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THE RELATION OF SULPHUR TO PETROLEUM DEPOSITS.

By Leland W. Jones.

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Petroleum that is free from sulphur is exceedingly rare. The association of sulphur and petroleum may be divided into two relationships:

1. Sulphur as a constituent of petroleum.
2. Sulphur that is merely associated with the petroleum.

In the majority of cases where sulphur is found in the vicinity of petroleum (associated with petroleum) sulphur is also found as a constituent.

1.

Sulphur as a constituent of petroleum.

Sulphur may be a constituent of petroleum in three forms.

1. Free sulphur.
2. Hydrogen sulphide or other inorganic compounds.
3. Organic compounds of sulphur.

Free sulphur.

Free sulphur is found as a constituent in the oils of the Mexico and Gulf Coast fields. " Both sulphur crystals and amorphous sulphur were found in the bottom of a tank car which held Beaumont petroleum." \*1.

In the Texas and Gulf Coast fields, the Petroleum undoubtedly contains sulphur because of the intimate relations of the two. There is so much sulphur associated with the petroleum that sulphur, sulphur dioxide, sulphuric acid, and hydrogen sulphide are taken to be signs showing the presence of oil in the vicinity in which they are found.

\*1. Eng. & Min. Jour. Vol 73, 1902. Page 353  
Chem. Ztg. Vol. 29, 1902. Page 896

" The oil found at the salt domes is in close contact with free sulphur, the two often occupying the same cavities. The limestone which contains the Beaumont oil contains free sulphur. In many of the Gulf Coast fields beds of free sulphur underly the oil horizons". \*1.

In view of the intimate association, it would be unusual if the oil did not contain a percentage of sulphur. This association of the two will be considered more fully under the heading of association.

"The oil from the Thornton Upton field contains from .1% to .095% of sulphur. The oil bearing sands lie immediately above the Greenhorn limestone in which shells of mollusks are very abundant. The oil is undoubtedly produced in part from the animal remains, and in part from carboniferous shales. There is gypsum found in the Red Beds below the oil, but no sulphur." \*2.

In this case, the sulphur was derived from the animal remains and formed with the petroleum at the same time, or has been added to the oil by percolating waters having sulphate in solution which was derived, possibly, from the gypsum of the Red Beds below. The latter explanation is unsatisfactory however, as the Red Beds are nearly 2000 feet below the Greenhorn limestone.

"The oil from the Coalinga field contains .03% to .77% of sulphur. The oil is of animal and vegetable origin and is found in sandy zones which are members of a diatomaceous and foraminiferal shale". \*3.

\*1. U.S.G.S. Bull. 716B.

\*2. U.S.G.S. Bull. 398 Pg. 209.

\*3. U.S.G.S. Bull 282 Texas Salt Domes.

In this case the sulphur was undoubtedly formed simultaneous with the petroleum and mixed with it during the formation process.

"The sulphur content of the oil from the Sunset-Midway fields seems to be related to the gravity of the oil. There is a direct relation between the gravity and the sulphur present. The heavier the oil, the greater the amount of sulphur present.

There are three producing formations:

The top zone produces oil of 14.9 Baume

The middle zone produces oil of 18.1 Baume

The bottom zone produces oil of 22.5 Baume "

"The top zone is the nearest to the water line, the water containing sulphate in solution. The oil zone nearest the water line contains the greatest amount of sulphur and is the heaviest ~~in~~ oil" \*1

"The sulphur content of Trinidad asphalt lead to a study of its percentages. There are two kinds of asphalt; hard and soft. The hard asphalts contain from 3.28 % to 9.76 % of sulphur while the soft varieties vary between .6 % and 2.29 %. The excess of sulphur in the hard asphalt over that in the soft would lead one to suspect that the sulphur had something to do with the hardening of the asphalt" \*2

When oil is exposed to the air for a period of time it becomes more viscous, darker, and heavier. This is due to the loss of volatile compounds and to oxidation. It has been demonstrated that oil will pass through the stages from light oil to heavy to asphalt if placed in proper conditions for either volatilization oxidation or both.

\*1 U.S.G.S. Prof. Paper 117

\*2 U.S.G.S. 695

Where asphalt is found far under the surface where conditions would be unfavorable for volatilization, it is reasonable to assume that oxidation in the absence of air has been responsible for the formation of the asphalt. \*1

As sulphates are oxidizing agents it is possible for them to combine with the hydrogen in hydrocarbons with the formation of hydrogen sulphide. Hydrogen sulphide is capable of further reduction resulting in free sulphur. With the oxidation the petroleum becomes denser and heavier. This change from sulphate to sulphide to free sulphur has been proven to take place under the influence of prolonged heat and pressure. This reaction also takes place under the action ~~the action~~ of certain bacteria which live in the presence of hydrocarbons.

In the example given of the oil from the Sunset-Midway field there seems to be little doubt but what the oil increases in density as the water zone is reached because the oil has been oxidized by sulphate which the water carries in solution. Hydrogen sulphide formed from the hydrocarbons has been found in the waters above the oil zones.

"Near the south end of the Sunset-Midway field there are commercial deposits of sulphur. No oil or tar seeps have been found in the immediate vicinity of the sulphur beds. Less than a mile away, however, there are deposits of brea". \*2. Undoubtedly there is some connection between their formation though as yet this relation has not been worked out.

\*1 References on the formation of asphalt  
 Proc. Amer. Phil. Soc. Vol 37 pg. 137  
 Jour. Soc. Chem. Ind. 1897 pg. 996  
 Geol. and Chem. Essays T. S. Hunt Ppgs. 87, 99, 145,  
 and 163 to 230

\*2. U.S.G.S. Prof. paper no. 117

\*1. "Sulphur is the most undesirable impurity in petroleum and is nearly everywhere present, except in the Appalachian oils and in certain heavy oils from shallow wells. The largest proportion that has ever come under my observation is 2.75% in the early Humble crude, about one third in solution, all that oil can hold; and two thirds combined. Sulphur was first observed in Canadian oil from Petrolia, which carried 1%. Next it was found in the oils of Ohio and later in those of Illinois, Oklahoma, Louisiana, and Kansas ; all carrying less than 0.5%".

"The presence of combined sulphur in petroleum has an especial interest to the geologist, for it is doubtless associated with the primary formation of the heavier varieties. Such large amounts as petroleum contain could not have had an origin in vegetable or animal matter; it must have been the result of secondary changes, in which the oil came in contact with beds of sulphur, the latter having been formed from sulphates in underground sulphate water by reduction of organic matter."

"In the formation of the heavier varieties of Ohio, Ill., Oklahoma, and Kansas in the great sea bed of this region there came the action of sulphur which increased the density of the oil and introduced sulphur in combination. This occurred concurrent with the decay of sea life yielding oil, or perhaps subsequently". \*1.

Mabery does not believe that so much sulphur could have had an origin in animal or vegetable matter. He reasons that a certain amount amount of animal or vegetable matter, containing a certain amount of sulphur, is productive of a certain definite amount of oil. Such reason is faulty because no one knows how

much animal or vegetable matter is necessary to produce a certain amount of petroleum. Different amounts of oil forming material may be needed under different conditions. It seems logical to me that the material which produces the oil also produces the sulphur. Perhaps in the oils with the highest percents of sulphur such as the early Humble crude with a sulphur content of 2.75% there is a possibility that some of the sulphur has been added from external sources. The great majority of oils only contain less than 0.1%, an amount which may easily be accounted for as having been formed by the same material which forms the oil and at the same time. The majority of authorities agree that oil is formed by the slow distillation of organic matter under anerobic conditions. This being the case, it would be odd if the oil did not contain sulphur as sulphur is a constituent of all organic matter.

#### Hydrogen Sulphide.

Hydrogen sulphide is a constituent of ~~the oils from~~ most of the oils from the Mexico and Gulf Coast fields. These fields produce the so called high sulphur crudes, oils which contain above 0.5% of sulphur and give off Hydrogen Sulphide. The following are a few examples.

Panhandle Field, Texas. \*1.

"A uniform water table underlies this field at about sea level. The zone of oil production is about 100 to 300 feet above this water table, and the big flow of gas is encountered about 100 feet above the oil. The surface elevations vary between 2900 and 3200 feet. There are two main producing zones in this area, the Granite Wash and the "Lime.

The Granite Wash development is confined to a small area several miles south of Borger, while the rest of the production is called the Lime.

"In the Granite Wash area, both the gas coming from the Big Gas" producing horizon above the oil and the gas coming from the oil contain less than 0.015% of hydrogen sulphide. No odor of  $H_2S$  could be detected!

" In the wells from the Lime district, both the gas from the Big Gas stratum and the gas coming with the oil contains between 0.20 and 0.65% of  $H_2S$  by volume. There appears to be a definite relation as to hydrogen sulphide content between different parts of the field. The gas from a well ten miles southeast of Borger, on what is probably the edge of the lime produces 0.20% of  $H_2S$ . Wells within a radius of 3 to 7 miles S-W, W, N-W, N, and N-E. of Borger contain from 0.45 to 0.55%. Two wells five and ten miles northwest of Borger produced 0.46 and 0.26% respectively. Wells from these areas produce so much of the poisonous hydrogen sulphide gas that precautions must be taken to prevent breathing in places where it may collect.

Big Lake field, Texas. \*1.

The Big Lake field is located 550 miles south of the Panhandle field. The average elevation is about 2700 feet above sea level. Gas is encountered in two zones. The upper zone contains a sweet gas in large quantities but small amounts of oil. This is in a "brown Sand" at a depth of about 2400 feet. Some of these wells have been known to flow 87 million cubic feet a day. The second from about 3000 feet below the surface contains a poison gas in

small amounts, 100 to 200,000 feet per day. This is the large producing horizon for oil. The lower gas is too corrosive and poisonous for use in gas engines, boilers and heating appliances. Analysis of eight samples show amounts of hydrogen sulphide ranging from 8.1% to 10.5%. The concentration seems to vary with the location of the wells. The wells in the extreme east part of the field produce the larger amount, and those in the southwest the lesser. Mccamey Field, Texas. \*1.

"The Mccamey oil field is located 35 miles west of the Big Lake Field. Although some gas producing strata are encountered above the oil, the poison gas in this field occurs with the oil in a lime formation. The gas is present in small amounts but the H<sub>2</sub>S percentage is high, averaging about 5.%".

The interesting fact concerning the Hydrogen sulphide production from these fields is that the H<sub>2</sub>S gas is, in all cases, intimately associated with the oil; and in the last two cases, the Big Lake and the Mccamey fields, H<sub>2</sub>S is found in the gas with the oil but not in the gas from the upper gas zones where there is no oil. Why is the hydrogen sulphide found with the oil only? It must be because of some relation between the two. This relation may be explained by theory of reduction of sulphates to sulphides by the presence of organic matter. As to why the reaction has not completed by reducing the H S to sulphur may only be a matter of time. As the oils do contain a large amount of sulphur, there is evidence that this reaction is or has been going on.

\*1. Bureau of Mines Serial No. 2776 H<sub>2</sub>S poisoning in the Texas Panhandle, Big Lake, and Mccamey fields of Texas. Yant & Fowler.

Also see Bureau of Mines Bull 231. H<sub>2</sub>S from Mexican oils.

There are innumerable cases where sulphur is found in petroleum but cases of hydrogen sulphide content are rather rare. This is to be expected as the  $H_2S$  would be completely reduced to sulphur

The following are a few other examples of oil with an  $H_2S$  content.

"Royalite well No.4 in Turner Valley, Calgary produces gas with a sulphur content which makes treatment in a scrubbing plant necessary". \*1.

"Hydrogen Sulphide gas in Texaco well". \*2. In Alberta.

Beaumont petroleum contains a large amount of  $H_2S$  gas. As the oil is underlain by large deposits of gypsum, it is not unreasonable to assume that the gypsum has been reduced by the action of the hydrocarbons to  $H_2S$  and has thus become a constituent of the oils.

Most of the oil from the salt dome region contains  $H_2S$ . This is to be expected because of the large amounts of sulphur which has been deposited, presumably by the reduction of gypsum or other sulphates. In a complete reduction of this kind, the  $H_2S$  stage is passed through and some of the gas left in the petroleum. In drilling through the salt domes, beds of gypsum are encountered which have probably been the source of the hydrogen sulphide and the free sulphur.

\*1. Montana Oil Jour. Feb. 12, 1927.

\*2. Oil and Gas Jour. 2/17/27 Pg. 130

Ammonium Sulphate.

"Oil shales taken from Sweetwater County, Wyoming yield from three to thirty four gallons per ton, and an average of sixteen pounds per ton of ammonium sulphate. The bitumen is known to be of animal origin." \*1.

The sulphur content as well as the ammonia present can easily be accounted for by the fact that the bitumen was produced by animal remains. The proportion of ammonium sulphate per ton of shale may seem large, but probably the amount of oil in the shale was much greater than it is now, the greater percent having been lost by volatilization. The ammonium sulphate would stay behind as an evaporation product.

Organic Compounds

Organic compounds of sulphur are a constituent of the Ohio, Lima Indiana, and Ontario fields. "Sulphides of the paraffine series have been isolated from the petroleum of the Lima Indiana fields which range from methyl sulphide  $C_2H_6S$  to hexyl sulphide  $C_{12}H_{26}S$ . In Canadian petroleum eight members of the paraffine series between  $C_7H_{14}S$  and  $C_{18}H_{36}S$  have been described."

This relationship indicates that there has been a chemical reaction between the petroleum and the sulphur. This reaction could have taken place in the formation process, the sulphur being produced by the organic material which gave rise to the oil.

\*1. U.S.G.S. 695 Pg. 727, 741.

\*2. J. Soc. Chem. Ind. 21(1902) 316.

There are several theories as to the origin of sulphur and sulphur compounds in petroleum.

1. If oil is derived from plant and animal remains it contains sulphur because of the sulphur contained in the original organic matter. See page six.
2. The sulphur might have been derived from gypsum or some other sulphate. It has been demonstrated that sulphate may be reduced by petroleum thus forming hydrogen sulphide and free sulphur, Many of the wells in the Gulf Coast fields are in close ~~pp~~ contact with beds of gypsum from which the sulphur could easily have been derived.
3. Sulphur might have been derived from the sulphates and sulphides present in percolating waters where the water is in close contact with the oil.
4. Percolating oil might dissolve sulphur which had been deposited at an earlier age and was present in the rocks through which the oil was percolating.

Sulphur as an associate of petroleum.

Sulphur may be associated with petroleum in the following forms:

1. Free sulphur.
2. Hydrogen sulphide.
3. Inorganic compounds other than hydrogen sulphide.

Free Sulphur.

In many cases, sulphur is found in the proximity of oil.

The following constitute examples.

The example of Beaumont petroleum containing free sulphur has been given. Beaumont oil is found very close to deposits of sulphur as are many wells of the Gulf Coast region.

"An analysis of the cap rock of Beaumont petroleum shows the following amounts of sulphur.

Free and organic sulphur	1.58%
Sulphuric acid in combination	.21% " *1.

"All of the salt mounds in this region are associated with sulphur. The limestones of the salt dome region are cavernous. In these spaces sulphur is frequently found. Many times the sulphur is chemically pure, crystals over an inch long having been found. Cavities that have been filled with water are often filled with sulphur crystals. In all cases, however, the sulphur is found in places where oil might have been at one time. Often cavities that contain oil are lined with sulphur. The following constitute a few of the examples that occur in the mound district."

"Spindletop. Sulphur occurs in, above, and below the oil bearing limestone.

\*1. U.S.G.S. 282.

It occurs largely in pores or openings in the limestone. Sulphur incrustations on the soil at gas or oil seeps are to be observed".

"Generalized column for Spindletop."

1. Sand, clay, thin limestone, occasional sulphur and pyrite.
2. Pyrite, most abundant just above the porous limestone.
3. Porous limestone containing sulphur and oil.
4. Gypsum, may be massive or mixed with clay or sand.
5. Rock salt to an unknown depth.

The sulphur in this case was probably derived from the gypsum by reduction. \*1.

"Matagora"

The sulphur occurs in caverns in the limestone. Some sulphur occurs in sediments near the oil horizon. \*1.

"Damon Mound".

Sulphur occurs in openings in the oil bearing limestone. In the sediments, and with gypsum underneath the oil horizon. There are from one to sixty feet of impure sulphur beds found above the cap rock of the oil horizon. Sulphur also outcrops on the surface, this together with gas showings led to the drilling.

"Sulphur mine" At Sulphur City, La.

Clay, sand, and gravel	300'	H <sub>2</sub> S
Shelly limestone	80 to 100'	Oil and tar.
Solid limestone	6 to 7'	
Sulphur and gypsum	110'	
Soft white rock	200'	

The sulphur alternates with beds of gypsum with the two occasionally mixed. The oil is black and tarry due to the association with the sulphur. Its gravity is only 7 Baume. \*1.

"Byran Heights"

Sulphur occurs in gypsum below the small showings of oil.

Regular occurrence of material in the mound district.

1. Unconsolidated sediments.
2. Porous limestone with oil.
3. Sulphur.
4. Gypsum.
5. Salt.

The sulphur is of varying thickness. The petroleum is associated with the porous limestone and the overlying sediments.

"Batson". \*1.

"The Batson Field produces the lightest oil of the costal plain. There is very little sulphur associated with the oil. This is additional evidence that the low specific gravity of some oils is produced by association with sulphur.

Excerpt from U.S.G.S. 540. The Sulphur Deposits in Park County, Wyoming. By D. F. Hewett. Pp 477-480.

"An interesting feature of the sulphur deposits is the proximity of a petroleum spring which lies within a hundred yards of the largest sulphur deposit. The oil is light and clear, enough being collected to run the lights at the camp. The sand at this point is dark brown and has an asphaltic odor."

Mr. Hewett does not say whither the oil is light colored or light in gravity when he states that the oil is light. Presumably he means that the color is light. The oil would undoubtedly be a heavy gravity oil.

Excerpt from U.S.G.S. Bull 540. Native Sulphur in

\*1. U.S.G.S. 282.

El Paso County, Texas. By G. B. Richardson. Pp 591.

" Concerning the origin of the sulphur, the most significant fact seems to be its association with gypsum, organic matter, and hydrogen sulphide. This association suggests their genetic relationship in as much as sulphur can be formed by the reduction of gypsum by organic matter. Gypsum plus organic matter results in calcium sulphide and carbonic waters which in turn produce calcium carbonate and hydrogen sulphide. Gypsum is however a stable compound and though it can be reduced by the action of heat, its reduction at ordinary temperatures except through the activity of alga or bacteria has not been proved. Possibly such favorable conditions existed during the formation of some of the sulphur which was apparently formed near the surface.

Example of occurrence: A bed three feet thick highly impregnated with undeterminable organic matter having a peculiar sulphurous odor and highly impregnated with sulphur crystals."

There is some question as to whether or not organic matter will, of itself, reduce sulphates. Some believe, rather, that it is the bacteria which all organic matter contains that is responsible for the reduction.

From U.S.G.S. 322 The Santa Maria Oil District, Calif.  
By Arnold and Johnson. Pp 48.

" Burning Monterey shale, burning underground with a disagreeable odor, oil cozing up at various points nearby, holes from which vapor issues were coated with delicate crystals of sulphur".

In this case, the relation between the sulphur and the oil\*  
is probably close. In all probabilities, the sulphur is contained in  
the shale. The sulphur may be the result of reactions between  
\*shale

organic matter and sulphates that led to the formation of the oil, in the shale by means of an oxidizing and thickening process. The Monterey shale is supposed by some to be the source of the oil in some of the fields of California.

Oil Shales. also see page 10.

The majority, if not all, of the oil shales contain sulphur in some form. It may occur as pyrite, sulphates, free sulphur, or organic sulphur. The shales contain from 0.3% to 4.0% of sulphur in its various forms. Such amounts of sulphur in oil shales can not be accidental. It must have had some part in the formation of the material that produces the oil.

Whither or nor oil shale contains oil as oil, or only organic matter which yields oil upon distillation is a question that has never been satisfactorily solved. If oil shales contain oil as such, the sulphur could account for the change from a liquid to a dry oil such as may be contained by the shale, on the other hand, if the shale does not contain oil as such but only organic matter that yields oil upon distillation, the sulphur is only the product of the organic matter being contained in it.

In the case where oil as oil is contained in the shale, part of the sulphur would come from the original material producing the oil, while part of it might have been added by any of the means hitherto mentioned.

The presence of the ~~oil~~ sulphur would indicate to me that oil as such was present in the shale, otherwise there would not have been reduction to free sulphur and the amounts that are present would not be so great.

### Tar and Asphalt.

The action of sulphur on petroleum leads to the formation of asphalt. The increase that takes place in the asphaltic content of oils has been shown to be produced either because of oxidation by sulphates or sulphides, or by means of evaporation or oxidation by air. When exposed to air as at seepages oxidation occurs without sulphur, the oxygen being derived from the air.

"A thick tar is usually formed where oil and mineral waters are in contact. Invariably where tar has been formed at depth, it has been found immediately above or below water bearing strata or has been found in contact with water at the outer edge of the pool. As tar is viscous, a small amount of it is able to seal in a reservoir thus protecting it from further action of the water". \*1.

### Hydrogen Sulphide.

Hydrogen sulphide seems to be a very common association of oil . This is especially true of the California oil fields. The following are examples:

\*2. "In the vicinity of the McKittrick and Midway fields there are a number of small springs which are sulphuretted. These springs are found in the region between Paso Robles and the San Joaquin Valley. The Hydrogen sulphide is probably derived from the sulphide minerals in the Tertiary sediments which border the plain."

\*1. U.S.G.S. Prof. Paper 117.

\*2. U.S.G.S. Water Supply Paper 338 Water Springs of Calif.  
By Gerald A. Waring.

The forementioned springs are only three miles from oil production.

\*1. "Santa Barbara County, Calif. Along the coast south of the Santa Maria oil field there are a number of springs containing sulphur and carbonate." These are located some 20 miles from the oil.

\*1. "Ventura county, Calif. The sulphur Mountain Spring located in the canyon of Sisar Creek six miles north of Santa Paula produces 15 gallons of sulphur water per minute.

Analysis:	Sulphate	584 parts per million by weight
	Sulphide	3.8
	H <sub>2</sub> S	2.2

This spring is very near to oil production.

\*1. "Los Angeles County, Calif. Near the Santa Maria oil fields on the south side of the Santa Susana Mts. 5 Miles north of Chatsworth. "

H <sub>2</sub> S	50
Sulphate	161 ( Parts per million by wt.)
Carbonate	338

These springs are very near to production.

There are ten sulphur springs in Venture and Los Angeles counties that are near to oil.

\*2. "Well n<sup>o</sup> 5 of the McKittrick oil co. ~~is the~~ ~~N.Y.~~ has been for several years the source of an immense quantity of warm sulphur water. The Arcola water well in the vicinity flows 3000 bbls. per day of strong sulphur water".

\*1. Water Supply Paper 335.

\*2. U.S.G.S. 406 Pg. 107 The McKittrick-Sunset Oil Region.  
By Arnold and Johnson.

From Oil and Gas Jour. 2/17/27 pg. 130.

"Hydrogen sulphide in Texaco well on the eastern end of Slave Lake, Alberta. At 1862 feet gas for 12 hours then water with  $H_2S$  and salt.

From U.S.G.S. 398 Coalinga Dist. By Arnold and Johnson.  
"At the Coalinga field, there is a very persistent water

zone which is called the Big Sulphur. The water from it is mal-odorous and blackish. It occurs just above the top producing horizon. No productive layer is found above this water zone. There are, however, several tar sands found above it in places. The water zone is considered the limit of upward migration of the ~~wil~~ oil in commercial quantities. In all of the seepages of the field where oil is accompanied with water, the water is heavily charged with  $H_2S$  hydrogen sulphide."

This is what one would expect according to the reduction oxidation theory. All of the sulphur springs in this area <sup>contain</sup> do not' oil, however, there is a decided possibility that the water is in close contact with oil ~~in~~ somewhere in its migration.

\*1. "Sulphur springs and sulphur water (water containing  $H_2S$ ) are associated with most of the oil fields of Wyoming. The Mowry shale throughout Wyoming contains a large amount of scales, bones, and teeth of fish, suggesting that their bodies might have been the source or partial source of the oil."

This being the case, some sulphur would have been derived f from the animal remains and would pass into the hydrogen sulphide stage. The presence of sulphur in these oil fields has usually been taken to denote animal origin.

\*1. U.S.G.S. 695 pg. 727.

From the U.S.G.S. 321 Oil and Gas of the Summerland District Santa Barbara County, California.

"The most prominent characteristics of the Summerland oil are its low gravity 12 to 16 degrees, its high percentage of asphalt (the highest of all Calif. oils.), its relatively high percent of nitrogen, and its relatively low sulphur content (.84%). The association of oil with oil has a deleterious effect upon the oil. For example, oil pumped from a certain sand in the Summerland field had a constant gravity until water began to enter the well. It then, after separation from the emulsion, had a lower gravity than it did before the water entered the well."

The absence of a large amount of sulphur may be accounted for by the fact that there is so much asphalt in the oil and the sulphur would be used up in its formation. The sulphur would be reduced to a sulphide and escape.

#### Organic compounds other than hydrogen sulphide.

##### Sulphuric acid. Sulphur dioxide.

The cap rock of Beaumont petroleum contains .21% of sulphuric acid. Sulphur dioxide and sulphuric acid are said to denote the presence of petroleum in the gulf coast regions. At present, there are no theories as to the relation between these and the oil.

##### Sulphates.

Analysis of the waters of the Appalachian fields show that sulphates are present in considerable amounts in the shallow non petroliferous rocks overlying the oil and gas strata, but are noticeably lacking in the waters associated with the oil and gas strata. This is in accordance with the oxidation-reduction theory.

From G. Sherburne Rodgers report on the Oil Field Waters of the San J Joaquin Valley, California. U.S.G.S. Bull. 653.

"In the fields of the San Joaquin Valley, as the oil zone is approached, the sulphates diminish in amount and sulphides appear. This shows that reduction has occurred. In the surface waters the sulphates of calcium and magnesium predominate. The amount of sulphide in the deeper waters is roughly proportionate to the amount of sulphate in the shallower waters."

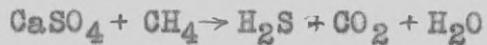
"The strata through which the water associated with the oil percolates contains a large amount of gypsum and other sulphates. In the normal ground waters of the west side of San Joaquin Valley, sulphate is the predominating radical. This is especially true near the surface."

"Outside of the oil fields, the deeper waters are characterized by high sulphate content. The amount bears no constant relation to depth and there is no sulphide present to speak of. In the oil fields, however, the sulphate concentration decreases with depth and practically disappears a certain distance above the oil zone. Many of the waters associated with the oil do not carry any sulphate and most of them contain less than one percent."

"The sulphide is undoubtedly formed by the reduction of sulphates. It may be still further reduced to free sulphur if it does not escape. As much gypsum is scattered throughout the rocks of this region it probably furnishes a source of the sulphates."

"Sulphide is found only near the hydrocarbons. The most pronounced sulphur waters are found in wells located near the outcrops of oil sands which draw their water from the strata below the oil. There is also found a high carbonate concentration near the oil, but no sulphate.

"It has been found that certain bacteria have the power to reduce sulphate to sulphide. This takes place under ordinary temperatures and pressures. This reduction can be accomplished by organic matter alone but high pressure and temperature are necessary. Excess of sulphur remaining in the organisms after death may form deposits of crystalline sulphur."



"Most of the sulphur of the McKittrick and Sunset regions is amorphous. This is intimately mixed with hydrocarbon material. Hydrocarbons seem to occupy 20% of the amorphous sulphur."

"The hydrocarbon gasses from most of the California fields contain a large amount of carbon dioxide. This is derived from the reaction between the oil and sulphates. Practically all of the waters contain enough of it to produce bicarbonate in the zone of alteration. The gas of the shallower western portion of the Coalinga and Midway-Sunset fields contains more carbon dioxide than in the deeper eastern portions. This is to be expected if the carbon dioxide is formed from the interaction of oil and sulphate for most of the waters enter the strata through their outcrops and it is there that the reaction would be most vigorous."

"That oxygen and sulphur may be important agents in determining the character of oil is evident because the oil in its migration is liable to encounter either or both of these elements in available form. Sulphur, however, is more accessible than oxygen."

"The percentage of sulphur bears a distinct relation to the gravity of the oil.

1.6% of sulphur gives a gravity of	1.2° to 10°
.75% of sulphur gives a gravity of	18° or over
.5% of sulphur gives a gravity of	25° to 30°

"In the deeper portions of the Midway-Sunset field the gravity runs from twenty to thirty degrees. As a general rule, the higher the producing sand the greater the gravity."

"The variations in the chemical character of the water as the water is approached may act as a guide in wildcatting. Marked changes as a rule do not occur more than a few hundred feet above the first showing of oil or gas or tar. For example, if a well reaches a depth of 4000 feet and there encounters water similar to that at the surface, the advisability of proceeding further may be questioned. However, if the water at this point contains no sulphate there are hopes of obtaining oil. Commercial quantities of gas or oil are not necessary to produce alteration however. As far as commercial quantities are concerned, it seems probable that when the evidences of the water are adverse it can be taken with more assurance than when it seems favorable. The decrease of sulphate, the appearance of sulphide and carbonate in the waters as the oil zone is approached indicates reactions between the oilfield waters and the constituents of the oil or gas".

From Calif. Oil Field Waters By Chase Palmer published in Economic Geology Vol 19 1924 Pg. 623.

"Within the oil field limits sulphate waters, the normal ground waters of the west side field, extend downward to a short distance above the oil measures. Outside of the oil field limits they often extend to much greater depths.

From Economic Geology Vol. 12 1917. Interpretation of Oil Field Waters By G. Sherburne Rodgers.

	%SO <sub>4</sub>	Parts per million	%CO <sub>2</sub>	parts million
Zone A. 1000' above oil.	38.3	2181	2.1	76
Zone B. 450' above oil.	28.7	1673	7.6	282
Zone C. 150' below tar sand. 250' above oil.	5.0	170	31.9	686
Zone D. 25' below oil.	0.2	23	18.1	1435

From Water Supply Paper 389 Ground Water of the San Joaquin Valley, California. By W. C. Mendenhall, R. B. Cole, Herman Stabler.

"The wells of the San Joaquin Valley, California yield three general types of water in relation to geographic position north of Tulare county. The east and west side types, named from their position in the valley are distinct from each other in their difference in sulphate content. The west side waters are nearly all high in sulphate content. None have a low sulphate content. Few wells on the east side north of Kern county contain more than ten parts per million." (See plate 2 of W.S.P. 389.)

Most of the production north of Kern County occurs west of the line dividing the high and low sulphate areas in the high sulphate territory. The sulphate content of the waters has not been worked out as far west as the producing fields. A few wells have been drilled in the low sulphate territory but most of them did not contain oil. Theoretically, oil should occur in the low sulphate area. Perhaps future drilling will find production in this area.

The Kern River field just north of Bakersfield is in an area of low sulphate concentration. No waters containing over six parts of sulphate per million. <sup>The majority contains only a trace.</sup> South of Bakersfield the sulphate concentration increases, running as high as 400 parts per million, in the area outside of production.

SUMMARY

Petroleum free from sulphur is exceedingly rare, although the amount of this constituent is usually small. Sulphur may be present in petroleum as free sulphur, organic sulphur, or hydrogen sulphide. Sulphur may be associated with petroleum as free sulphur, organic sulphur, hydrogen sulphide, sulphuric acid, or sulphates.

THEORIES AS TO THE CAUSE OF SULPHUR IN AND ABOUT PETROLEUM DEPOSITS.

(1) Sulphur is a constituent of all proteids. If oil is formed from organic matter, the sulphur is formed with the oil from the same source.

(2) Percolating oil would dissolve sulphur that had been deposited at an earlier age and was present in the rocks through which the oil migrated.

(3) Gypsum and other sulphates have been reduced by contact with the oil forming hydrogen sulphide and free sulphur.

(4) Reduction of sulphates in percolating ground waters by contact with the oil.

THEORIES AS TO THE RELATIONSHIP OF THE TWO.

(1) Change from a light oil to heavy with the ultimate formation of asphalt by association of oil with sulphur.

(a) Proven by laboratory experiments.

(b) Proven by analysis of oils of different gravity.

The more sulphur the heavier the oil.

(c) The relation of tar beds and sulphur waters.

Deep beds chosen to exclude chance of increase in gravity by loss of volatile compounds.

(d) Increased gravity of oil as water strata containing sulphate water is approached.

(2) Change from sulphate to sulphide in water as oil reservoir is approached.

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