alkalies:							
Sodium (rNa)	*a* 48.3	*a* 48.2	33.3	47.1	40.5	*a* 33.8	46.0
Potassium (rK)			.6	.1	1.3		.5
Alkaline earths:							
Calcium (rCa)	.9	1.8	6.8	2.3	2.4	10.7	1.1
Magnesium (rMg)	.8		9.3	.5	5.8	5.5	2.4
Strong acids:							
Sulphate (rSO₄)	5.3	10.7	15.3	2.6	13.0	18.1	.5
Chloride (rCl)	1.7	13.8	7.4	7.5	9.3	10.2	38.2
Weak acids:							
Carbonate (rCO₃)	*c* 39.5	*c* 25.5	0	0	8.3	*c* 21.7	0
Bicarbonate (rHCO₃)			24.3	39.9	19.4		11.3
Sulphide (rS)	3.5		3.0				
ANALYSIS AS REPORTED. *d*							
Sodium sulphate	18.41	32.60				8.91	
Sodium chloride	5.25	34.14				4.17	
Sodium carbonate	106.45	53.40				2.03	
Sodium sulphide	7.34						
Calcium sulphate	1.00						
Calcium carbonate	1.80	3.74				3.74	
Magnesium sulphate	.39						
Magnesium carbonate	1.48	Trace.				1.59	
Iron and alumina	.28					.28	
Silica	3.49					.56	
	145.89	123.88				21.28	

a Reported and calculated as sodium but includes potassium.
b Fe₂O₃+Al₂O₃.
c Reported and calculated as carbonate but probably in part bicarbonate.
d In hypothetic combinations, in grains per U. S. gallon.

Coalinga field:
27. California Oilfields (Ltd.) well 16, sec. 26, T. 19 S., R. 15 E. Water from 2,415 to 2,450 feet (above the oil). Analyst, Smith, Emery & Co., November, 1915. Authority, California Oilfields (Ltd.).
28. Union Oil Co. well La Vista 4, sec. 4, T. 20 S., R. 15 E. Water from 3,191 feet, or about 400 feet above first show of oil reported. Analyst, E. H. Miller, April, 1911. Authority, Union Oil Co.
29. Coalinga Homestake water well, sec. 26, T. 20 S., R. 14 E. Sulphur water from 336 to 354 feet, or at top of tar sand zone and 200 to 300 feet above the oil. Sampled by G. S. Rogers, October, 1915. Analyst, S. C. Dinsmore.
30. Santa Rosa Oil & Development Co. water well, sec. 12, T. 21 S., R. 14 E. Sulphur water from 2,077 feet, or about 600 feet below the oil. Temperature, 118° F. Sampled by G. S. Rogers, October, 1915. Analyst, S. C. Dinsmore.
Midway and Sunset fields:
31. Stratton Water Co. well 3, sec. 7, T. 32 S., R. 23 E. Probably a mixture of waters from above and below the oil. Temperature, 90° F. Sampled by G. S. Rogers, August, 1914. Analyst, S. C. Dinsmore.
32. Midway Basin Oil Co. well in sec. 28, T. 31 S., R. 24 E. Water from 2,980 feet. No oil encountered, though possibly present at greater depth. Analyst, Standard Oil Co., November, 1910.
33. Union Oil Co. water well Diamond 2, sec. 13, T. 11 N., R. 24 W. Sulphur water from about 650 feet, or about 100 feet above the oil. Sampled by G. S. Rogers, September, 1915. Analyst, S. C. Dinsmore.

ALTERED GROUND WATER.

Reversed type.—When a pure sulphate water is altered by the action of hydrocarbons it apparently becomes a pure carbonate water, a reversal from complete salinity to complete alkalinity taking place. However, there are few waters anywhere that do not contain some chloride, and in oil fields, where the underground circulation is normally restricted, a large concentration of chloride is generally found. It is probable therefore that oil-field waters of the reversed type, in which chloride is practically lacking, are rare, and so far as the writer knows the only fields in which they constitute the rule rather than the exception are the Eastside Coalinga and possibly the Kern River fields. (See p. 85.) Tables 6 and 7 show analyses of this type of water. The type is characterized by low primary salinity and high primary alkalinity, by a moderately low concentration, and by a high ratio of carbonate to sulphate. Owing to the small amount of chloride present the sulphate salinity ratio (per cent of rSO_4 in $rSO_4 + rCl$) is much higher than in most altered waters, though generally below 10 per cent. In some waters, however, the actual amount of sulphate seems to be abnormally large for a water associated with the oil, and it is possible that in some localities sulphate water is entering at the outcrop and percolating down faster than it is being altered.

All the analyses in Table 6 and four of those in Table 7 represent water from the Coalinga field. No. 34 is a sulphur water which occurs a short distance above the oil measures at the upper end of the Coalinga syncline. Circulation is doubtless restricted in this locality and a considerable proportion of chloride has been retained. The primary salinity is 35 per cent and the primary alkalinity only 52 per cent, and the water is therefore a mixed type, approaching that shown in Table 10, but characterized by a lower concentration. The presence of hydrogen sulphide together with a small amount of sulphate indicates that the alteration of this water is not entirely complete. Analyses 37, 38, and 39 represent waters from the deep territory on the east side of the Coalinga anticline near its southern end. These waters resemble 34 in that a considerable proportion of chloride is present, indicating an admixture of connate water. The properties of these waters are very similar, and all of them are characterized by a high proportion of carbonate as compared with either chloride or sulphate. However, a rather large amount of sulphate is present, especially in No. 39, which may be the normal condition or which may be due to an admixture of upper water in the samples analyzed. It may also indicate that these waters occur above the oil measures instead of in or below them, as generally believed. Analysis 42, which is very similar to these, represents

a water definitely reported to occur at 4,022 feet, or near the base of the main oil measures. It will be noted that this analysis shows only about half as much sulphate as analyses 37, 38, and 39.

Analyses 35, 36, and 40 contain an even lower proportion of chloride than analysis 42 and represent the extreme of the reversed type. These waters occur on the east flank of the anticline, farther north and in shallower territory than those discussed above. Apparently in this locality the connate water has been entirely drained away and replaced by meteoric water. In Nos. 36 and 40 primary salinity is only 1.4 per cent, and these waters are therefore practically pure solutions of sodium carbonate. No. 36 contains no sulphate whatever, but a small amount of the hydrogen sulphide formed by the reduction of the sulphate that it formerly contained is still present. In Nos. 35 and 40 the sulphate seems high when compared with the chloride, but is negligible in comparison with the carbonate. Analysis 41 represents a water similar to No. 40, but characterized by higher salinity, both chloride and sulphate. Sulphate is relatively high, and the presence of hydrogen sulphide presumably indicates that alteration is not complete.

Analysis 43 represents a water similar to No. 41, but occurring under very different conditions in the Westside Coalinga field This water was obtained from a well drilled to a depth of only 410 feet (probably in the brown shale, Oligocene?) a mile west of the developed oil field. The strata dip steeply in this locality and the water sand outcrops not far west of the well. The occurrence of an almost completely altered water so close to the surface is very unusual, but it is known that small quantities of oil or gas are disseminated through the formation, and there is said to be an oil seep within a mile of the well. Furthermore, only a very small supply of this water was found and the action of reducing agents would therefore have been localized. Ordinarily, however, the water obtained from the brown shale in similar relative locations is only partly modified.

Analyses 44 and 45 represent waters of the reversed type from the northern part of the Midway field. No. 44 was obtained from a depth of 3,860 feet or probably several thousand feet below the main oil measures, but it is reported that a "stray" oil sand was found just below the water. It is said that the production of this well increases perceptibly after the rains, which is not inconsistent with the fact that the water is chiefly of meteoric origin. No. 45 is a similar type of water, though it contains an even smaller proportion of chloride and is less concentrated. It occurs above the oil measures and probably in the zone of tar sands. These waters are very different from those found 2 miles to the southeast and described in the following section.

Analysis 85 (Table 14, p. 85) shows a similar water from the Kern River field. It resembles the waters of the west side very closely, although its concentration is lower and its secondary alkalinity is somewhat higher.

TABLE 6.—*Analysis of essentially meteoric water altered by action of oil (reversed type), from oil wells in the Coalinga oil fields, Cal.*

	34	35	36	37	38	39
PROPERTIES OF REACTION IN PER CENT.						
Primary salinity	34.8	4.6	1.4	28.6	30.6	34.4
Secondary salinity	0	0	0	0	0	0
Primary alkalinity	51.8	75.8	94.4	69.4	68.6	59.2
Secondary alkalinity	13.4	19.6	4.2	2.0	.8	6.4
Per cent of rSO₄ in rSO₄+rCl	2.8	4.4	0	10.5	9.2	13.4
Ratio of rCO₃+rHCO₃ to rSO₄	65.2	477	∞	23.8	24.8	14.3
CONSTITUENTS IN PARTS PER MILLION.						
Sodium (Na) and potassium (K)[a]	799	1,123	1,458	3,699	3,968	2,610
Calcium (Ca)	62	60	22	13	6.3	122
Magnesium (Mg)	28	109	22	37	16	21
Iron oxide (Fe₂O₃) and alumina (Al₂O₃)	15	38	3.4	4.8	1.5	
Sulphate (SO₄)	22	8	0	238	228	262
Chloride (Cl)	480	95	32	1,494	1,700	1,280
Carbonate (CO₃)[b]	784	1,737	1,953	3,514	3,634	2,382
Silica (SiO₂)	86	69	41	53	29	37
	2,276	3,239	3,531.4	9,052.8	9,582.8	6,714
Hydrogen sulphide (H₂S)	26	0	6.3			
REACTING VALUES IN PER CENT.						
Alkalies:						
Sodium (rNa) and potassium (rK)[a]	43.3	40.2	47.9	49.0	49.6	46.8
Alkaline earths:						
Calcium (rCa)	3.8	2.4	.8	.2	.1	2.5
Magnesium (rMg)	2.9	7.4	1.3	.8	.3	.7
Strong acids:						
Sulphate (rSO₄)	.5	.1	.0	1.5	1.4	2.3
Chloride (rCl)	16.9	2.2	.7	12.8	13.9	14.9
Weak acids:						
Carbonate (rCO₃)[b]	32.6	47.7	49.3	35.7	34.7	32.8
ANALYSIS AS REPORTED.[c]						
Sodium sulphate	1.89			20.61	19.68	21.39
Sodium chloride	46.21		2.03	143.97	163.86	123.43
Sodium carbonate	64.18	150.95	193.69	351.42	370.29	222.96
Calcium sulphate		.48				.40
Calcium chloride			.55			
Calcium carbonate	9.05	8.39	2.79	1.91	.92	17.46
Magnesium sulphate		.15				.73
Magnesium chloride		7.45	.43			
Magnesium carbonate	5.74	15.52	4.07	7.56	3.26	3.70
Iron oxide and alumina	.85	2.22	.19	.28	.09	
Silica	5.05	4.05	2.45	3.07	1.72	2.18
	132.97	189.21	206.20	528.82	559.82	392.25
Hydrogen sulphide	1.52	.00	.37			

[a] Reported and calculated as sodium but includes potassium.
[b] Reported and calculated as carbonate but probably in part bicarbonate.
[c] In hypothetic combinations, in grains per U. S. gallon.

34. California Oilfields (Ltd.) well 5, sec. 29, T. 19 S., R. 15 E. Sulphur water from 2,655 feet, or a short distance above oil zone. Analyst, Standard Oil Co., October, 1915.
35. California Oilfields (Ltd.) well 37, sec. 27, T. 19 S., R. 15 E. Analyst, Smith, Emery & Co., October, 1915. Authority, California Oilfields (Ltd.).
36. California Oilfields (Ltd.) well 15, sec. 34, T. 19 S., R. 15 E. Analyst, Smith, Emery & Co., November, 1915. Authority, California Oilfields (Ltd.).
37, 38, 39. Water from oil wells in secs. 35 and 36, T. 19 S., R. 15 E., and sec. 2, T. 20 S., R. 15 E., respectively. This water is thought by most of the operators to occur at the base of the main oil zone; it is certainly closely associated with the oil. Analyst, Kern Trading & Oil Co.

TABLE 7.—*Analyses of essentially meteoric water altered by action of oil (reversed type), from wells in the Coalinga and Midway oil fields, Cal.*

	40	41	42	43	44	45
PROPERTIES OF REACTION IN PER CENT.						
Primary salinity	1.4	14.4	33.8	27.8	40.2	22.4
Secondary salinity	0	0	0	0	0	0
Primary alkalinity	88.4	83.6	64.2	69.8	57.8	60.4
Secondary alkalinity	10.2	2.0	2.0	2.4	2.0	17.2
Per cent of rSO$_4$ in rSO$_4$+rCl	11.4	36.0	5.3	1.4	1.5	Trace.
Ratio of rCO$_3$+rHCO$_3$ to rSO$_4$	493	16.5	36.8	180	99	....
CONSTITUENTS IN PARTS PER MILLION.						
Sodium (Na)	a1,087	a1,007	3,295	a 718	2,052	a 1,010
Potassium (K)	....	....	23	....	9.7	....
Calcium (Ca)	25	10	31	7.2	19	56
Magnesium (Mg)	50	6.3	19	5	11	77
Iron (Fe)	} b 3.9	b 1.7	{ Trace.	....	Trace.	....
Aluminum (Al)					3.1	....
Sulphate (SO$_4$)	4.1	111	135	5.8	28	Trace.
Chloride (Cl)	22	147	1,695	310	1,293	421
Carbonate (CO$_3$)	c1,555	c1,148	36	c 691	342	c 1,236
Bicarbonate (HCO$_3$)	....	....	5,956	....	2,732	....
Silica (SiO$_2$)	68	19	46	10	72	Trace.
	2,815	2,450	8,214	1,747	5,175.8	2,800
Hydrogen sulphide (H$_2$S)	14	5	....	....	....	Present.
REACTING VALUES IN PER CENT.						
Alkalies:						
Sodium (rNa)	a 44.9	a 49.0	48.8	a 48.8	48.9	a 41.4
Potassium (rK)	....	....	.2	....	.1	....
Alkaline earths:						
Calcium (rCa)	1.2	.5	.5	.6	.5	2.6
Magnesium (rMg)	3.9	.5	.5	.6	.5	6.0
Strong acids:						
Sulphate (rSO$_4$)	.1	2.6	.9	.2	.3	....
Chloride (rCl)	.6	4.6	16.0	13.7	19.8	11.2
Weak acids:						
Carbonate (rCO$_3$)	c 49.3	c 42.8	.4	c 36.1	6.2	c 38.8
Bicarbonate (rHCO$_3$)	....	....	32.7	....	23.7	....
ANALYSIS AS REPORTED.d						
Sodium sulphate	....	9.57	....	.50	....	....
Sodium chloride	.98	14.17	....	29.93	....	....
Sodium carbonate	145.25	115.38	....	69.04	....	....
Calcium sulphate	.34	Trace.	....	....	....	....
Calcium carbonate	3.41	1.46	....	1.04	....	....
Magnesium sulphate	.02	....	....	....	....	....
Magnesium chloride	.92	....	....	....	....	....
Magnesium carbonate	9.28	1.28	....	1.01	....	....
Iron oxide and alumina	.23	.10	....	....	....	....
Silica	3.97	1.13	....	.59	....	....
	164.40	143.09	....	102.11	....	....
Hydrogen sulphide	.80	.29	....	....	....	....

 a Reported and calculated as sodium but includes potassium.
 b Fe$_2$O$_3$+Al$_2$O$_3$.
 c Reported and calculated as carbonate but probably in part bicarbonate.
 d In hypothetic combinations, in grains per U. S. gallon.

Coalinga field:
 40. California Oilfields (Ltd.) well 1, sec. 34, T. 19 S., R. 15 E. Analyst, Smith, Emery & Co., November, 1915. Authority, California Oilfields (Ltd.).
 41. California Oilfields (Ltd.) well 31, sec. 34, T. 19 S., R. 15 E. Water from about 2,156 feet, or a short distance above main oil zone. Analyst, Smith, Emery & Co., November, 1915. Authority, California Oilfields (Ltd.).
 42. Kern Trading & Oil Co. well, in sec. 11, T. 20 S., R. 15 E. Water from 4,022 feet or near base of lower oil zone. Sampled by G. S. Rogers, October, 1915. Analyst, S. C. Dinsmore.
 43. Kern Trading & Oil Co. water well 1, sec. 15, T. 20 S., R. 14 E. Water from 410 feet. Well is probably in brown shale (Oligocene?) and is located close to the outcrop of the water sand. Analyst, Kern Trading & Oil Co.
Midway field:
 44. General Petroleum Co., Carnegie water well, sec. 9, T. 31 S., R. 22 E. Water from brown shale at 3,860 to 3,880 feet, or probably over 3,000 feet below horizon of main oil zone. Temperature, 131° F. Sampled by G. S. Rogers, July, 1914. Analyst, S. C. Dinsmore.
 45. Potter Oil Co. well 2, sec. 15, T. 31 S., R. 22 E. Water from about 500 feet, or in tar sand zone and 200 to 300 feet above the oil. Analyst, Smith, Emery & Co., May, 1915. Authority, Potter Oil Co.

Brine.—In Tables 8 and 9 are shown analyses of brine, or connate water, altered presumably by the action of hydrocarbons. For convenience in discussion the term brine is here restricted to waters that are practically sulphate-free and that are characterized by secondary salinity. The primary salinity generally ranges upward from about 80 per cent and the secondary salinity downward from about 20 per cent; the concentration is generally between 25,000 and 45,000 parts per million, and secondary alkalinity is therefore very low. The greatest actual amount of sulphate in any of the waters shown is 34 parts per million, and owing to the large amounts of chloride present the sulphate salinity ratio is less than 0.5 per cent. Owing to the very small amount of both carbonate and sulphate the ratio between them generally has little significance. To facilitate comparison an analysis of ocean water is included in Table 8 as No. 52.

Analysis 46 represents a very exceptional water from the Coalinga field, which is exactly on the dividing line and exhibits neither secondary salinity nor primary alkalinity. Carbonate is low and only a trace of sulphate is reported, so that this water is essentially a solution of sodium chloride. The concentration is unusually low and secondary alkalinity is present in corresponding high proportion. A partial analysis of a deeper water from the same well showed more chloride and less carbonate, indicating a true (secondary saline) brine. Both these waters are said to be from the brown shale below the oil measures. Apparently no brines have been encountered in the main Coalinga field south of this well, though they probably exist in the deeper unexplored portion of the syncline.

The remaining analyses in Table 8 represent brines from the Midway syncline and the Buena Vista anticline. All these waters occur close to the oil, some a short distance above and others below. In all of them the sulphate salinity ratio is less than 0.1 per cent and two of them contain no sulphate whatsoever. In all other respects they closely resemble sea water, the properties of reaction varying within the limits stated above and the concentration ranging between 29,000 and 39,000 parts. No. 48 is the only oil-field water that has come to the writer's attention in which secondary salinity is as high as it is in sea water.

Table 9 contains analyses of seven brines from the Midway and Sunset fields. Nos. 53 and 55 to 58 are in every way similar to those already described and are believed to be representative of the water associated with the oil in the central and eastern parts of these fields. Nos. 54 and 59 are somewhat different types, having a very much lower concentration than the rest. No. 54 contains an exceptionally high proportion of the calcium and carbonate radicles and primary and secondary salinity are therefore unusually low. No. 59, which is

a water from a considerable depth, probably in the Vaqueros formation, is characterized by a lower concentration than many surface waters, although its properties resemble those of the other brines. Nos. 54 and 59 contain only minute amounts of sulphate. Analysis 88 (Table 14) represents a brine associated with the oil in the Lost Hills field.

TABLE 8.—*Analyses of brine or connate water altered by action of oil, from oil wells in the Coalinga and Midway oil fields, Cal., and of ocean water.*

	46	47	48	49	50	51	52
PROPERTIES OF REACTION IN PER CENT.							
Primary salinity	96.2	86.6	75.9	83.8	91.8	82.0	78.6
Secondary salinity	.0	12.2	22.5	13.4	6.6	17.0	21.1
Primary alkalinity	0	0	0	0	0	0	0
Secondary alkalinity	3.8	1.2	1.6	2.8	1.6	1.0	.3
Per cent of rSO_4 in rSO_4+rCl	Trace.	0	.01	.06	0	.01	9.2
CONSTITUENTS IN PARTS PER MILLION.							
Sodium (Na)	a4,137	11,160	a10,522	a13,253	a10,704	11,011	10,710
Potassium (K)		124				156	390
Calcium (Ca)	81	848	2,894	1,089	284	1,188	420
Magnesium (Mg)	40	425	7.2	685	326	510	1,300
Iron oxide (Fe_2O_3) and alumina (Al_2O_3)	32		35	11			
Sulphate (SO_4)	Trace.	0	31	18	0	9	2,700
Chloride (Cl)	6,367	20,694	20,955	23,553	17,631	18,750	19,410
Carbonate (CO_3)	b 218	48	b 293	b 626	b 243	0	b 70
Bicarbonate (HCO_3)		359				280	
Silica (SiO_2)	49	102	18	65	12	123	
	10,924	33,578	34,755.2	39,300	29,200	31,885	35,000
REACTING VALUES IN PER CENT.							
Alkalies:							
Sodium (rNa)	a 48.1	43.0	a 37.95	a 41.9	a 45.9	40.6	38.5
Potassium (rK)		.3				.4	.8
Alkaline earths:							
Calcium (rCa)	1.0	3.7	12.00	4.0	1.4	5.3	1.8
Magnesium (rMg)	.9	3.0	.05	4.1	2.7	3.7	8.9
Strong acids:							
Sulphate (rSO_4)	Trace.	.0	.05		.0	Trace.	4.6
Chloride (rCl)	48.1	49.4	49.15	48.5	49.2	49.5	45.2
Weak acids:							
Carbonate (rCO_3)	b 1.9	.1	b.80	b 1.5	b.8	.0	b.2
Bicarbonate ($rHCO_3$)		.5				.5	
ANALYSIS AS REPORTED.c							
Sodium sulphate	Trace.						
Sodium chloride	605.36		1,560.10	1,954.36	1,575.11		
Sodium carbonate	7.34			9.53	10.90		
Calcium sulphate	Trace.		2.57	1.47			
Calcium chloride	2.98		434.50	167.26	45.99		
Calcium carbonate	9.13		28.50	6.95			
Magnesium sulphate	Trace.						
Magnesium chloride	4.24		1.64	114.05	61.88		
Magnesium carbonate	4.37			37.95	11.24		
Iron and alumina	1.88		2.05	.63			
Silica	2.84		1.08	3.83	.70		
	638.14		2,030.44	2,296.03	1,705.82		

a Reported and calculated as sodium but includes potassium.
b Reported and calculated as carbonate but probably in part bicarbonate.
c In hypothetic combinations, in grains per U. S. gallon.

Coalinga field:

46. Acorn Oil Co. well 1, sec. 2, T. 20 S., R. 14 E. Flowing water from 1,104 feet (in brown shale), or about 1,000 feet below main oil horizon. Temperature, 86° F. Analyst, Luckhardt & Co. Authority, H. W. Bell. A partial analysis by H. W. Bell of water struck in this well at 2,528 feet shows about 7,700 parts per million of Cl and 175 parts of CO_3. This deeper water thus probably resembles No. 50 in its properties of reaction.

Midway field:

47. Mays Consolidated Oil Co. well 6, sec. 28, T. 31 S., R. 23 E. Flowing water from 3,000 feet, or a few feet beneath the oil sand. Temperature, 125° F. Sampled by G. S. Rogers, September, 1915. Analyst, S. C. Dinsmore.

48. Standard Oil Co. well 6, sec. 22, T. 31 S., R. 23 E. Water from 2,700 feet, or in oil zone. Analyst, Standard Oil Co., September, 1915.

49. Associated Oil Co. well 2, sec. 32, T. 31 S., R. 23 E. Water from a short distance above 3,100 feet, or more than 100 feet above the oil. Analyst, Smith, Emery & Co. Authority, Associated Oil Co.

50. Associated Oil Co. well Pioneer Midway 7, sec. 30, T. 31 S., R. 23 E. Water probably from 2,840 to 2,885 feet, or in oil measures. Analyst, Smith, Emery & Co. Authority, Associated Oil Co.

51. Honolulu Oil Co. well 6, sec. 10, T. 32 S., R. 24 E. Water from 2,755 feet, or close to the horizon. of the oil. Sampled by Paul Paine. Analyst, S. C. Dinsmore.

Ocean water:

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

TABLE 9.—*Analyses of brine or connate water altered by the action of the oil, from oil wells in the Midway and Sunset oil fields, Cal.*

	53	54	55	56	57	58	59
PROPERTIES OF REACTION IN PER CENT.							
Primary salinity	84.2	48.6	84.0	84.6	83.4	83.6	85.0
Secondary salinity	14.6	5.0	11.4	13.8	16.2	16.0	12.6
Primary alkalinity	0	0	0	0	0	0	0
Secondary alkalinity	1.2	46.4	4.6	1.6	.4	.4	2.4
Per cent of rSO_4 in rSO_4+rCl	.01	Trace.	0	.20	Trace.	.0	.48
CONSTITUENTS IN PARTS PER MILLION.							
Sodium (Na)	a15,015	a1,323	a9,855	10,548	a11,656	11,176	} 671
Potassium (K)				72		86	
Calcium (Ca)	1,895	1,223	1,064	772	1,281	1,100	69
Magnesium (Mg)	342		345	570	443	503	21
Iron (Fe)	} b 11	b 1.7	b 5	{ .1			
Aluminum (Al)				8.4			
Sulphate (SO_4)	32	3.6	0	34	4.3	0	7.8
Nitrate (NO_3)				0		45	0
Chloride (Cl)	27,102	2,254	17,231	19,624	21,415	20,421	1,170
Iodide (I)						29	
Carbonate (CO_3)	c 275	c1,645	c692	0	c90	0	0
Bicarbonate (HCO_3)				573		162	48
Silica (SiO_2)	60	4.1	10	43	39		5
	44,732	6,454.4	29,202	31,953.5	34,928.3	33,440	1,967.8
Carbon dioxide (CO_2)				Present.		Present.	Present.
REACTING VALUES IN PER CENT.							
Alkalies:							
Sodium (rNa)	a 42.1	a 24.3	a 42.0	42.1	a 41.7	41.6	} 42.5
Potassium (rK)				.2		.2	
Alkaline earths:							
Calcium (rCa)	6.1	25.7	5.2	3.5	5.3	4.7	5.0
Magnesium (rMg)	1.8		2.8	4.2	3.0	3.5	2.5
Strong acids:							
Sulphate (rSO_4)				.1		.1	.2
Nitrate (rNO_3)							
Chloride (rCl)	49.4	26.8	47.7	49.1	49.8	49.7	48.6
Weak acids:							
Carbonate (rCO_3)	c. 6	c 23.2	c 2.3	.0	c .2	.0	.0
Bicarbonate ($rHCO_3$)				.8		.2	1.2
ANALYSIS AS REPORTED.[d]							
Sodium chloride	2,226.21	196.25	1,461.20				
Calcium sulphate	2.64	.30					
Calcium chloride	274.80	19.92	97.36				
Calcium carbonate	26.78	160.25	67.39				
Magnesium chloride	78.40		78.93				
Iron oxide and alumina	.64	.10	.29				
Silica	3.50	.24	.62				
	2,612.97	377.06	1,705.79				

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.
d In hypothetic combinations, in grains per U. S. gallon.

Midway field:
53. Standard Oil Co. well 7, sec. 12, T. 32 S., R. 23 E. Water from 2,600 feet, or 400 feet below a gas sand and about 100 feet above the oil. Analyst, Standard Oil Co., June, 1913.
54. Standard Oil Co. well 3, sec. 20, T. 32 S., R. 24 E. Water from 3,250 feet, or about 200 feet below the oil. Analyst, Standard Oil Co., February, 1911.
55. Standard Oil Co. well 1, sec. 28, T. 32 S., R. 24 E. Water from 2,390 feet, or about 400 feet above the oil. Analyst, Standard Oil Co., August, 1909.
Sunset field:
56. M. J. & M. M. Oil Co. well M. J. 6, sec. 36, T. 12 N., R. 24 W. Flowing water from 2,270 feet, or about 200 feet below top oil sand and above lower oil sand. Sampled by G. S. Rogers, July, 1914. Analyst, S. C. Dinsmore.
57. Kern Trading & Oil Co. well, in NE. ¼ sec. 31, T. 12 N., R. 23 W. Water from 2,924 feet, or about 200 feet below horizon of top oil sand. Analyst, Kern Trading & Oil Co., January, 1915.
58. Midway Northern Oil Co. well 5, sec. 32, T. 12 N., R. 23 W. Flowing water from 2,505 feet, or below top oil sand and about 100 feet above second oil sand. Temperature, 115° F. Sampled by G. S. Rogers, August, 1914. Analyst, Chase Palmer.
59. Sunset Security Oil Co. well 1, sec. 29, T. 11 N., R. 23 W. Flowing water, probably from sands between 2,992 and 3,997 feet, or below several shows of oil. Sampled by G. S. Rogers, September, 1915. Analyst, S. C. Dinsmore.

Mixed type.—In Tables 10 and 11 are shown analyses of waters of mixed meteoric and connate origin, altered presumably by the action of hydrocarbons. This type naturally overlaps on the two preceding, for few waters can be considered wholly meteoric or wholly connate, but it appears to have a fairly definite geographic distribution. (See p. 88.) The type may be defined as comprising primary alkaline waters that are characterized by less than 50 per cent of primary alkalinity and that contain practically no sulphate. Primary salinity usually ranges between 55 and 85 per cent and secondary alkalinity between 1 and 10 per cent. The concentration is intermediate between that of the reversed type and that of the brine, but generally ranges between 6,000 and 12,000 parts. (See fig. 4.)

Table 10 includes five analyses of this type of water from the Westside Coalinga field. In this locality the mixed type everywhere occurs in or below the oil measures and constitutes the bottom water, but so far as is known it does not occur above them. The only exception to this statement is found in the water which in the deeper portion of the field replaces the oil in the highest oil sand, the so-called "upper edge water." This is represented by analysis 62 and the bottom water by analyses 60, 61, 63, and 64. Two of these waters contain no sulphate whatever, in two others it is negligible, and in the other it amounts to 37 parts per million. The primary alkalinity ranges between 23 and 42 per cent and the other properties vary accordingly. The concentration ranges between 4,000 and 8,000 parts.

Analyses 65 to 73, Tables 10 and 11, represent waters of the mixed type in the Midway and Sunset fields. Generally speaking, these waters exhibit lower primary alkalinity and higher concentration than the Coalinga types; in other words, the mixture contains a somewhat larger proportion of connate water. In the Midway and Sunset fields this type of water is found both below and above the oil, No. 70, for example, occurring 700 feet above the main oil zone. The type is confined to the western edge of the fields or to the zone nearest the outcrop.

In No. 73 the sulphate amounts to 27 parts per million; in the remainder it is either absent entirely or present in negligible amount. The properties of reaction and the concentration show essential regularity within the limits defined, although Nos. 66 and 72 show lower primary alkalinity and higher concentration, indicating a larger proportion of connate water. Analysis 82 (p. 83) shows another example of this type from the Midway field.

Analysis 86 (Table 14, p. 85), represents a water of the mixed type encountered near the bottom of a well 5,135 feet deep in the Kern River field. It is similar in every way to the waters of this type from the fields on the west side of the valley, except that its concentration is

somewhat lower. In parts of the McKittrick field water of the mixed type, whose original source is generally believed to have been below the oil, has flooded the oil measures. About 30 analyses of the water obtained from oil wells in this field have been made available for the writer's study. All of them are very similar and belong to the same type. which is represented by analysis 89 (Table 14, p. 85).

TABLE 10.—*Analyses of mixed meteoric and connate water altered by action of oil, from oil wells in the Coalinga and Midway oil fields, Cal.*

	60	61	62	63	· 64	65	66
PROPERTIES OF REACTION IN PER CENT.							
Primary salinity	54.8	60.2	74.4	56.6	67.6	74.8	83.6
Secondary salinity	0	0	0	0	0	0	0
Primary alkalinity	35.6	36.0	22.8	42.2	30.2	24.4	11.8
Secondary alkalinity	9.6	3.8	2.8	1.2	2.2	.8	4.6
Per cent of rSO_4 in rSO_4+rCl	0	1.0	0	Trace.	.01	0	.01
CONSTITUENTS IN PARTS PER MILLION.							
Sodium (Na)	} 2,273	{ 2,951	1,885	a 1,749	} 3,315	{ 3,140	a 7,090
Potassium (K)		77	20	....		24	....
Calcium (Ca)	77	19	17	10	19	9.3	73
Magnesium (Mg)	81	53	18	6.3	28	·3.6	135
Iron (Fe)	22	Trace.	Trace.	} b 2.6	{ Trace.		} b 13
Aluminum (Al)	....	....	....		....		....
Sulphate (SO₄)	0	37	0	0.7	4.9	0	4.5
Chloride (Cl)	2,119	2,960	2,170	1,543	3,526	3,662	9,566
Carbonate (CO₃)	0	192	120	c 1,001	0	219	c 1,588
Bicarbonate (HCO₃)	3,013	3,013	1,049	....	2,903	1,708	....
Silica (SiO₂)	61	119	75	33	68	40	44
	6,116	7,891	4,822	4,345.6	8,390.9	7,939.9	18,513.5
Carbon dioxide	....	....	....	18	....	....	0
REACTING VALUES IN PER CENT.							
Alkalies:							
Sodium (rNa)	} 45.2	{ 47.4	48.3	a 49.4	} 48.9	{ 49.4	a 47.7
Potassium (rK)		.7	.3	....		.2	....
Alkaline earths:							
Calcium (rCa)	1.8	.3	.5	.3	.3	.2	.6
Magnesium (rMg)	3.0	1.6	.9	.3	.8	.1	1.7
Strong acids:							
Sulphate (rSO₄)	0	.3	....	Trace.	Trace.	0	Trace.
Chloride (rCl)	.27.4	29.8	37.2	28.3	33.8	37.4	41.8
Weak acids:							
Carbonate (rCO₃)	0	2.3	· 2.4	c 21.7	0	2.6	c 8.2
Bicarbonate (rHCO₃)	22.6	17.6	10.4	....	16.2	10.1	....

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.

Coalinga field:
   60. Section Seven Oil Co. well 5, sec. 7, T. 20 S., R. 15 E. Sampled by S. H. Hain, October, 1915. Analyst, S. C. Dinsmore.
   61. American Petroleum Co. well 2 N, sec. 30, T. 20 S., R. 15 E. Water from 1,916 feet, or 3 feet below main oil. Sampled by T. J. Crumpton, August, 1912. Analyst, S. C. Dinsmore, November, 1915.
   62. American Petroleum Co. well 21, sec. 30, T. 20 S., R. 15 E. Water from a short distance above the producing oil sand ("upper edge water"). Sampled by T. J. Crumpton, August, 1912. Analyst, S. C. Dinsmore, November, 1915.
   63. Nevada Petroleum Co. well 1, sec. 20, T. 20 S., R. 15 E. Water from 3,305 feet, or about 25 feet below lowest oil. Analyst, Smith, Emery & Co. Authority, Nevada Petroleum Co.
   64. Lucile Oil Co. wells 1 and 2, sec. 6, T. 21 S., R. 15 E. Water from sand probably in oil zone. Sampled by G. S. Rogers, October, 1915. Analyst, S. C. Dinsmore.
Midway field:
   65. Associated Oil Co. well 1, sec. 35, T. 31 S., R. 22 E. Water from 1,495 to 1,727 feet, or about 100 feet below lowest oil sand. Temperature, 120° F. Sampled by G. S. Rogers, July, 1914. Analyst, Chase Palmer.
   66. North American Oil Consolidated Co. well 71, sec. 16, T. 32 S., R. 23 E. Water probably from about 3,200 feet, or below the oil. Analyst, Smith, Emery & Co., March, 1914. Authority, North American Oil Consolidated Co.

TABLE 11.—*Analyses of mixed meteoric and connate water altered by action of oil, from wells in the Midway and Sunset oil fields, Cal.*

	67	68	69	70	71	72	73
PROPERTIES OF REACTION IN PER CENT.							
Primary salinity	64.0	62.6	76.0	77.2	69.0	82.0	74.2
Secondary salinity	0	0	0	0	0	0	0
Primary alkalinity	33.2	35.4	20.2	21.6	29.2	13.8	23.0
Secondary alkalinity	2.8	2.0	3.8	1.2	1.8	4.2	2.8
Per cent of rSO₄ in rSO₄+rCl	Trace.	.2	.01	.01	.1	Trace.	.4
CONSTITUENTS IN PARTS PER MILLION.							
Sodium (Na)	} 3,921	{ 3,627	a 3,595	a 5,933	4,188	} 8,437	{ 3,649
Potassium (K)		30			52		24
Calcium (Ca)	37	41	50	29	31	163	57
Magnesium (Mg)	41	17	48	21	21	94	23
Iron (Fe)	Trace.	.3	} b 1.7	{	Trace.		.3
Aluminum (Al)		6.6			5.2		4.5
Sulphate (SO₄)	1	14	3.2	6	11	3	27
Chloride (Cl)	3,977	3,608	4,370	7,125	4,593	11,123	4,364
Carbonate (CO₃)	0	0	c1,172	c1,784	108	0	0
Bicarbonate (HCO₃)	3,855	3,793			3,477	4,270	2,818
Silica (SiO₂)	136	122	47	117	125	108	98
	10,011	9,333.9	9,286.9	15,015	10,846.2	22,031	9,633.8
REACTING VALUES IN PER CENT.							
Alkalies:							
Sodium (rNa)	} 48.6	{ 48.8	a 48.1	a 49.4	48.8	} 47.9	{ 48.4
Potassium (rK)		.2			.3		.2
Alkaline earths:							
Calcium (rCa)	.5	.6	.8	.3	.4	1.1	.8
Magnesium (rMg)	.9	.4	1.1	.3	.5	1.0	.6
Strong acids:							
Sulphate (rSO₄)	Trace.	.1	Trace.	Trace.	.1	Trace.	.2
Chloride (rCl)	32.0	31.2	38.0	38.6	34.4	41.0	36.9
Weak acids:							
Carbonate (rCO₃)	0	0	c 12.0	c 11.4	.9	0	0
Bicarbonate (rHCO₃)	18.0	18.7			14.6	9.0	12.9

a Reported and calculated as sodium but includes potassium.
b Fe₂O₃+Al₂O₃.
c Reported and calculated as carbonate but probably in part bicarbonate.

Midway field:
 67. General Petroleum Co. water well 2, sec. 15, T. 32 S., R. 23 E. Water from 1,765 to 1,820 feet, or about 150 feet below the oil. Temperature, 102° F. Sampled by G. S. Rogers, July, 1914. Analyst, S. C. Dinsmore.
 68. Crescius Oil Co. water well 6, sec. 25, T. 32 S., R. 23 E. Water from 1,460 feet, or about 50 feet below the oil. Temperature, 97° F. Sampled by G. S. Rogers, June, 1914. Analyst, S. C. Dinsmore.
 69. Standard Oil Co. well 3, sec. 24, T. 32 S., R. 23 E. Water from 1,505 feet, or below tar sand and above oil sand. Temperature, 96° to 103° F. Analyst, Standard Oil Co., April, 1909.
 70. Standard Oil Co. well 2, sec. 14, T. 32 S., R. 23 E. Water from 2,000 feet below a show of gas but about 700 feet above the oil. Analyst, Standard Oil Co., July, 1909.
 71. August Water Co. well 3, sec. 31, T. 32 S., R. 24 E. Water from sands between 1,334 and 1,609 feet, or below the oil. Temperature, 109° F. Sampled by G. S. Rogers, July, 1914. Analyst, S. C. Dinsmore.
Sunset field:
 72. Sunset Monarch Oil Co. well F, sec. 26, T. 12 N., R. 24 W. Flowing water from 2,540 to 2,560 feet, or about 125 feet below top oil sand. Temperature, 93° F. Sampled by G. S. Rogers, July, 1914. Analyst, S. C. Dinsmore.
 73. Good Roads Oil Co. well 14, sec. 12, T. 11 N., R. 24 W. Flowing water from 3,550 feet, or about 2,500 feet below the oil. Temperature, 104° F. Sampled by G. S. Rogers, July, 1914. Analyst, S. C. Dinsmore.

RELATIONS OF THE TYPES.

Reference has already been made to figure 4, in which are shown the broader relations of the several types of water discussed above. The chief factors determining the character of the oil-field waters are the amount of alteration by the hydrocarbons that they have undergone and the proportions in which connate and meteoric waters have

entered into their composition. Broadly considered, the first factor is a function of the depth, but the second depends on structural conditions and is therefore a function of the geographic position. In figure 4 these two factors can not well be distinguished, and therefore in the following sections several groups of analyses are presented in which the two lines of variation may be studied separately.

VERTICAL RELATIONS.

Analyses 74 to 77, Table 12, represent four waters occurring in the southwestern corner of the Westside Coalinga field. The samples were collected at different times from four wells, and are therefore not as satisfactory as if taken from one well. However, the four wells are located within 1,200 feet of a central point, and as the water sands appear to be persistent within this area the four waters may be considered as occurring in the same well. Analysis 74 represents water from a depth of about 800 feet, and may include some water from a sand at 600 feet. Analysis 75 represents a water that corroded the casing at 1,160 feet; its exact position is not reported in the log, but a study of the logs of neighboring wells reveals a persistent water sand which would occur in this well at about 1,100 feet, and which is doubtless the source of this water. Analysis 76 represents water from a depth of 1,347 feet, or below the tar sands and about 250 feet above the oil, and No. 77 is the "bottom water" which occurs 25 feet below the main oil zone. It will be noted that Nos. 74 and 75 are secondary saline waters of the normal group, and that Nos. 76 and 77 are primary alkaline waters. No. 76 may be referred to the modified group and No. 77 to the mixed type of the altered group. The sulphate salinity ratio decreases from 80 per cent in the highest water to 0.6 per cent in the lowest and the ratio of carbonate to sulphate increases from 0.05 in the highest to 90.5 in the lowest.

In order to show the relations of these waters graphically the four analyses have been plotted in figure 5, A, as though they represented waters occurring in the same well. The vertical scale shows the distance in feet between the water sands and the oil zone. On the horizontal lines representing the water sands are plotted the percentages of the radicles in reacting values and the concentration of the water in parts per 5,000, and the points thus obtained are connected by lines to show the variations of each constituent. A glance at the figure is sufficient to show that the most marked changes take place near the zone of tar sands or between the second and third waters; the two upper waters are very similar and the lowest differs from the third chiefly in its higher chloride. The heavy line representing sulphate shows the most pronounced and regular variation, decreasing from 38 per cent in the highest water to 0.2 per cent in the lowest.
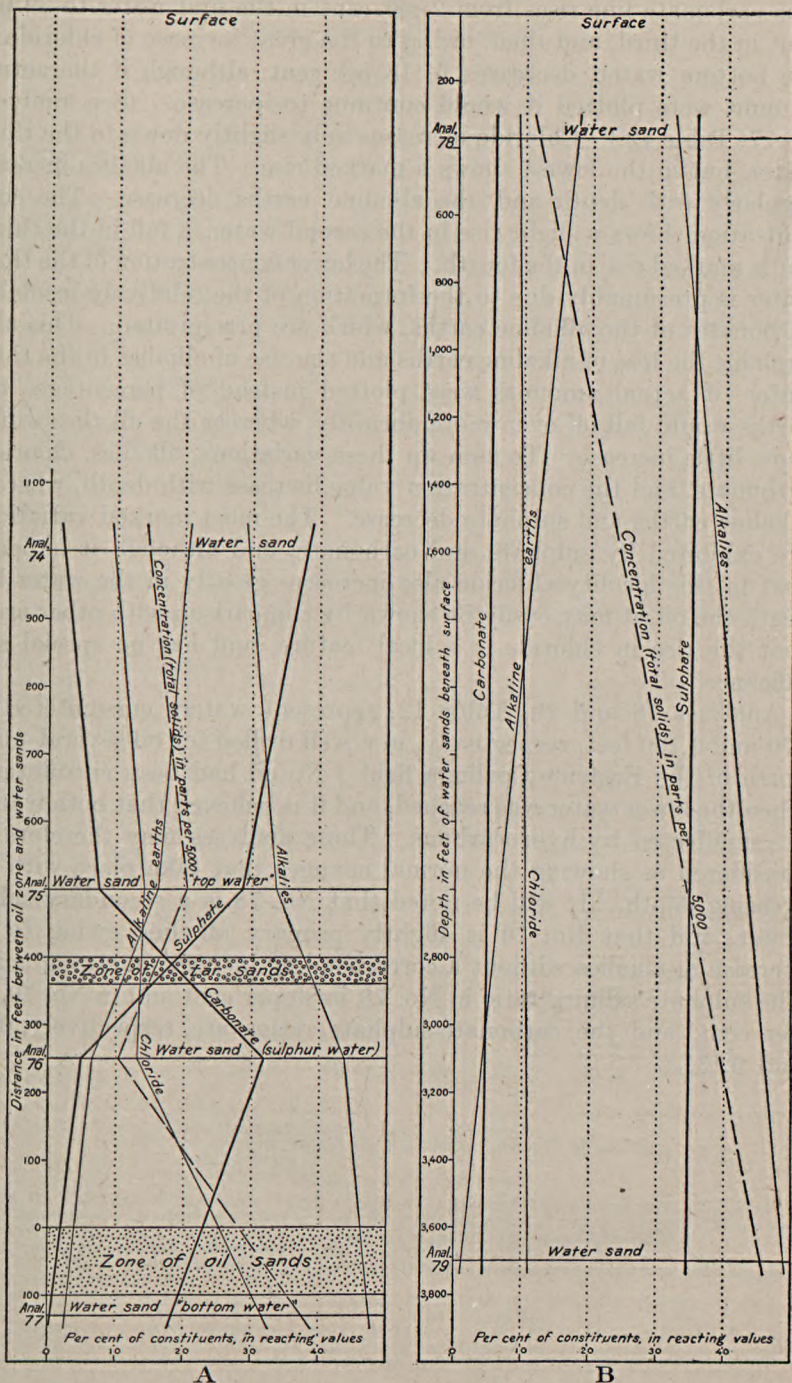
FIGURE 5.—Variation in chemical character of waters from different depths, showing alterations by hydrocarbons. The horizontal lines represent the horizon of the waters and on these lines are plotted their analyses. (See analyses 74 to 79, Table 12.) A, Four waters from neighboring oil wells in sec. 36, T. 20 S., R. 14 E., Coalinga field. (Note reversal of sulphate and carbonate values as the oil zone is approached.) B, Two waters from a well in sec. 27, T. 18 S., R. 15 E., several miles north of Coalinga field. (No oil was found to a depth of more than 3,700 feet, and the waters are probably unaffected by hydrocarbons. Note constancy of sulphate and carbonate values.)

The carbonate line rises from 2 per cent in the first water to 32 per cent in the third, and then, owing to the great increase of chloride in the bottom water, decreases to 18 per cent, although if the actual amount were plotted it would continue to increase. (See analyses 74–77, Table 12.) Chloride increases only slightly down to the third water, but in the lowest shows a marked rise. The alkalies increase regularly with depth and the alkaline earths decrease. The concentration shows a slight rise in the second water, a fall in the third, and a marked rise in the fourth. The lower concentration of the third water is presumably due to the formation of the relatively insoluble carbonates of the alkaline earths, which are precipitated. This also explains the loss of alkaline earths and the rise of alkalies in the third water; if actual amounts were plotted instead of percentages the earths would fall off even more abruptly, whereas the alkalies would show little increase. To sum up these variations, alkalies, chloride, carbonate, and the concentration value increase with depth, whereas alkaline earths and sulphate decrease. The most marked variations are exhibited by sulphate and carbonate, and although it happens that in this locality chloride also increases greatly in the water beneath the oil, it may easily be shown by comparison with other areas that the rise in chloride is a local feature, and has no special significance.

Analyses 78 and 79, Table 12, represent waters encountered at 370 and 3,700 feet, respectively, in a well drilled for oil several miles north of the Eastside Coalinga field. No oil had been encountered when the lower water was reached, and it is believed that both waters are unaffected by hydrocarbons. These analyses may therefore be considered as showing the normal changes that take place with increasing depth. It will be noted that No. 78 is a secondary saline water, and that No. 79 is slightly primary alkaline owing to an increase in alkalies without a corresponding increase in strong acids. The sulphate salinity ratio in No. 78 is 80 per cent and in No. 79, 76 per cent, and the carbonate-sulphate ratios are, respectively, 0.16 and 0.13.

TABLE 12.—*Analyses of ground water at different depths in the Coalinga oil field, Cal., showing alteration by oil or coal.*

[See fig. 5, p. 79.]

	74	75	76	77	78	79	80
PROPERTIES OF REACTION IN PER CENT.							
Primary salinity	59.0	67.0	36.2	63.8	64.6	91.2	21.8
Secondary salinity	36.8	18.6	0	0	24.0	0	0
Primary alkalinity	0	0	50.8	30.8	0	6.6	74.4
Secondary alkalinity	4.2	14.4	13.0	5.4	11.4	2.2	3.8
Per cent of rSO_4 in rSO_4+rCl	80.0	67.0	27.6	.6	80.0	76.0	29.4
Ratio of rCO_3+rHCO_3 to rSO_4	.05	.26	6.38	90.5	.16	.13	8.8
CONSTITUENTS IN PARTS PER MILLION.							
Sodium (Na) and potassium (K)[a]	804	933	717	2,872	544	3,000	526
Calcium (Ca)	303	193	27	75	124	28	13
Magnesium (Mg)	112	121	40	44	82	19	2.6
Iron oxide(Fe_2O_3) and alumina (Al_2O_3)	14	19	3	56	....	Trace.	4.6
Sulphate (SO_4)	2,181	1,673	170	23	1,243	4,421	74
Chloride (Cl)	404	606	332	2,961	232	1,040	130
Carbonate (CO_3)[b]	76	282	686	1,435	125	355	400
Sulphide (S)							83
Silica (SiO_2)	c 54	c 249	95	c 67	57	29	18
	3,948	4,076	2,070	7,533	2,407	8,892	1,251.2
Hydrogen sulphide (H_2S)			104				
REACTING VALUES IN PER CENT.							
Alkalies:							
Sodium (rNa) and potassium (rK)[a]	29.5	33.5	43.5	47.3	32.3	48.9	48.1
Alkaline earths:							
Calcium (rCa)	12.7	7.9	1.9	1.4	8.5	.5	1.4
Magnesium (rMg)	7.8	8.2	4.6	1.3	9.2	.6	.5
Strong acids:							
Sulphate (rSO_4)	38.3	28.7	5.0	.2	35.3	34.6	3.2
Chloride (rCl)	9.6	14.1	13.1	31.7	9.0	11.0	7.7
Weak acids:							
Carbonate (rCO_3)[b]	2.1	7.6	31.9	18.1	5.7	4.4	28.1
Sulphide (rS)							11.0
ANALYSIS AS REPORTED.[d]							
Sodium sulphate	96.76	100.33	14.37	1.90	70.80	382.05	5.84
Sodium chloride	38.93	56.81	31.99	286.00	22.37	100.30	12.52
Sodium carbonate	.66	1.35	56.68	126.00		27.54	39.01
Sodium sulphide							11.85
Calcium sulphate	59.08	10.12	.10		8.22		.50
Calcium carbonate	.82	20.76	3.90	10.90	12.13	4.07	1.54
Magnesium sulphate	25.42	28.53	.21		23.77		Trace.
Magnesium carbonate	4.99	4.54	7.95	8.90		3.82	.52
Iron oxide and alumina	.84	1.13	.16	3.30		Trace.	.27
Silica	c 3.15	c 14.54	5.63	c 3.90	3.33	1.70	1.03
	230.65	238.11	120.99	440.90	140.62	519.48	73.08
Hydrogen sulphide			6.09				

  a Reported and calculated as sodium but includes potassium.
  b Reported and calculated as carbonate but probably in part bicarbonate.
  c Includes suspended matter.
  d In hypothetic combinations, in grains per U. S. gallon.

74, 75, 76, 77. Water from different horizons in four wells of the Associated Oil Co., sec. 36, T. 20 S., R. 14 E. These wells are all within 1,200 feet of a central point, and the four waters probably occur in the same vertical section. Analyst, Smith, Emery & Co. Authority, Associated Oil Co.

74. Water well, 996 feet deep. Water chiefly from about 800 feet, or about 1,000 feet above the oil.

75. Oil well. Water corroded casing at 1,160 feet, and probably occurs in water sand at about 1,100 feet. Top of oil sand 1,542 feet.

76. Oil well. Sulphur water from 1,347 feet. Tar sand 1,170 to 1,205; top of oil sand 1,593 feet.

77. Oil well. "Bottom water" from 1,802 feet. Oil sand 1,712 to 1,778 feet.

78, 79. Standard Oil Co. well Domengine 1, sec. 27, T. 18 S., R. 15 E. No. 78 represents water from 370 feet; No. 79, water from 3,700 feet, at which depth no oil had been encountered. These analyses probably represent the normal changes that occur with increasing depth in waters unaltered by the oil. Analyst, Standard Oil Co.

80. Water from upper coal mine, sec. 26, T. 20 S., R. 14 E. Water issues from point just above the coal bed (in Tejon formation) and is probably unaffected by oil. Analyst, Smith, Emery & Co.

Figure 5, B, shows these two analyses plotted according to the scheme followed in figure 5, A, except that the vertical scale used is only about half as great.   Even on a smaller scale, however, the contrast between the two figures is striking.   The percentage values of sulphate and carbonate, instead of crossing, run practically parallel. The alkaline earths decrease greatly and the alkalies therefore increase. The percentage of chloride is about the same in the two waters.   The concentration figure increases greatly, however, so that all these constituents except the alkaline earths increase in actual amount. Analyses of water from other deep wells outside the oil fields on the west side of the San Joaquin Valley indicate that these changes are representive and that the amount of sulphate does not decrease and generally increases with depth.[1]   In general, the concentration increases and in many localities chloride shows a marked increase with depth, but this does not affect the relative proportions of sulphate and carbonate.

The analyses given above show that in the Coalinga field the alteration of the waters as the oil zone is approached is extensive, but in the Midway field the changes are less striking.   Analyses 81 and 82, Table 13, represent waters from the same well at depths of 1,380 and 1,947 feet, respectively.   A gas sand occurs at about 1,810 feet and an oil sand a short distance below the lower water, so that the section represented is roughly comparable to that shown in the lower part of figure 5, A.   These waters, however, are of partly connate origin and the proportion of sulphate even in the upper water is small.

The properties of reaction show only a slight change, primary alkalinity increasing from 28.6 to 31.8 per cent and the sulphate salinity ratio decreasing from 2.3 to 0.2 per cent.   The carbonate-sulphate ratio shows the most pronounced change, from 20 in the upper water to 165 in the lower.   There is also a marked difference in concentration, that of the lower water being over twice that of the upper.   It is evident that these waters differ in composition along the same lines followed by the Coalinga waters but that the total changes are much smaller.   In the Midway field water 600 feet apart may show only a slight difference in sulphate content, whereas in the Coalinga field waters in the same relative positions usually differ widely.

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

TABLE 13.—*Analyses of water from different depths in an oil well in the Midway oil field, Cal.*

	81	82		81	82
PROPERTIES OF REACTION IN PER CENT.			REACTING VALUES IN PER CENT.		
Primary salinity	68.6	67.0	Alkalies:		
Secondary salinity	0	0	Sodium (rNa) and potassium (rK) [a]	48.6	49.4
Primary alkalinity	28.6	31.8			
Secondary alkalinity	2.8	1.2	Alkaline earths:		
			Calcium (rCa)	.6	.5
Per cent of rSO$_4$ in rSO$_4$+rCl.	2.3	.2	Magnesium (rMg)	.8	.1
Ratio of rCO$_3$+rHCO$_3$ to rSO$_4$.	20	165	Strong acids:		
			Sulphate (rSO$_4$)	.8	.1
CONSTITUENTS IN PARTS PER MILLION.			Chloride (rCl)	33.5	33.4
			Weak acids:		
			Carbonate (rCO$_3$) [b]	15.7	16.5
Sodium (Na) and potassium (K) [a]	1,059	2,809			
Calcium (Ca)	11	26	ANALYSIS AS REPORTED.[d]		
Magnesium (Mg)	9.6	2.9			
Iron (Fe$_2$O$_3$) and alumina (Al$_2$O$_3$)	1.7		Sodium sulphate	3.31	.76
			Sodium chloride	108.40	281.50
Sulphate (SO$_4$)	38	8.7	Sodium carbonate	41.64	121.80
Chloride (Cl)	1,125	2,920	Calcium carbonate	1.65	3.80
Carbonate (CO$_3$) [b]	443	1,226	Magnesium carbonate	1.92	.61
Silica (SiO$_2$)	12	17	Iron oxide and alumina	.10	
			Silica	.71	1.00
	c 2,699.3	7,009.6		c 157.73	409.47

a Reported and calculated as sodium but includes potassium.
b Reported and calculated as carbonate but probably in part bicarbonate.
c Potassium, iodide, and borate absent.
d In hypothetic combinations, in grains per U. S. gallon.

81,82. Standard Oil Co. well, sec. 30, T. 32 S., R. 24 E. No. 81 represents water from 1,380 feet and No. 82 water from 1,947 feet. A small gas sand occurs between the two waters, and an oil sand a short distance below the lower. Both samples taken while drilling and analyzed by Standard Oil Co.

Analyses 83 to 85, Table 14, represent the vertical gradation in the Kern River field. As these waters are primary alkaline there is no sharp change in character comparable with the change from secondary salinity to primary alkalinity in the waters of the west side, but the same order of succession is observed, carbonate increasing and sulphate decreasing as the oil zone is approached. Analysis 86 represents water from a depth of 5,135 feet or over 3,000 feet below the main oil zone. Although occurring over 3,000 feet below the deepest of the waters just mentioned it is very similar to it in character, showing high alkalies, chloride, and carbonate, and no sulphate.[1] However, a water encountered at least 2,500 feet above this in the same well close to (probably below) the oil zone is very different in character; it is a secondary saline brine rather than a primary alkaline water, though as would be expected from its position it contains no sulphate. So far as is known, this water is much the most concentrated water and is the only brine that has been found in the Kern River field. An idea of its composition may be obtained from the following partial analysis,[2] and the properties of reaction estimated from this analysis are as follows: Primary salinity 89.5 per cent, secondary salinity 10 per cent, secondary alkalinity 0.5 per cent.

[1] Compare analysis 44, Table 7, p. 70, which represents water from a depth of 3,860 feet, or about 3,000 feet below the oil measures at the northern end of the Midway field.
[2] Mendenhall, W. C., Dole, R. B., and Stabler, Herman, Ground water in San Joaquin Valley, Cal.: U. S. Geol. Survey Water-Supply Paper 398, Table 60, p. 294, 1916.

Field assay of water occurring between 1,030 and 2,609 feet in Petroleum Development Co.'s deep well, sec. 4, T. 29 S., R. 28 E.

Parts per million.

Bicarbonate (HCO_3)	132
Sulphate (SO_4)	5
Chloride (Cl)	15,100
Total hardness calculated as $CaCO_3$	2,300
Total solids	25,000

Although definite groups of analyses showing the vertical gradation in other fields are not available, there is every reason to believe that the order of succession is the same. The total extent of the alteration may differ in different fields, and the point at which alteration is complete may be higher in some localities than in others, but these are merely local variations which remain to be determined in each field. In some localities an incompletely altered water may be found below the oil measures, but such occurrences are doubtless due to unusual geologic conditions. Thus, analysis 30, already discussed, indicates an only partly altered water occurring 600 feet below the oil measures, but this water is in Cretaceous strata and has probably had a very different history from the altered water more closely associated with the oil (analysis No. 64). However, as the migration and accumulation of oil in the fields of the San Joaquin Valley has been greatly influenced by angular unconformities in the strata, it is conceivable that surface water might enter at the outcrop of a lower formation, barren of oil, and migrate through it without complete alteration to a point below the oil measures. In a region of such complex geologic structure some apparent irregularities in the alteration of the water are to be expected.

TABLE 14.—*Analyses of waters from various horizons in the Kern River, Lost Hills, and McKittrick oil fields, Cal.*

	83	84	85	86	87	88	89
PROPERTIES OF REACTION IN PER CENT.							
Primary salinity	34.4	41.6	12.2	58.8	87.6	94.0	72.8
Secondary salinity	0	0	0	0	10.4	1.6	0
Primary alkalinity	4.4	33.0	76.2	40.2	0	0	24.0
Secondary alkalinity	61.2	25.4	11.6	1.0	2.0	4.4	3.2
Ratio of rSO₄ to rSO₄+rCl	62.8	20.2	8.0	0	5.7	Trace.	.6
Ratio of rCO₃+rHCO₃ to rSO₄	3	7	88	∞	.36	44.0	68.0
CONSTITUENTS IN PARTS PER MILLION.							
Sodium (Na)	22	*a* 51	*a* 296	1,550	*a* 4,773	*a* 7,635	*a* 4,132
Potassium (K)							
Calcium (Ca)	18	13	20	10	214	195	38
Magnesium (Mg)	4.2	1.2	8.6	1.2	228	144	52
Iron (Fe)	.1	*b* 5		.1	*b* 16	*b* 21	*b* 2.7
Aluminum (Al)							
Sulphate (SO₄)	21	12	7.5	0	634	17	28
Chloride (Cl)	9.1	35	58	1,418	7,744	11,946	4,766
Carbonate (CO₃)	0	*c* 52	*c* 384	0	*c* 145	*c* 464	*c* 1,513
Bicarbonate (HCO₃)	71			1,708			
Silica (SiO₂)	18	23	52		46	48	67
	127.4	192.2	826.1	3,821.3	13,800	20,470	10,598.7
REACTING VALUES IN PER CENT.							
Alkalies:							
Sodium (rNa)	19.4	*a* 37.3	*a* 44.2	49.5	*a* 43.8	*a* 47.0	*a* 48.4
Potassium (rK)							
Alkaline earths:							
Calcium (rCa)	22.2	11.0	3.4	.4	2.2	1.3	.5
Magnesium (rMg)	8.4	1.7	2.4	.1	4.0	1.7	1.1
Strong acids:							
Sulphate (rSO₄)	10.8	4.2	.5	.0	2.8	Trace.	.2
Chloride (rCl)	6.4	16.6	5.6	29.4	46.2	47.8	36.2
Weak acids:							
Carbonate (rCO₃)	0	*c* 29.2	*c* 43.9	.0	*c* 1.0	*c* 2.2	*c* 13.6
Bicarbonate (rHCO₃)	32.8			20.6			
ANALYSIS AS REPORTED.*d*							
Sodium sulphate		1.06	.65		705.65	1,116.23	459.11
Sodium chloride		3.39	5.56		1.79	14.30	139.32
Sodium carbonate		3.01	34.30				
Calcium sulphate					40.58	1.42	.71
Calcium chloride						6.85	
Calcium carbonate		1.88	2.96		1.35	21.15	5.01
Magnesium sulphate					10.50		1.40
Magnesium chloride					33.25	22.93	.27
Magnesium carbonate		.26	1.75		9.36	8.93	9.30
Iron and alumina		.30			.92	1.20	.16
Silica		1.36	3.06		2.69	2.83	3.89
		11.26	48.28		806.09	1,195.84	619.17

a Reported and calculated as sodium but includes potassium.
b Fe₂O₃+Al₂O₃.
c Reported and calculated as carbonate but probably in part bicarbonate.
d In hypothetic combinations, in grains per U. S. gallon.

Kern River field:
83. Kern River water at Bakersfield. Mean of 35 analyses of samples collected every 10 days in 1906. Analysts, F. M. Eaton and P. L. McCreary (U. S. Geol. Survey Water-Supply Paper 237, p. 56, 1910).
84. Standard Oil Co. water well, sec. 5, T. 28 S., R. 27 E. Water from 380 to 397 feet. Analyst, Standard Oil Co., October, 1913.
85. Standard Oil Co. well 1, sec. 27, T. 28 S., R. 27 E. Water from 1,990 feet to 2,018 feet or about 200 feet above tar and oil sands. Analyst, Standard Oil Co., January, 1915.
86. Petroleum Development Co., sec. 4, T. 29 S., R. 28 E. Well 5,135 feet deep. Water is from brown shale, containing shows of oil, but over 3,000 feet below producing oil zone. (U. S. Geol. Survey Water-Supply Paper 398, Table 61, p. 294, 1916.)
Lost Hills field:
87. Lindsay Incorporated Oil Co. well 1, sec. 7, T. 27 S., R. 21 E. Water from 180 feet, and probably not affected by oil. Analyst, Smith, Emery & Co.
88. Associated Oil Co. well 3, sec. 13, T. 26 S., R. 20 E. Water probably from a short distance above the oil. Analyst, Smith, Emery & Co. Authority, Associated Oil Co.
McKittrick field:
89. Associated Oil Co. well Del Monte 38, sec. 18, T. 30 S., R. 21 E. Water pumped with the oil. Analyst, Smith, Emery & Co. Authority, Associated Oil Co. This analysis is typical of the water associated with the oil in the McKittrick field.

AREAL RELATIONS.

The oil-field waters vary horizontally as well as vertically, but the horizontal or areal variation is due simply to the mingling in various proportions of meteoric and connate waters. No matter how effectually connate water may be trapped in a structural trough, it is evident that near the surface of the ground and also around the edges of the trough where the rocks outcrop there will be a certain admixture of meteoric water. Although a few very salty waters have been found close to the surface (see No. 87, Table 14, p. 85) they are generally confined to lower levels, and a marked increase of alkalies and chlorides with depth appears to be the rule. This phase of the mixing of fresh and salt waters has been sufficiently discussed in the preceding section, and the gradation from the outcrop toward the center of the trough will now be considered. Two phases of this gradation present themselves, first, the increase in chloride, which is a factor of simple mixing, and second, the change in the properties of the water, which is the net result of various chemical reactions. Since the chloride is not affected by hydrocarbons it furnishes a simple and convenient basis for comparing normal and modified as well as altered waters. The properties of reaction, however, furnish a more adequate basis for comparison and in studying waters of the altered group are especially valuable.

The examples given below are drawn from the Midway and Sunset fields, where it happens that the most complete data are available, but similar gradations have been observed in the Coalinga field and can doubtless be worked out elsewhere.

Variation in chloride.—Normal connate water contains about 19,000 parts per million of the chloride radicle and 16,000 parts of other constituents; ordinary surface water contains very little chloride and generally less than 3,000 parts of dissolved solids. The figures representing chloride and total solids show the greatest contrast and are therefore convenient indices for comparing mixtures of the two types. The carbonate figure also shows considerable variation, being very low in brine and generally higher in meteoric water.

In the accompanying table are shown a series of partial analyses of water from wells near Fellows in the northern part of the Midway field. The wells fall roughly along a line about coincident in direction with the dip of the strata. In the table they are arranged in order of their distance from the outcrop—American Oilfield Co.'s well 92 being about 1,600 feet from the outcrop and Associated Oil Co.'s well 3 about 10,000 feet beyond well 92. The analytical figures given for the water from the first four wells represent partial analyses made by the American Oilfields Co.; the figures given for the water from the last two wells are taken from complete analyses made by Smith,

Emery & Co. for the Associated Oil Co. The chloride values are accurately determined and are comparable throughout. The figures reported for soluble solids in the first four analyses are assumed to represent all the constituents except silica and the alkaline earth carbonates, and on this basis are comparable with the figures shown for the last two analyses. The "alkalinity" values of the first four waters are mutually comparable but do not represent alkalinity in the sense used elsewhere in this report; no comparable figures for the last two waters are available, but their alkalinity is known to be considerably lower than that of the others.

Partial analyses of water from oil wells near Fellows, Midway field, showing increase of salinity with distance from the outcrop.

	Parts per million.		"Alkalinity," per cent.
	Chloride (Cl).	Soluble solids.	
American Oilfields Co. well 92	400	6,630	0.01300
American Oilfields Co. well 73	2,840	8,660	.01350
American Oilfields Co. well 57	7,720	20,720	.01158
American Oilfields Co. well 23	14,480	26,480	.00625
Associated Oil Co. well 7a	17,631	28,970	....
Associated Oil Co. well 3	24,398	39,700	....

a See analysis 50, Table 8, p. 73.

In order to show these relations graphically the determinations have been plotted in figure 6. In the figure the horizontal scale represents the distance between the wells along a line between American Oilfields Co.'s well 92 and Associated Oil Co.'s well 3. All the wells fall close to this line except Associated Oil Co.'s well 7, which lies about 1,200 feet to the northwest. The figure shows fairly well the gradation from an essentially meteoric water to a connate water. If an analysis of water from still nearer the outcrop could be added it would doubtless show a still smaller amount of solids. On the other hand, the water from Associated Oil Co.'s well 3 is somewhat more concentrated than sea water and contains a slightly larger amount of chloride, and waters from points still farther from the outcrop do not show any further increase.

The remarkably regular increase in chloride and soluble solids shown by these analyses is not entirely a horizontal gradation, for the waters are not all from the same horizon. The water in American Oilfields Co.'s well 92 probably occurs about 600 feet stratigraphically higher than that in the Associated Oil Co.'s wells. This is suggested by the slight irregularities in the curves shown in figure 6, but the vertical component is not great enough to detract seriously from the significance of this regular and essentially horizontal gradation.

Relations of the mixed type.—Besides causing a simple variation in the chloride content the mingling of connate and meteoric waters leads to a series of reactions between the other constituents and produces corresponding changes in the properties of the waters. These changes may be observed in the waters of any one zone along a line leading away from the outcrop, but may best be studied in the waters of the altered group, whose complete alteration by the oil affords a uniform basis for comparison. The fact that the altered waters along the western or shallow edge of the Midway and Sunset fields are of the chloride-carbonate type, whereas those farther east are secondary saline brines, is due to the entrance of meteoric water at the outcrop,
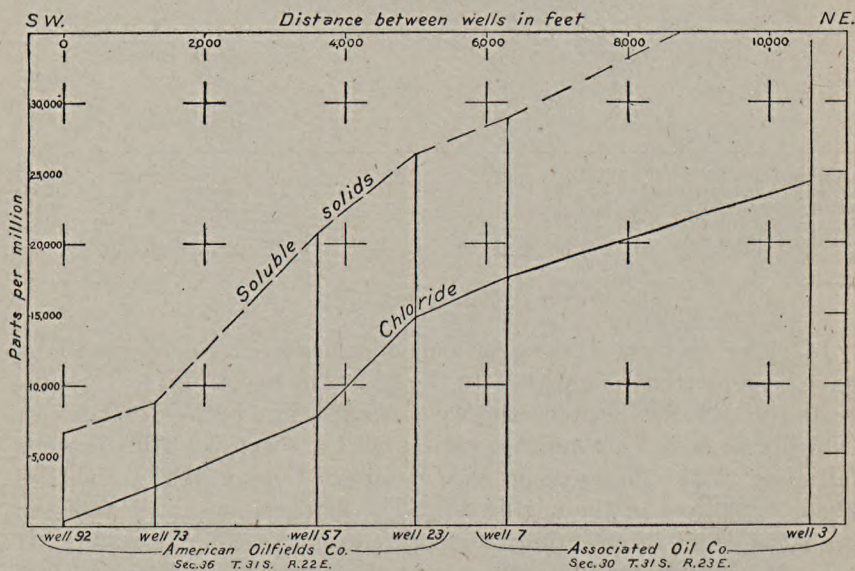
FIGURE 6.—Diagram showing increase in salinity of waters in the northern part of the Midway field with distance from the outcrop.

and the gradations that may be traced between this mixed type and the brines afford an interesting study of the mixing of meteoric and connate waters. The relations and derivation of the mixed type may more easily be understood if some of the reactions involved are first considered.

The reactions involved in the conversion of a sulphate water into a carbonate water, which forms the basis of the vertical gradation already described, are discussed on pages 94–99. Let it be assumed for the present that the process is a simple substitution of carbonate for sulphate. In unaltered sea water sulphate and chloride exceed the alkalies in 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 value of alkaline earths balanced by carbonate that can be retained represents only a very small percentage of the total concentration value, 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 is characterized by 21.1 per cent of secondary salinity, of which 9.2 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 value of primary salinity will be raised. If it be assumed, first, that the sulphate in sea water is entirely removed and an equal value of carbonate introduced, and secondly, that 7.6 per cent, or 2,660 parts per million of alkaline-earth carbonates are lost through precipitation, the properties will change as follows:

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

	Primary salinity.	Secondary salinity.	Secondary alkalinity.	Concentration.
Normal sea water...............................	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....................................	85.1	12.8	2.1	32,340

Since these reactions take place after the water has been entrapped in the sediments they are of course complicated by many indeterminable factors, and any attempt to reduce them to exact figures must be regarded as speculative. There is little doubt, however, that the oil-field brines have been derived from connate water by the general processes outlined above, as shown by their properties of reaction. (See Tables 8 and 9.)

The changes involved in the alteration of a meteoric water are similar but more extensive. The chief constituents of the surface and shallow ground waters of the fields of the west side are sulphate, alkalies, and alkaline earths. (See Tables 1 to 4.) If carbonate is substituted for the sulphate in these waters, it may be pre-

[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, 1892-93.

sumed that a considerable proportion of alkaline earth carbonates will be formed and removed by precipitation, leaving the chief constituents of the water alkalies and carbonate. These waters, however, are less concentrated than sea water, and therefore the amount of alkaline earths that can be held in solution in the presence of carbonate, if expressed as a percentage, will be much greater. The alteration of a meteoric water results essentially in a change from primary and secondary salinity to primary and secondary alkalinity, the percentage of the last property being only moderate. These changes are partly shown by the first three analyses in figure 5, A, and the complete transition from normal through modified to altered waters of meteoric origin by the analyses in Tables 4, 5, and 6.

Altered waters of the mixed type are derived by the mixing of primary alkaline waters (reversed type) and brines. It has been shown above that if all of the sulphate is removed from sea water and carbonate substituted the resulting brine will still be characterized by a considerable proportion of secondary salinity, which must be chloride salinity. The reaction that ensues when a sodium carbonate water is added may be written thus:

Secondary salinity+Primary alkalinity=Primary salinity+Secondary alkalinity

$$CaCl_2 \quad + \quad Na_2CO_3 \quad = \quad 2NaCl \quad + \quad CaCO_3$$
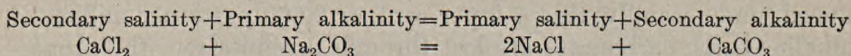
The addition of a primary alkaline water to a brine increases the alkalies without corresponding increase in strong acids and secondary salinity is therefore reduced. Secondary alkalinity may be somewhat increased, as the concentration of the brine is decreased by the addition of the more dilute water, but this change is not likely to be pronounced. If a sufficient amount of the sodium carbonate water is added it is evident that all the secondary salinity will be destroyed and that the water will then be characterized by only two properties, primary salinity and secondary alkalinity. (See analysis 46, Table 8, p. 73.) 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 most of the primary alkaline (meteoric) waters is only about 3,000 parts; hence, the concentration of the mixed water will be some intermediate figure, depending on the proportions of the mixture. If the brine component predominates primary salinity and the concontration will be high and primary alkalinity low, but as more and more of the meteoric water is added primary alkalinity will increase and primary salinity and concentration will decrease. (See analyses 60, Table 10, p. 76, and 72, Table 11, p. 77.)

The transition from brine to the mixed type is shown in figure 7, in which are plotted the reaction properties of the waters from four wells along the east-west line that separates the Midway and Sunset

fields. This line is oblique to the strike of the beds and the changes are therefore more gradual than they would be along a line normal to the strike. The total distance is about 18,300 feet, the wells being equally spaced. All the waters occur below the top oil sand and are believed to come from the same general horizon.

Complete analyses of the waters are given in Tables 9 and 11 (pp. 74 and 77). As shown in figure 7, the waters of the two wells near the outcrop are primary alkaline, whereas those farther east are brines. With 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.
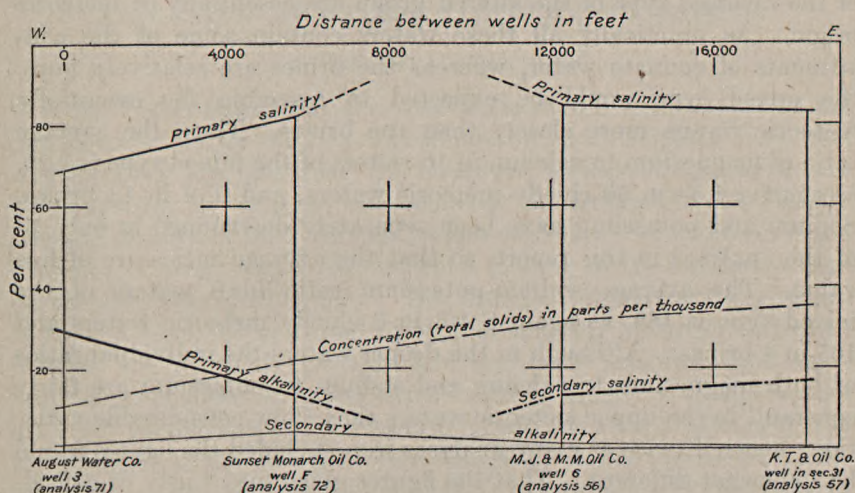
FIGURE 7.—Diagram showing gradation between waters of the mixed type in the western part of the Midway-Sunset field and the brines that occur at the same general horizon in the deeper territory to the east. Section extends from SE. ¼ sec. 31, T. 32 S., R. 24 E., to NE. ¼ sec. 31, T. 12 N., R. 23 W.

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 with distance from the outcrop, and in the distance covered by the figure more than trebles. It will be noted that there is much less difference between the waters of the two wells farthest from the outcrop than between those of the two 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. Between the first well and the outcrop, however, the water probably increases rapidly in primary alkalinity and near the outcrop passes to the reversed type.

The belief that this chloride-carbonate water, which is associated with the oil in the Westside Coalinga and in the western or shallower portion of the Midway and Sunset fields, is in reality a mixture of meteoric and connate waters is corroborated by other observations. Thus, the average ratios of magnesium to calcium and of sodium to potassium in waters of the mixed type are intermediate between those in the brines on the one hand and in the chiefly meteoric waters on the other. These ratios have been calculated in all the analyses given in this report, and the averages for each type are presented in the following tables. For the purposes of this comparison it may be assumed that all the waters of the normal and modified groups and of the reversed type of the altered group are essentially of meteoric origin. As practically all these waters contain some of the constituents of connate water, whereas the brines are relatively pure, the mixed type would be expected to resemble the essentially meteoric waters more closely than the brines. Thus, the average ratio of magnesium to calcium in 16 waters of the mixed type is 1.29, as against 1.34 in 50 chiefly meteoric waters, and 0.71 in 13 brines. Sodium and potassium have been separately determined in only 16 of the analyses in this report, so that the average ratios are of less value. The average sodium-potassium ratio in 6 waters of the mixed type is 188, as against 246 in 6 chiefly meteoric waters and 165 in 4 brines. Although in the deeper waters the individual ratios of both magnesium to calcium and sodium to potassium are fairly constant, in the upper meteoric waters they show considerable variation; hence if twice as many analyses were included the figures would be somewhat different. That the figures given may fairly be considered representative, however, is indicated by the writer's study of a large number of analyses not included in this report.

Average ratios of magnesium to calcium in reacting values $\left(\frac{rMg}{rCa}\right)$ in 79 analyses of different types of water from the Coalinga, Midway, and Sunset fields.

Type of water.	Coalinga field.		Midway-Sunset field.		Both fields.	
	Average ratio.	Number of analyses.	Average ratio.	Number of analyses.	Average ratio.	Number of analyses.
Surface water................	3.08	2	0.90	5	1.52	7
Ground water:						
Normal...................	1.04	18	1.35	4	1.09	22
Modified.................	.90	4	1.70	3	1.25	7
Reversed................	1.70	12	1.65	2	1.69	14
Brine....................	.90	1	.70	12	.71	13
Mixed...................	1.62	5	1.15	11	1.29	16
Averages:						
All meteoric waters......	1.35	36	1.31	14	1.34	50
All types...............	1.37	42	1.06	37	1.23	79

Average ratios of sodium to potassium in reacting values $\left(\frac{rNa}{rK}\right)$ *in 16 waters from the Coalinga, Midway, and Sunset fields.*

	Average ratio.	Number of analyses.
Chiefly meteoric water	246	6
Mixed type	188	6
Brine	165	4
Average of all types	204	16

CHEMICAL RELATIONS BETWEEN WATER AND THE HYDROCARBONS.

ALTERATION OF WATERS BY THE HYDROCARBONS.

NATURE OF ALTERATIONS.

It has been shown that the waters associated with the oil in the San Joaquin Valley oil fields are almost or quite sulphate-free, 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. In regions where sulphates are rare or only locally distributed the alternative hypothesis— that sulphide has accompanied the oil from below and that sulphate is formed by its oxidation—may have to be considered, but as this condition does not prevail in the oil fields of San Joaquin Valley this hypothesis need not be discussed.

REDUCTION OF SULPHATE.

The observation that waters associated with oil contain no sulphate is by no means new, for it was pointed out in 1882 by Potiiitzin [1] that the waters associated with oil in the Caucasian oil fields contain no sulphate, and this has been amply confirmed by later workers there

[1] Potilitzin, A., Zusammensetzung des die Naphta begleitenden und aus schlammvulkanen ausströmenden Wassers (abstract); Deutsche chem. Gesell., Ber., Band 15, p. 3099-b, 1882,

and in other fields.   Höfer [1] 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. However, neither Höfer nor, so far as the writer knows, any other writers on this subject have attempted to work out the chemical relations of the various types of water in any one field, but present merely isolated analyses of ''oil-field water,'' the position of which with regard to the oil is generally not stated.   The waters differ widely in chemical composition, some of them being concentrated brines very high in secondary salinity and others closely resembling the mixed (carbonate) type found in the San Joaquin Valley fields. The mixed type is less common but appears to be characteristic of the Russian and Galician fields.   The nearly pure alkali carbonate water (reversed type) found in the Eastside Coalinga field has apparently not been found elsewhere.   Some of the analyses show unusually large amounts of iodine and bromine, and several other rare elements have been reported, but the common characteristic of all the waters examined is the absence of sulphate.   In some waters this is so complete that barium salts have been found in the solution.[2]

The earlier investigators apparently regarded these sulphate-free waters more as chemical curiosities than as normal and reasonable phenomena, but the absence of sulphate has since been attributed to the reducing action of the hydrocarbons.   The reaction between sulphate and organic matter was suggested by Bischof [3] to explain the origin of certain sulphur deposits.   It is supposed that the sulphate is reduced to sulphide, which passes off as hydrogen sulphide, and that an equivalent portion of the oil or gas is oxidized to carbon dioxide and carbonate.   Höfer writes the reaction substantially as follows:

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

or

$$CaSO_4 + CH_4 = CaS + CO_2 + 2H_2O = CaCO_3 + H_2S + H_2O$$
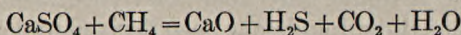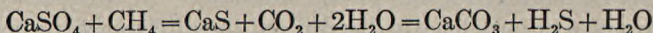
These reactions, however, are hypothetic and are open to several objections.   It has long been known that sulphate solutions are decomposed under some conditions in the presence of organic matter with the formation of hydrogen sulphide.[4]   It was shown by Meyer [5] and more definitely by Plauchud,[6] however, that this decomposition

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

[2] Idem, p. 28.

[3] Bischof, G., Chemische und physikalische Geologie, 2, pp. 144–164, 1851.

[4] Lersch, B. M., Hydro-chemie, pp. 235–238, Berlin, 1864.   Clarke, F. W., The data of geochemistry, 3d ed.: U. S. Geol. Survey Bull. 616, p. 111, 1916.

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

[6] 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.   Ètard, A., and Olivier, L., De la réduction des sulfates par les êtres vivants: Idem, vol. 95, p. 846, 1882.

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 [1] and whose importance from the standpoint of geochemistry appears to be considerable.   It has been found that certain bacteria have the function of reducing sulphate to sulphite or thiosulphate and that others reduce oxygenated sulphur compounds to hydrogen sulphide.[2]   On the other hand, certain bacteria can exist only in solutions containing hydrogen sulphide, which they oxidize and secrete as sulphur.   This sulphur is further oxidized in the course of metabolism to sulphate, but the excess of sulphur remaining in the organism after death may accumulate to form deposits of crystalline sulphur.[3]   In general, the sulphide-producing bacteria are anaerobic, being able to exist in the absence of air, whereas those which secrete sulphur are probably aerobic. The hydrogen sulphide in many natural waters is thus doubtless derived from aqueous sulphate solutions by the action of bacteria.

The action of similar organisms in ocean water has also been studied.   Van Delden,[4] in experimenting with a species that inhabits the estuaries on the coast of Holland, finds that these bacteria liberate in 27 days 843 milligrams of hydrogen sulphide per liter, which represents the reduction of 1,984 milligrams of sulphur trioxide. In this experiment he used sea water, to which was added a little potassium phosphate and organic matter; in another experiment with the same bacteria he used a prepared solution containing slightly more sodium chloride and more sulphate than sea water, and found that in 19 days 1,030 milligrams of hydrogen sulphide, equivalent to 2,424 milligrams of sulphur trioxide, were liberated. In the latter experiment the amount of sulphate reduced slightly exceeds that present in normal sea water.   Van Delden notes also that the activity of this species increases with the concentration of sodium chloride up to 60,000 parts per million, but that the addition of more sodium chloride produces a marked diminution in their activity.

Hydrogen sulphide has been repeatedly observed in sea water and has been quantitatively determined by several observers. Lebedinzeff [5] finds that water from a depth of 8,290 feet in the

[1] Winogradsky, Sergius, Ueber Schwefelbacterien: Bot. Zeitung, Nos. 31 to 37, 1887.

[2] See, for example, Beyerinck, M. W., Ueber *Spirillum desulfuricans* als Ursache von Sulfatreduction: Centralbl. Bakteriologie, Band 1, Abt. 2, pp. 1–9, 49–59, 104–114, 1895.   Also Saltet, R. H., Ueber Reduktion von Sulfaten in Brackwasser durch Bakterien: Idem, Band 6, Abt. 2, p. 648, 1900.

[3] For a summary see Stutzer, O., Die Wichtigsten Lagerstätten der Nicht Erze, Berlin, 1911; Phalen, W. C., The origin of sulphur deposits (translation from Stutzer's work): Econ. Geology, vol. 7, pp. 732–743, 1912.

[4] Van Delden, A., Beitrag zur Kenntnis der Sulfatreduktion durch Bakterien: Centralbl. Bakteriologie, Band 11, Abt. 2, pp. 92–94, 113–119, 1903.

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

Black Sea contains 6,550 parts per million of hydrogen sulphide, and Zelinsky[1] 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. Murray and Irvine[2] report the formation of unstable sulphide in sea water associated with the blue muds on the floor of the ocean and by a series of analyses show that some of the sea water drained from the muds contains only 50 per cent as much sulphate as normal sea water. They note a concomitant increase in the alkalinity of the water, due principally to the formation of carbonate, and a slight loss of lime, due to the precipitation of calcium carbonate. This implies a decrease in secondary salinity and an increase in secondary alkalinity, limited by the solubility of the calcium carbonate; or, in other words, an approach to the oil-field brines along the lines explained above.

It is therefore well established that sulphate may be reduced by bacteria in the presence of organic matter, but the bearing of this process on the development of the composition of oil-field waters is conjectural. It may be assumed, if desired, that the connate water was completely altered by the action of bacteria shortly after being entrapped in the sediments, as suggested by the observations of Murray and Irvine, but the alteration of the meteoric water is more difficult to explain. There is no evidence to show that even anaerobic bacteria can continue to exist in the muds after they have been covered with a thousand feet or more of other sediments and elevated into land, and certainly some time must have elapsed after the elevation before meteoric water penetrated to the zone of alteration. In fact, the writer is inclined to believe that in some localities meteoric waters are percolating down to this zone and are being reduced at the present time. Hence, unless it be assumed that bacteria are present in the strata to depths of several thousand feet the formation of the sulphate-free waters can not be ascribed to bacterial action, except perhaps in part.

The belief that hydrocarbons can reduce sulphate at moderate temperatures in the absence of bacteria has been tacitly accepted for many years, and few attempts have been made to prove it in the laboratory. In the anhydrous condition gypsum ($CaSO_4$) is a very stable compound, and it has been found that a temperature of about 700° C. is required for its reduction, even with a fairly active reducing agent, such as carbon monoxide.[3] In solution, however,

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[1] 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. Geog. Jour., vol. 1, p. 49, 1893.

[2] Murray, John, and Irvine, Robert, On the chemical changes which take place in the composition of sea water associated with blue muds on the floor of the ocean: Roy. Soc. Edinburgh Trans., vol. 37, p. 481, 1892–93.

[3] Hofman, H. O., and Mostowitsch, W., The reduction of calcium sulphate by carbon monoxide and carbon, and the oxidation of calcium sulphide: Am. Inst. Min. Eng. Bull., pp. 913–939, 1910.

sulphate is more readily reduced. The experiments of the earlier workers are discredited by the fact that no precautions were taken to exclude bacteria, and certain more recent attempts proved unsuccessful, but recently Kharitschoff [1] has published a note on some simple experiments that were 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. Cadmium chloride was used to indicate the formation of sulphide. Three samples exposed to direct sunlight for six months at ordinary temperatures showed no sign of reduction. Other samples, sealed and heated for 420 hours on a water bath, under which conditions a pressure of not less than three atmospheres must have been developed, showed a very faint coloration due to the formation of a trace of sulphide. In still other samples left open and heated for 420 hours at 96° C. some sulphide was formed. A solution of magnesium sulphate mixed with kerosene and heated in the open for 420 hours 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 necessary to insure complete reduction.

If it be admitted that the reduction of sulphate is accomplished directly by the constituents of oil it must still be recognized that the reaction as generally written, involving methane, is improbable. Methane, being itself a decomposition product, is the most stable member of the paraffin series, which are the most inert of the hydrocarbons; and although methane becomes much more active at higher temperatures and pressures it seems that the reduction of a sulphate solution would be accomplished less readily by this hydrocarbon than by others. The different members of the hydrocarbon series probably react with sulphate solutions in different degree, but this phase of the subject has apparently not been investigated. The unsaturated chain compounds, such as the olefines, acetylenes, and terpenes, doubtless behave in different manner from the paraffins, the naphthenes, or the aromatic hydrocarbons, not only in the ease of reaction but in the stages involved. In the reactions between some substances hydrolysis is probably important, and in those between other substances the action of oxidizing agents may enter. It is quite possible that certain constituents of the oil other than true hydrocarbons are active in the reduction of sulphate solutions, although for the sake of brevity the term hydrocarbon is used in this report to include all oil constituents. In any event, the reaction as written by Höfer (p. 94) can be considered only a condensed repre-

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

sentation of the type of change that takes place, the intermediate stages in the decomposition of the hydrocarbons on the one hand and of the sulphate on the other being as yet unknown.

Just as sulphate by reduction yields sulphide, so sulphide under other conditions may oxidize to sulphate. Whether alkaline sulphide is the first product of reduction or not, the final product is hydrogen sulphide, and this gas is readily oxidized to produce free sulphur, probably in accordance with the equation

$$2H_2S + O_2 = 2H_2O + 2S$$

Thus, free sulphur has been found in a number of marine muds, where it is doubtless formed by the oxidation of hydrogen sulphide derived from the sulphate in the sea water.[1] Under more strongly oxidizing conditions, or in the presence of certain bacteria, the sulphur becomes thiosulphate, sulphite, and finally sulphate. The complete reversion of hydrogen sulphide to sulphate is probably not widespread in deeply buried strata, but the change to free sulphur, which may take place even on the floor of the ocean, must be taken into account. It may also be noted that the oxidation of hydrogen sulphide to sulphur or sulphate results in the evolution of much heat,[2] and if the earth temperatures in oil regions are higher than elsewhere, as suggested by Koenigsberger and Mühlberg,[3] some of the excess may be contributed by this reaction.

FORMATION OF CARBONATE.

In the few published accounts of oil-field waters special stress is laid on the absence of sulphate as discussed in the preceding section, but no attempt has been made, so far as the writer can learn, to work out the relations of the various types of water or to explain the significance of the carbonate. If the reduction of the sulphate is to be ascribed to the action of hydrocarbons, however, the formation of carbonate is a necessary concomitant, and the presence of unusual amounts of carbonate in oil-field waters may be explained by this reaction.

The proportion of carbonate formed during the reduction of a definite amount of sulphate is not known and can not be determined until the stages involved in the reaction have been critically studied. Murray and Irvine report that the increase in the alkalinity of sea water associated with bottom muds is proportional to its loss in sul-

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[1] Buchanan, J. Y., On the occurrence of sulphur in marine muds and nodules, and its bearing on their mode of formation: Roy. Soc. Edinburgh Proc., vol. 18, p. 17, 1890–91; Clarke, F. W., The data of geochemistry, 3d ed.: U. S. Geol. Survey Bull. 616, p. 514, 1916.

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

[3] Koenigsberger, J., and Mühlberg, M., Über Messungen der geothermischen Tiefenstufe: Neues Jahrb., Beilage Band 31, pp. 107–157, 1911.

phate, but this observation merely indicates that the two changes are the result of the same process and does not throw much light on the proportions involved. In the transition from normal to altered waters in the oil fields the increase in carbonate is roughly proportional to the decrease in sulphate, but the loss by precipitation of alkaline-earth carbonates prevents the deduction of exact figures. The assumption made on page 88 that for the value of sulphate removed from the water an equivalent value of carbonate is introduced, is perhaps the best that can be made at the present time and is fairly adequate if the water alone is considered. As a matter of fact, however, the waters in the zone of alteration contain sufficient half-bound carbon dioxide to allow the formation of bicarbonate almost exclusively, and in addition many of these waters contain considerable free carbon dioxide. The amount of free and half-bound carbon dioxide in the zone of alteration seems disproportionately large in relation to the amount of hydrogen sulphide, even if the ready oxidation of hydrogen sulphide is taken into account.

The apparent disparity between the total amount of carbon dioxide formed and the amount of sulphate removed may be due to the fact that all the carbon dioxide is not derived from the oxidation of hydrocarbons. Several reactions are known by which carbonate may be derived from inorganic sources. Hilgard [1] finds that a solution containing free carbon dioxide in the presence of sodium sulphate dissolves calcium carbonate and forms sodium bicarbonate and a precipitate of gypsum. This reaction would partly explain the disappearance of sulphate and the formation of carbonate, but it would not account for the formation of hydrogen sulphide. If it is assumed, however, that the hydrogen sulphide is derived through the reduction of sulphate, the presence of free carbon dioxide may be explained by the following reaction, first investigated by Béchamp [2]

$$CaCO_3 + 2H_2S = Ca(SH)_2 + H_2O + CO_2.$$
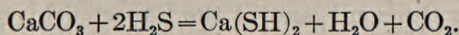
Under other conditions hydrogen sulphide may unite with calcium carbonate to form calcium sulphate and sulphur.[3] It is evident, therefore, that the disappearance of sulphate and the formation of carbonate may be the net result of several reactions. As the strata in the oil fields of the San Joaquin Valley do not contain much calcium carbonate, the reactions just discussed have probably not entered largely into the development of the chemical character of the waters, but the possibility that they have played some part should be duly considered.

[1] Hilgard, E. W., The geologic efficacy of alkali carbonate solution: Am. Jour. Sci., 4th ser., vol. 2, pp. 100-107, 1896.
[2] Béchamp, A., Recherches sur l'état du soufre dans les eaux minérales sulfurées: Annales chimie et phys., 4th ser., vol. 16, p. 234, 1869.
[3] Spezia, G., Sull' origine del solfo nei giacimenti solfiferi della Sicilia, Torino, 1892.

PRODUCTION OF GASES.

Whatever the reactions controlling the character of the oil-field waters may be, it is clear that sulphide, free hydrogen sulphide, carbonate, bicarbonate, and free carbon dioxide are formed. The particular significance of the gases hydrogen sulphide and carbon dioxide will be briefly considered.

Although the sulphide radicle is probably first formed during the reduction of sulphate, it is ordinarily so unstable that hydrogen sulphide may be considered the final product. 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. The strong odor of hydrogen sulphide may readily cause overestimation of the amount present in a water. The greatest amounts that have come to the writer's attention, which are reported in waters from the Eastside Coalinga field, do not exceed 350 parts per million, and few waters carry more than 50 parts. As the complete reduction of 10 parts of sulphate would yield 3.5 parts of hydrogen sulphide, it is evident that either the sulphate in the upper waters is not all reduced directly to hydrogen sulphide or else the hydrogen sulphide is being removed from the solution nearly as rapidly as it is being formed. Some of it may unite with iron to form iron sulphide, which is precipitated. A small amount of hydrogen sulphide has been found in some of the hydrocarbon gas, but the total quantity accounted for in this way is not great.

As hydrogen sulphide readily oxidizes to sulphur, even under very feebly oxidizing conditions, considerable amounts of it are doubtless oxidized to sulphur and so removed by precipitation from the waters above the oil measures.[1] 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 the Sunset field, in sec. 21, T. 11 N., R. 23 W., in pockets and fissures in the McKittrick formation, 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 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

[1] 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).

disseminated sulphur are not uncommon along the western edges of the Coalinga and Midway-Sunset fields, and it seems probable that these accumulations have been derived from sulphate by the reducing action of hydrocarbons.

The other important gaseous product of the reaction between sulphate and the hydrocarbons is carbon dioxide. As already stated, there is almost invariably sufficient carbonic acid to form bicarbonate exclusively in the waters in the zone of alteration, and in addition many of these waters contain a dissolved excess of free carbon dioxide. Unfortunately, the few determinations that have been made of the quantity of free carbon dioxide give no idea of the amount present in the water underground. The writer has seen several waters so heavily charged that they effervesced when they were brought to the surface, and the dissolved gas may cause some waters to rise or flow. Free carbon dioxide is present also in many of the modified waters above the zone of alteration, but it has not been observed in the normal waters, in many of which a deficiency of carbon dioxide and the consequent presence of some normal carbonate are observable.

The hydrocarbon gas of many of the California fields contains a considerable proportion of carbon dioxide, much of which, in the writer's opinion, has probably been formed in the same manner as the free, half-bound, and combined carbonic acid associated with the oil-field waters. In general, the gas in the shallower western portions of the Coalinga and Midway-Sunset fields contains more carbon dioxide than that in the deeper eastern portions. In other words, the natural gas near the outcrop generally contains more carbon dioxide than that several miles away. This is to be expected if the carbon dioxide is formed by the interaction of the sulphate water and the hydrocarbons, for most of the sulphate water enters the strata at their outcrops and it is therefore in this locality that the reaction should be most vigorous. The percentage of carbon dioxide in the gas generally ranges between 3 and 25, but the gas from a well about 600 feet deep in sec. 22, T. 19 S., R. 15 E., in the Eastside Coalinga field, contains 49 per cent of carbon dioxide. As carbon dioxide is inert it acts as a diluent in natural gas and lowers its heating value. The following table shows analyses of gas from wells in the Coalinga, Midway, and Sunset fields.[1] Analysis 7 represents gas from the deep eastern part of the Midway field; it will be noted that the carbon dioxide is low in this gas, and a number of other analyses of gas from the same locality show still smaller amounts.

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[1] A few other analyses are given by I. C. Allen and W. A. Jacobs (Physical and chemical properties of the petroleums of the San Joaquin Valley of California: U. S. Bur. Mines Bull. 19, p. 56, 1912)

Analyses of natural gas from Coalinga, Midway, and Sunset fields, Cal.

	1	2	3	4	5	6	7
Carbon dioxide	5.1	11.1	34.2	20.0	19.7	20.0	7.6
Carbon monoxide			.9				
Oxygen	1.1		.3	.0	.0	.0	.0
Methane	92.8	88.0	61.8	74.7	73.8	62.5	76.5
Ethane			.7	4.4	5.7	16.4	15.2
Nitrogen		.9	2.1	.9	.8	1.1	.7
Hydrogen sulphide	.5	.0					
	99.5	100.0	100.0	100.0	100.0	100.0	100.0
Heating value (British thermal units per cubic foot)		937	663	904	892	971	1,097

Coalinga field:
1. Well in sec. 11, T. 19 S., R. 15 E.   Analyzed by Kern Trading & Oil Co.
2. Several wells in sec. 25, T. 20 S., R. 14 E.   Analyzed by U. S. Bureau of Mines.   (Bur. Mines Bull. 19, p. 56, 1912.)
3. Well in sec. 36, T. 20 S., R. 14 E.   Analyzed by Smith, Emery & Co.   Authority, Associated Oil Co.
Midway-Sunset fields (samples 4, 5, 6, and 7 collected by G. S. Rogers in July, 1914, and analyzed by G. A. Burrell, of the Bureau of Mines):
4. Well 5, Hale-McLeod Oil Co., sec. 8, T. 32 S., R. 23 E.
5. Well 6, Chanslor-Canfield Midway Oil Co., sec. 31, T. 31 S., R. 23 E.
6. Well 5, Spreckles Oil Co., sec. 32, T. 12 N., R. 23 W.
7. Well 5, Honolulu Oil Co., sec. 6, T. 32 S., R. 24 E.

ALTERATION OF HYDROCARBONS BY WATER.

Despite the close association of petroleum and water in most oil fields the chemical relations of the two have apparently never received much attention.   Many oil men have developed from personal observation opinions concerning the effect of water on petroleum, but these opinions differ widely and little attempt has been made to corroborate them in the laboratory.   In fact, petroleum chemists have been occupied so largely in working out the complex constitution of petroleum and the processes of refining it that we know little of the effect on petroleum of any of the substances with which it comes in contact underground.   The great differences between petroleum in different regions are doubtless due largely to differences in the composition of the original organic matter and to differences in age and degree of metamorphism; but some of these broader differences, as well as most of the minor variations in the character of the oil from any one field, are probably due to the local action of natural agents.   Of these oxygen and sulphur are probably among the most important.

When oil is exposed to the air for some 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 a so-called paraffin oil for several hours the oil becomes black and asphaltic.[1]   Similarly, if solid paraffin or a paraffin oil is digested with sulphur it becomes black and asphaltic,[2] or if a light asphaltic oil of the type

[1] 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.
[2] See Köhler, H., Die Chemie und Technologie der natürlichen und künstlichen Asphalte, p. 119, Braunschweig, 1904.

produced in the Buena Vista Hills is used it also becomes heavier and more viscous and passes to a substance resembling solid asphalt. The chemical reactions involved in this change are probably of two kinds. A part of the sulphur may combine with certain oil constituents to form simple sulphur compounds or complex sulphur derivatives; another portion may unite with some of the hydrogen of the oil and pass off as hydrogen sulphide. By the loss of hydrogen a condensation or polymerization of the hydrocarbon molecules is effected, and this change is reflected in the increase in the gravity of the oil itself as it approaches solid asphalt. Oxygen acts in a similar way; some of it may be taken into combination to form complex acids or phenols and part of it may unite with the hydrogen of the oil to form water.[1] Oxygen has been determined in so few analyses of oil from the San Joaquin Valley fields that its relation to the gravity of the oil, except in a very broad way, is not known; but the percentage of sulphur has been determined in a great many samples and appears to bear a fairly constant relation to the gravity of the oil. If more than 0.75 per cent of sulphur is present the specific gravity of the oil is generally greater than 0.945 (18° Baumé). The sulphur content of oils of 0.985 to 1.000 specific gravity (12° to 10° Baumé) is usually 1 per cent or more, whereas that of oils of 0.875 to 0.905 gravity (30° to 25° Baumé) is generally less than 0.50 per cent.[2]

That oxygen and sulphur may be important agents in determining the character of petroleum is evident from the likelihood that the oil in its migration will encounter one or both of these common elements in some available form. Oxygen is probably the less important under ordinary conditions, but in some places the oil doubtless derives oxygen from oxygenated waters, and in others it may possibly be contributed locally by oxidizing agents such as manganese dioxide. The action of sulphur is probably more widespread, and sulphur is believed to be afforded abundantly by the reduction of the sulphate waters. There are other possible sources of sulphur, but they need not be considered here.

It is evident that in any one field the action of both oxygen and sulphur on the oil will be more or less localized, since ordinarily the quantity of these substances available is insignificant as compared with that of the petroleum. Most of the oil in the San Joaquin

[1] Mabery, C. F., and Byerly, J. H., The artificial production of asphalt from petroleum: Am. Chem. Jour., vol. 18, p. 141, 1896. See also Hausmann, J., and Pilat, S., Studien über die Oxydation der Petrolkohlenwasserstoffe: Cong. internat. pétrole Compt. rend. sess. 3, p. 378, 1907.

[2] Analyses of oil from the oil fields of San Joaquin Valley are given in the following publications: Arnold, Ralph, and Anderson, Robert, Geology and oil resources of the Coalinga district, Cal., with a report on the chemical and physical properties of the oils, by I. C. Allen: U. S. Geol. Survey Bull. 398, pp. 264–272, 1910. Allen, I. C., and Jacobs, W. A., Physical and chemical properties of petroleums of the San Joaquin Valley of California: Bur. Mines Bull. 19, 1912. Allen, I. C., Jacobs, W. A., Crossfield, A. S., and Matthews, R. R., Chemical and physical properties of the petroleums of California: Bur. Mines Tech. Paper 74, 1914.

Valley fields has migrated up from lower formations, and there is reason to believe that some of the variation in its composition and properties is the result of changes that have taken place during this migration. The free chemical energy of reacting substances and the time of contact are potent factors in chemical change, and these factors should be recognized in accounting for variations in the properties of oil that has migrated. An oil that is the first to traverse a given course comes in contact with reacting substances at their highest potential, and therefore becomes changed more radically than does the oil that follows it at the same rate. As soon as these reacting substances have become exhausted, then oil may pass them unaffected. Again, oil that moves with extreme slowness and remains a very long time in contact with reacting substances may undergo changes just as marked as though it had moved more rapidly in a new channel. In general, therefore, that portion of the oil which migrated first or farthest will be the most altered. Moreover, the oil nearest the surface or nearest the outcrop of the oil-bearing zone may be further altered by fresh supplies of descending sulphate waters. Therefore, the oil around the upper edges of the main body should as a rule be the most altered or, in other words, the heaviest and most asphaltic.

This reasoning is well borne out by the variations in the gravity of the oil in the valley fields. In the deeper portion of the Midway-Sunset field, for example, the specific gravity of the oil ranges between 0.933 and 0.875 (20° and 30° Baumé), but as the outcrop is approached the oil becomes heavier and most of the wells nearest the outcrop produce oil of specific gravity about 0.985 to 0.972 (12° to 14° Baumé). A part of this difference is probably due to the escape of the more volatile constituents of the oil in the zone along the outcrop, but variation in gravity several miles away from the outcrop can hardly be explained in this way. Furthermore, as a general rule, to which there are local exceptions, the highest producing oil sand carries heavier oil than the sands below. In portions of the Coalinga, Midway, and Sunset fields the producing oil sands are overlain at a distance of several hundred feet by the tar-sand zone, which contains sands partly impregnated with a very heavy, viscous tar. Some of the sands in this zone carry water of the modified type (sulphur water), and most of the tar sands become water bearing farther down the dip. So far as the writer knows this very heavy tar has never been analyzed, but the analyses of several samples of oil of 0.993 (11° Baumé) gravity show about 1.15 per cent of sulphur, and it may be presumed that the tar carries at least as much as this. In a general way the tar-sand zone marks the farthest limit of migration of the oil. It has been observed that oil which has migrated for some distance into sands that lie in angular unconformity with the

main oil zone generally becomes heavier with distance from the main body and finally passes to tar. Purely on the basis of field evidence, therefore, it would appear that among the important factors influencing the gravity of the oil are the distance that the oil has migrated, its present distance from the outcrop or its depth below the surface, and the extent to which it is or has been subject to contact with waters, especially meteoric (sulphate) waters.

There seems little doubt therefore that the local variations in the character of the oil are in part, at least, due to the action of sulphur and probably also of oxygen. Sulphate waters descending from the surface are to a large extent altered in the zone of tar sands, and the tar itself is thereby rendered still more asphaltic. To some extent, therefore, the tar sands may be conceived as protecting the main body of oil in the sands below. The same process goes on near the outcrop, although how far descending meteoric waters have affected the main body of the oil since it attained its present position is a matter of conjecture. It seems more reasonable to suppose that the oil which migrated first and farthest was considerably altered by the water that had previously occupied the sands, and that most of its alteration took place before it had come to rest in its present position.

SOLUBILITY OF PETROLEUM CONSTITUENTS IN WATER.

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.

The solubilities of some of the simple gaseous hydrocarbons have been investigated, with the results shown in the following table. The solubility decreases with increasing temperature, and at 40° C. (104° F.) may be only two-thirds to three-fourths of the solubility at 20° C. (68° F.). The solubility is generally decreased by the presence of mineral salts in the water but is increased to some extent by pressure.

Solubility of certain gaseous hydrocarbons in water.

[At 20° C. and 760 millimeters pressure, except propane, which is at 17.8° C. and 753 millimeters pressure.]

Name.	Formula.	Volumes soluble in 100 volumes of water.	Authority.
Methane	CH_4	3.31	Winkler.[a]
Ethane	C_2H_6	4.72	Do.
Propane	C_3H_8	6.50	Lebeau.[b]
Butane	C_4H_{10}	0	Frankland.[c]
Ethylene	C_2H_4	12.2	Winkler.[d]
Propylene	C_3H_6	22.1	Von Than.[e]

[a] Winkler, L. W., Die Löslichkeit der Gase in Wasser: Deutsche chem. Gesell. Ber., Band 34, pp. 1417–1421, 1901.

[b] Lebeau, Paul, Sur quelques propriétés physiques du propane: Compt. Rend., vol. 140, pp. 1454–1456, 1905.

[c] Frankland, Edward, Ueber die Isolirung der organischen Radicale: Annalen der Chemie, Band 71, p. 171, 1849. (Frankland states that butane is insoluble in water, but it is desirable that this early work be checked with the more refined methods now in use.)

[d] Winkler, L. W., unpublished data cited by Landolt-Börnstein, Physikalisch-chemische Tabellen, p. 604, 1905.

[e] Von Than, Carl, Der Absorptionscoefficient des Propylengases: Annalen der Chemie, Band 123, p. 187, 1862.

Methane and ethane are the predominating constituents of most natural gas, and water which has been in contact with gas is therefore likely to contain these hydrocarbons in solution. Propane has been found in some gas, but propane and butane are more commonly associated with light paraffin oil. Ethylene and perhaps propylene may occur in natural gas but are not common.

The hydrocarbons dissolved in the California oil-field waters are doubtless chiefly methane and ethane. Their presence in the water flooding an oil well is of little value in determining the source of that water, as they are rapidly soluble and may be taken up by the water while it is being raised to the surface. Their presence in water from a wildcat well in which no oil or gas has yet been found might be taken merely as a suggestion of the proximity of petroleum, but certainly could not be considered conclusive evidence. Methane in particular is so widely distributed that its presence in a water has little significance; ethane and ethylene are more generally associated with petroleum deposits and therefore have somewhat greater diagnostic value. The presence of propane would be still more significant, but as this hydrocarbon is not common in California oil or gas it would seldom be a factor in practical work.

The more complex hydrocarbon derivatives that are soluble in water are chiefly compounds containing oxygen, the commonest of which are probably the naphthenic acids. All the waters near the oil zone in the San Joaquin Valley fields are alkaline, and the presence of organic acids may be determined by acidulating the water. Organic acids if present in moderate amounts appear as a milky precipitate, but in some waters are present in so large amount that they separate out in large oily globules. Many of the waters near the oil measures or in the diatomaceous shale below respond to this reaction.

The naphthenic acids are the oxygen derivatives of the naphthenes (polymethylenes) and have the general formula $C_nH_{2n-2}O_2$. These compounds were observed by Hell and Medinger [1] in 1874, and in 1890 Aschan [2] studied them in detail and gave them the name naphthene carboxylic acids. The naphthenes are prominent constituents of much of the Russian, Galician, and Roumanian oil, and when such oil is exposed to the air, especially in sunlight, the acids tend to form.[3] These acids have been observed in waters associated with the Russian oil and have been studied by Kharitschoff,[4] who in recent years has published a number of papers on their properties and nature. Inasmuch as the naphthenes are, according to Mabery and Hudson,[5] important constituents of the California and other American oils, it is probable that naphthenic acids are to be found in the water associated with these oils also. Fatty acids have been reported in oil-field waters by several of the earlier investigators,[6] but their identification has since been questioned. However, Thompson [7] has more recently reported fatty acids (probably oleic and palmitic acids) in the waters from wells in the Grosny district, Russia. Kharitschoff,[8] in waters from the same locality, reports carbonates of ammonia and the amines, and Schidkoff [9] reported in the oil itself small quantities of formic and oxalic acids. Hydroxyl derivatives of the nature of phenols have been reported in California and other oils,[10] and these compounds may also be present in the oil-field waters. However, the naphthenic and perhaps the fatty acids, which may be grouped under the general term petroleum acids, are probably the commonest petroleum derivatives in oil-field waters. In alkaline waters these acids are doubtless present as alkali salts rather than as free acids.

So far as the writer knows, no attempt has been made to study or even to determine quantitatively the petroleum acids in California oil-field waters, although, as already stated, several chemists have detected them qualitatively. It has been suggested that the presence

[1] Hell, C., and Medinger, E., Ueber das Vorkommen und die Zusammensetzung von Säuren im Rohpetroleum: Deutsche chem. Gesell. Ber., Band 7, pp. 1216–1223, 1874; Ueber die Oxydation der im Rohpetroleum enthaltenden Säure, $C_{11}H_{20}O_2$: Idem, Band 10, pp. 451–456, 1877.

[2] Aschan, O., Ueber die in dem Erdöl aus Baku vorkommenden Säuren von niedrigerem Kohlenstoffgehalt: Deutsche chem. Gesell. Ber., Band 23, pp. 867–875, 1890; Band 24, pp. 2710–2724, 1891; Band 25, pp. 3661–3670, 1892.

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

[4] Kharitschoff's papers appeared mostly in Russian journals, but adequate summaries of them are given in the Chemical Abstracts and in the Journal of the Chemical Society of London.

[5] Mabery, C. F., and Hudson, E. J., On the composition of California petroleum: Am. Acad. Arts and Sci. Proc., vol. 36, pp. 255–283, 1901.

[6] Potilitzin, A., Zusammensetzung des die Erdöl begleitenden und aus Schlammvulkanen ausströmenden Wassers (abstract): Deutsche chem. Gesell. Ber., Band 16, p. 1395–a, 1883.

[7] Thompson, A. B., Oil fields of Russia, p. 93, London, 1908.

[8] Kharitschoff, K. V., Ueber die Analyse des Wassers aus den Bohrlöchern des Grosnyschen Bezirkes: Chem. Centralbl., vol. 78, p. 295, 1907.

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

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

or absence of these substances in a water may serve to determine whether the water is from a horizon very near the oil zone or far above it, but the validity of such a distinction obviously depends on the ease and rapidity with which the 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. In refining oil the naphthenic acids are usually removed by the addition of caustic soda, for the alkali salts of these acids are readily soluble in water. The alkaline-earth salts of the naphthenic acids are somewhat less soluble. Hence, when alkali carbonate water of the type associated with the hydrocarbons in many parts of the San Joaquin Valley fields is brought in contact with oil containing petroleum acids it may be inferred that alkali naphthenates or soaps will readily form and go into solution. The oil-field brines, however, contain no alkali carbonates and only small quantities of alkaline-earth carbonates, and the rapid formation of organic salts in these waters would probably be less common. In washing the ether solutions of the acids Holde [1] uses a concentrated solution of sodium sulphate in order to avoid dissolving the acids. As the acids are thus practically insoluble in strong solutions of sodium sulphate, and as most of the shallower oil-field waters are essentially solutions of sodium sulphate and chloride, it seems probable that brief contact of a shallow water with the oil would not suffice for the solution of these organic compounds.

It may therefore be inferred that alkali carbonate waters which occur near the oil zone or which have been mixed with the oil before being raised to the surface, are most likely to contain salts of the petroleum acids; that brines may or may not contain these compounds, and that normal top waters rarely contain them unless they have been allowed to stand in contact with the oil for some time. When oil stands exposed to the air, as in a sump, it is probable that naphthenic acids are formed by oxidation; hence most sump water, especially if it be of the alkali carbonate type, probably contains petroleum acids. Water which has been intimately mixed with oil in the form of an emulsion is also more likely to contain them. For these reasons it would seem that the value of petroleum acids as indicators of the original position of a water with respect to the oil zone is open to question. The rapidity with which they are extracted by different types of water must be investigated before their evidence can be positively relied on.

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[1] Holde, D., and Mueller, E., The examination of hydrocarbon oils, p. 232, New York, 1915.

Those who desire to examine oil-field waters for petroleum acids may find the following simple test of value. This test, which depends on the green color of copper naphthenates, was recently devised by Kharitschoff.[1]

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. The filtrate is added with 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.

VALUE OF WATER ANALYSES TO THE OIL OPERATOR.

Much of the foregoing discussion of the chemical relations of water and oil is necessarily hypothetic, owing to the unfortunate lack of chemical experimentation bearing on the subject, and although for the sake of simplicity only one broad hypothesis has been presented it is realized that discussion is by no means closed. However, the conjectural nature of the conclusions advanced do not affect the validity of the main facts presented in this paper, which relate to the composition and chemical properties of the oil-field waters themselves. There is no question that the normal ground waters are very different from those close to or below the oil measures, and that, broadly speaking, the horizon at which a water occurs is indicated by its chemical composition. According to the few analyses published the water associated with the oil in most oil fields is characterized by the absence of sulphate, but probably in few regions do these waters present such marked contrast with the shallower waters as in the San Joaquin Valley, in which sulphate is especially abundant. It would seem peculiarly unfortunate therefore if the operators do not take advantage of these favorable conditions to use the character of the water as a general index of its horizon, for the need for some easy means of determining the source of the water flooding a well is yearly becoming more pressing.

The gradations between the strong sulphate waters near the surface and the sulphate-free water near the oil measures have already been described. There is little question that in all the San Joaquin Valley fields the same order of change from the surface downward is to be observed, but the total extent of the change and the point above the oil at which it becomes complete are subject to variation. In the Westside Coalinga field all the data at hand indicate that the alteration of the water is not complete until the oil measures are reached, whereas in the Midway and Sunset fields completely altered

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

waters are found several hundred feet above the oil zone. In these fields, moreover, waters containing only small amounts of sulphate are found comparatively near the surface, and the change in the character of the water with depth is therefore less marked. It may be inferred by analogy that similar conditions exist in the Lost Hills fields and in the other structures of this type which are believed to contain oil. In the Eastside Coalinga field very different conditions prevail, and all gradations from a pure sulphate water to a pure carbonate water may be observed. At the same time the waters near the oil measures in this field generally contain some sulphate, and may in fact contain more than the waters 500 feet above the oil in the Midway and Sunset fields. These local variations do not affect the broad principles involved, but they are evidently of great practical importance, and only general conclusions can be drawn from an analysis until these variations have been worked out in the area in which the water occurs.

In order to work out the detailed changes between successive water sands in each area it is necessary that as many reliable analyses as possible be placed on record. The analyses given in this report are sufficient to show the general type of the chemical changes that take place, but they are not intended to constitute a description of local conditions. It is believed by the writer that within small areas the chemical character of water from the same horizon is sufficiently constant to justify correlations on the basis of the analyses, and hence that when a sufficient number of analyses of reliable samples have been collected and made available for comparison the horizon of an unknown water may be closely estimated. Thus, one of the larger companies in the Midway field is making a practice of collecting water samples while drilling the well and preserving the samples, or analyses of them, for future reference. If the well later "goes to water" a sample of this water is analyzed and the analysis is compared with those of the waters encountered while drilling. A marked difference in composition between the waters first above the oil measures and the water flooding the well is taken to indicate that the water flooding the well is from strata below the oil or that it has invaded the oil sand at some other point and has migrated to the well. This use of water 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 Midway-Sunset 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, it is probable that this method will be essential in the accumulation of an adequate amount of data regarding the character of the water in the 500 feet or so on either side of the oil measures. In the Westside Coalinga

field, however, fairly accurate estimates of the horizon of the waters can often be made on the basis of much less complete information.

A factor which might militate against the success of this method in some regions is the possibility that a flow of water may change in character during lapse of time. When large quantities of water are removed by one well from a sand, water which may be different in composition is drawn toward the well from distant parts of the sand. The variation in character is most noticeable when the water withdrawn from the sand is salty and is being replaced by fresh water, which enters at the outcrop. Replacement by fresher water is of course most likely to take place in shallow sands, and in general little or no change in character takes place in flows from deep-lying sands.[1] This condition should hold especially in the oil fields, where usually no effort is made to produce water from the deeper sands and where their normal contents are therefore disturbed as little as possible. Changes in the concentration of the water may be observed, but the relative proportions of the several constituents probably remain about constant, unless a considerable circulation is set up.

The variations in the chemical character of the waters as oil is approached may also be used as a guide in wildcatting. In many prospect holes this evidence will probably be put to little practical use, for marked changes in the character of the water generally do not occur more than a few hundred feet above the first showings of tar or gas. Contingencies may readily arise, however, in which corroborative evidence of the probable presence of hydrocarbons below will be of value. For example, if a well reaches a depth of 4,000 feet, and there encounters water very similar in character to that near the surface, and if at this point serious drilling difficulties involving great extra expense are encountered, the advisability of proceeding farther may be questioned. On the other hand, if the water at this depth contains no sulphate the prospect of finding oil a short distance below is decidedly more encouraging. It should be pointed out, however, that commercial quantities of oil or gas may not be necessary to produce an altered water. The writer has a number of analyses of water from prospect wells of the Standard Oil Co. in southern California, and although the water in all the wells which produced commercial quantities of oil is sulphate-free, that in several wells which gave only shows of oil also contains only small amounts of sulphate. However, in other unsuccessful wells the deep water, so far as the tests have been applied, contains more sulphate than the water near the surface. As far as commercial quantities of the hydrocarbons are concerned it seems probable that

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[1] Sanford, Samuel, Saline artesian waters of the Atlantic Coastal Plain: U. S. Geol. Survey Water-Supply Paper 258, p. 85, 1910.

when the evidence of the water is adverse it can be taken with more assurance than when it seems favorable.

The remarks in the preceding paragraph concerning the use of water analyses in prospecting are intended to apply only to the San Joaquin Valley region. If the writer's conception of the principles involved is correct, then, as oil is approached, similar variations in the character of the water should occur also in other regions. So far as is known, however, these variations have never been studied elsewhere, and in advance of definite knowledge it must be recognized that an extension of this method to other regions is based wholly on theory.

In using water analyses to predict conditions in unexplored districts a complication arises from the fact that the rate of change in the composition of the waters and the distance above the oil measures at which sulphate disappears are different in different areas. The chemical character of the oil itself may be involved in these differences, but observations in the San Joaquin Valley fields indicate that stratigraphic and structural conditions are of prime importance. If the bedding is sufficiently irregular to permit transverse migration of either the water or the hydrocarbons the water may be considerably altered some distance above the main body of oil. If the course of the water is influenced by fault planes or unconformities the variations in its character may be irregular. Structural conditions influencing the freedom of circulation are also very important, for they determine in a measure the quantity of sulphate that is brought down to be acted upon by the oil. In other words, a given quantity of oil may be able to reduce the sulphate in a large body of stagnant water, but if the water is in circulation and fresh supplies of sulphate are constantly penetrating to the oil measures the reduction may not be complete. Hence, if structural conditions in the area in question are such as to prevent circulation, a high concentration of chloride is to be expected; sulphate will probably be present in rather small amount even in the shallower waters and may be entirely absent in the waters several hundred feet above the oil zone. If, on the other hand, the circulation is relatively free and the outcrop of the beds not far distant, chloride will probably be low and a considerable concentration of sulphate may be present in the waters close above the oil measures.

In comparing the analyses of two different waters all the constituents must be taken into account; their relative values as criteria for comparison have been indicated elsewhere. General comparisons may be made of analyses reported in hypothetic combinations, but much more satisfactory results are obtained if the analyses are recalculated and the comparison made on the basis of the reacting values of the radicles themselves. The practice of attempting to estimate

the horizon of a water on the basis of a partial analysis can not be too strongly 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 distinguishing or correlating waters, chiefly because this constituent can readily be detected by its odor or by its ability to darken a silver coin immersed in the water. As many top waters contain hydrogen sulphide, whereas the waters below the oil contain it only in some localities along the border of the fields, this simple test may sometimes be of value. Owing to the ease with which hydrogen sulphide is oxidized, however, it can not be regarded as a very stable constituent of the water and its value as a criterion for comparison is limited. A complete analysis is always the most satisfactory. In conclusion, it may be reiterated that an analysis is of no value in comparison unless the sample is properly taken and the analytical work accurately performed, for otherwise very misleading conclusions may be drawn.

SUMMARY OF CONCLUSIONS.

Water-bearing sands are generally encountered above, below, and, in many places, in the oil measures in the oil fields bordering the San Joaquin Valley. The strata are lenticular and the correlation of individual beds except within limited areas is impracticable. The high pressure of the water in many of the sands renders it difficult to prevent the water from invading the oil sands and thus greatly reducing their productivity.

Some of the ground waters are as salty as ocean water, but others are fresh. This difference is believed to be the result of difference in freedom of circulation, which is controlled chiefly by the geologic structure. Where the structure prevents free circulation the ground water is salty, but where it does not and circulation is relatively free meteoric water has entered the beds and replaced much of the strong chloride water originally present. The ground water near the surface and near the outcrops of the beds is comparatively fresh, but the content of chloride generally increases with depth and with distance from the outcrop. The deeper waters trapped in structural troughs, like the Midway syncline, closely resemble ocean water in most respects and are believed to be only slightly altered connate water or fossil sea water.

The surface waters and shallow ground waters and also the deeper ground waters outside the oil fields on the west side of the San Joaquin Valley contain much sulphate. In the oil fields, however, the content of sulphate decreases with depth and ground waters near and

in the oil measures are practically free from sulphate. This decrease in sulphate is attended by a corresponding increase in carbonate, and in districts in which chloride is not abundant the waters near the oil measures are nearly pure carbonate waters. Where chloride is the predominating acid radicle, even in the shallower waters, carbonate is unimportant, and the chief change in character with depth is due to the disappearance of the sulphate. Sulphide and hydrogen sulphide appear near the horizon at which sulphate begins to decrease and are present in many of the waters above the oil measures, but the complete disappearance of the sulphate and of the sulphide are coincident. The amount of sulphide in the deeper waters is roughly proportional to the amount of sulphate in the waters directly above them, or nearer the surface.

Calcium and magnesium predominate in many of the surface waters, but sodium and potassium greatly predominate in the deeper waters. Most of the waters associated with the oil are therefore variously proportioned mixtures of solutions of alkaline carbonates and chlorides, the proportion of carbonate depending chiefly on the extent to which meteoric water is able to enter at the outcrop. Besides the change in character with depth the oil-field waters therefore exhibit progressive variations with distance from the outcrop, the predominantly carbonate waters being found near the outcrop and the predominantly chloride waters farther away. The final stage in this gradation is represented by the very salty waters, which are believed to be connate. Coincident with these changes in composition is a great increase in the total amount of dissolved solids.

The decrease of sulphate, appearance of sulphide, and increase of carbonate in the waters as the oil zone is approached all point to reactions between the oil-field waters and constituents of the oil or gas. It is probable that sulphate is reduced to sulphide by certain oil constituents whose carbon is simultaneously oxidized to products which eventually yield carbonate, though the stages involved in these reactions and the conditions under which they take place are not yet understood. These reactions not only alter the character of the waters but they also produce the gases carbon dioxide and hydrogen sulphide. Carbon dioxide, presumably thus produced, occurs in the natural gas of these fields in amounts ranging from 5 to more than 30 per cent. The greatest proportions of carbon dioxide are usually found in gas near the outcrop, where sulphate water can most readily enter the beds and where the reaction would naturally be vigorous. A large part of the hydrogen sulphide formed is probably changed to sulphur, some of which apparently reacts again with the oil to make it heavier and more asphaltic. It is significant that the oils contain-

ing the largest proportion of sulphur are in general the heavy oils close to the surface or to the outcrop of the oil measures.

The marked differences in chemical composition between the waters close to the oil measures and those at higher levels are believed to afford a means of estimating the position of a water with respect to oil. This knowledge should be useful in determining the source of water flooding an oil well and also in prospecting for oil or gas. The distance above the oil measures at which the marked changes in the composition of the water occur depends on local conditions, which remain to be determined in each field. The order of change, however, has been found to be uniform, and it is believed that the use of analyses in estimating the position of a water with regard to the oil will prove valuable to those engaged in the exploitation and development of the California oil fields.

List of water analyses.

Owner.	Designation.	Location.			Analysis No.	Page.
		Sec.	T.	R.		
Coalinga field:						
Acorn Oil Co	Well No. 1	2	20 S.	14 E.	46	73
American Petroleum Co	Well No. 2 N	30	20 S.	15 E.	61	76
	Well No. 21	30	20 S.	15 E.	62	76
Associated Oil Co	Water well	36	20 S.	14 E.	74	81
	Oil well	36	20 S.	14 E.	75	81
	Oil well	36	20 S.	14 E.	76	81
	Oil well	36	20 S.	14 E.	77	81
Associated Pipeline Co	Water well	18	20 S.	15 E.	10	59
California Oil & Gas Co	Water well No. 1	6	21 S.	15 E.	12	59
California Oilfields (Ltd.)	Well No. 2	10	19 S.	15 E.	15	62
	Well No. 16	14	19 S.	15 E.	16	62
	Well No. 16	26	19 S.	15 E.	27	66
	Well No. 37	27	19 S.	15 E.	35	69
	Well No. 5	29	19 S.	15 E.	34	69
	Well No. 1	34	19 S.	15 E.	40	70
	Well No. 15	34	19 S.	15 E.	36	69
	Well No. 31	34	19 S.	15 E.	41	70
	Oil well	2	20 S.	15 E.	39	69
Coalinga Homestake Oil Co	Water well	26	20 S.	14 E.	29	66
Coal mine		26	20 S.	14 E.	80	81
Diaz Creek			19 S.	14 E.	2	57
Kern Trading & Oil Co	Oil well	35	19 S.	15 E.	37	69
	Oil well	11	20 S.	15 E.	42	70
	Oil well	13	20 S.	14 E.	19	62
	Water well	15	20 S.	14 E.	43	70
	Oil well	25	20 S.	14 E.	22	63
	Oil well	25	20 S.	14 E.	23	63
	Oil well	25	20 S.	14 E.	24	63
Los Gatos Creek			20 S.	14 E.	1	57
Lucille Oil Co	Wells Nos. 1 and 2	6	21 S.	15 E.	64	76
Nevada Petroleum Co	Well No. 1	20	20 S.	15 E.	63	76
	Well No. 3	30	20 S.	15 E.	20	62
Ozark Oil Co	Well No. 3	26	20 S.	14 E.	21	62
Premier Oil Co	Well No. 3	24	19 S.	14 E.	18	62
Record Oil Co	Well No. 5	22	19 S.	15 E.	17	62
Santa Rosa Oil & Development Co.	Water well	12	21 S.	14 E.	30	66
Section Seven Oil Co	Well No. 5	7	20 S.	15 E.	60	76
Standard Oil Co	Domengine No. 1	27	18 S.	15 E.	78	81
	Domengine No. 1	27	18 S.	15 E.	79	81
	Water well No. 3	28	19 S.	15 E.	8	59
	Oil well	36	19 S.	15 E.	38	69
	Water well No. 2	36	19 S.	15 E.	9	59
Traders Oil Co	Water well	24	20 S.	14 E.	11	59
Union Oil Co	La Vista No. 4	4	20 S.	15 E.	28	66

List of water analyses—Continued.

Owner.	Designation.	Location.			Analysis No.	Page.
		Sec.	T.	R.		
Midway and Sunset fields:						
Associated Oil Co	Well No. 1	35	31 S.	22 E.	65	76
	Pioneer Midway No. 7	30	21 S.	23 E.	50	73
	Well No. 2	32	31 S.	23 E.	49	73
August Water Co	California Amalgamated Well No. 2.	35	32 S.	23 E.	26	63
	California Amalgamated Well No. 3.	31	32 S.	24 E.	71	77
Bitterwater Creek		29	11 N.	24 W.	5	57
Crescius Oil Co	Water well No. 6	25	32 S.	23 E.	68	77
Crocker Spring		18	31 S.	22 E.	4	57
General Petroleum Co	Carnegie water well	9	31 S.	22 E.	44	70
	Water well No. 2	15	32 S.	23 E.	67	77
Good Roads Oil Co	Well No. 14	12	11 N	24 W.	73	77
Honolulu Oil Co	Well No. 6	10	32 S.	24 E.	51	73
Kern County Land Co	Spring	23	10 N.	23 W.	6	57
Kern Trading & Oil Co	Oil well	31	12 N.	23 W.	57	74
Mays Consolidated Oil Co	Well No. 6	28	31 S.	23 E.	47	73
Midway Basin Oil Co	Oil well	28	31 S.	24 E.	32	66
Midway Northern Oil Co	Water well	32	12 N.	23 W.	14	59
	Well No. 5	32	12 N.	23 W.	58	74
M. J. & M. M. Oil Co	Well M. J. 6	36	12 N.	24 W.	56	74
North American Oil Consolidated Co.	Well No. 71	16	32 S.	23 E.	66	76
Potter Oil Co	Well No. 2	15	31 S.	22 E.	45	70
San Emigdio Creek a					7	57*
Standard Oil Co	Well No. 6	22	31 S.	23 E.	48	73
	Well No. 6	12	32 S.	23 E.	25	63
	Well No. 7	12	32 S.	23 E.	53	74
	Well No. 2	14	32 S.	23 E.	70	77
	Well No. 3	20	32 S.	24 E.	54	74
	Well No. 3	24	32 S.	23 E.	69	77
	Well No. 1	28	32 S.	24 E.	55	74
	Well No. 1	30	32 S.	24 E.	81	83
	Well No. 1	30	32 S.	24 E.	82	83
Stratton Water Co	Well No. 3	7	32 S.	23 E.	31	66
Sunset Monarch Oil Co	Well F	26	12 N.	24 W.	72	77
Sunset Security Oil Co	Well No. 1	29	11 N.	24 W.	59	74
Union Oil Co	Diamond well No. 2	13	11 N.	24 W.	53	74
Western Water Co	Water wells	5	31 S.	25 E.	13	59
Other fields:						
Associated Oil Co	Well No. 38	18	30 S.	21 E.	89	85
	Well No. 3	13	26 S.	20 E.	88	85
Frazers Spring		2	30 S.	21 E.	3	57
Kern River b					83	85
Lindsay Incorporated Oil Co	Well No. 1	7	27 S.	21 E.	87	85
Petroleum Development Oil Co	Oil well	4	29 S.	28 E.	86	85
Standard Oil Co	Water well	5	28 S.	27 E.	84	85
	Well No. 1	27	28 S.	27 E.	85	85
Ocean water					52	73

a San Emigdio Land Grant.   b Bakersfield.

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