

## Chlorides in Oil-Field Waters

BY C. W. WASHBURN, WASHINGTON, D. C.

(New York Meeting, February, 1914)

THE waters of many oil fields have been regarded as buried sea water which has been retained in the sediments since the time of their deposition. The preservation of connate water through geological time has seemed improbable to only a few geologists, but there is room for doubt that buried sea water could remain in the strata during their periods of deformation and during the many subsequent epochs of the circulation of meteoric ground-water. Some have even suggested that the calcium chloride water in the deep mines of the Lake Superior region is ancient sea water buried in the Algonkian lavas, but it is hard to understand how such water could be derived from the highly sodic and sulphatic water of the sea. It would seem more plausible to connect the calcium chloride with the highly calcic magmas of the greenstones in which it is found.

Chemical analyses of waters associated with oil differ widely from the composition of sea water, requiring extensive alteration of the latter, if the former is truly its derivative. The first notable difference is the general absence of sulphates from oil-field waters, but this has been explained satisfactorily through reduction by hydrocarbons and organic matter. Oil reduces sulphates with the production of hydrogen sulphide (or sulphur), water, and carbonates (or carbon dioxide).

The second striking difference is in the high ratio of chlorine to sodium. An examination of the analyses of chloride waters from oil fields shows that they contain a large relative excess of chlorine over that in sea water. Moreover, there is difficulty in finding chemical reactions that are probable in nature, by which sea water could be converted into anything like the chloride waters of oil fields. In the latter a large part of the chlorine occurs as calcium and magnesium chloride. This condition might be produced by the removal of sodium carbonate, which, however, cannot be precipitated in the presence of much calcium or magnesium.

## Composition of Chloride Waters from Oil Fields

	Sea Water	Pennsylvania		Kansas	
	A	B	C	D	E
Cl.....	55.29 <sup>a</sup>	62.31 <sup>a</sup>	161.80 <sup>b</sup>	49,285 <sup>c</sup>	30,066.0 <sup>c</sup>
Br.....	0.19	0.53	0.70	79	.....
I.....	.....	0.01	.....	8.4	.....
SO <sub>4</sub> .....	7.69	0.03	0.05	40	.....
CO <sub>3</sub> .....	0.21	0.27	0.00	0	.....
B <sub>4</sub> O <sub>7</sub> .....	.....	.....	.....	150	.....
Na.....	30.59	18.35	64.55	} 2,791	} 4,216
K.....	1.11	1.55	5.16		
Li.....	.....	0.04	.....	.....	.....
NH <sub>4</sub> .....	.....	0.23	.....	.....	.....
Ca.....	1.20	13.86	25.19	1,425	2,792
Ba.....	.....	.....	trace	.....	.....
Sr.....	.....	.....	3.55	.....	.....
Mg.....	3.72	2.53	2.48	2,844	6,310
Al <sub>2</sub> O <sub>3</sub> .....	.....	0.02	0.00	.....	.....
Fe <sub>2</sub> O <sub>3</sub> .....	.....	.....	.....	} 56	} 48
Fe.....	.....	0.25	0.16		
SiO <sub>2</sub> .....	.....	0.02	0.00	43	85
	100.00	100.00	263.64	56,721	43,517
Ratio $\frac{\text{Cl}}{\text{Na}}$ .....	1.8	3.5	2.5	18.2 <sup>≠</sup>	7.5 <sup>≠</sup>

a. Percentage of total salts.

b. Grams per kilogram of water.

c. Parts per million (?).

A. Dittmar's summary of the principal salts in sea water, from Clarke, *Data of Geochemistry, Bulletin No. 491, U. S. Geological Survey*, p. 113, 1911. Placed here for comparison.

B. Brine from well 2,667 ft. deep at Conneautsville, Pa. Salinity about nine times that of sea water. Analysis by Robinson and Mabery, quoted by Clarke, *loc. cit.*, p. 174.

C. Brine from depth of 6,300 ft. in well near Imperial, Allegheny county, Pa. Analysis by George Steiger, *Journal of the Washington Academy of Sciences*, vol. iii, p. 423, 1913. Well record described by White, *Bulletin of the Geological Society of America*, vol. xxiv, No. 2, pp. 275-282, June, 1913. The salinity is eight times that of sea water.

D. Hudson well, Fredonia, Wilson county, Kan. Depth 400 ft. Analysis by Bailey and Davies, quoted in *Water Supply Paper No. 273, U. S. Geological Survey*, p. 199 (1911).

E. Flowing salt well in Pennsylvanian strata at Lawrence, Kan., depth 1,400 ft. Analysis by Bartow and Thompson, *Kansas Geological Survey*, vol. vii, p. 151 (1902).

The following American analyses were gathered by Hofer,<sup>1</sup> the first four (A-D) being from oil wells near Tarentum, Pa. (analyses by Charles Lenny), and the last two (E-F) from oil and gas wells in Ohio (analyses by W. J. Root). The high percentage of calcium and magnesium chlorides is noteworthy.

	A	B	C	D	E	F
NaCl.....	3.2000	5.0203	4.7152	32.978	71.645	30.128
NaI.....					0.013	0.024
KCl.....				0.041		
NH <sub>4</sub> Cl.....				0.007		
CaCl <sub>2</sub> .....	0.5587	1.6462	0.9657	8.578	18.665	48.969
CaI <sub>2</sub> .....				0.080		
CaCO <sub>3</sub> .....				2.764		
MgBr <sub>2</sub> .....				0.1154	0.271	0.592
MgCl <sub>2</sub> .....	0.2933	0.3193	0.3132	2.166	9.826	20.201
MgCO <sub>3</sub> .....				1.377		
BaCl <sub>2</sub> .....	0.0380	0.0642	0.0759	0.006		
BaCO <sub>3</sub> .....				0.004		
SrCO <sub>3</sub> .....				0.059		
Al <sub>2</sub> O <sub>3</sub> .....						
Fe <sub>2</sub> O <sub>3</sub> .....					0.096	0.054
FeCO <sub>3</sub> .....				0.038		
SiO <sub>2</sub> .....				0.102	0.024	0.032
CO <sub>1</sub> .....				1.953		
CO <sub>2</sub> .....				0.008		

Two working hypotheses may be entertained to account for the great excess of chlorine over sodium in the water of oil fields. By the first hypothesis, we may explain the disappearance of sodium by the precipitation of sodium chloride from ancient sea water after its burial in the sediments, assuming that the Paleozoic ocean contained less sodium than the modern seas. It is improbable that the average water originally buried in the sediments of oil fields could have been a concentrated brine from which much sodium chloride had been previously precipitated. But the dryness of deep sands in oil fields, and the downward increase in salinity, suggest that beneath the zone of ground water there is a deeper dry zone from which water has been extracted, possibly through the drying influence of the ascending rock gases, which consist mainly of nitrogen, carbon dioxide, and methane. This process would precipitate sodium chloride on the surfaces of deep rock pores, leaving a residual water relatively rich in the soluble magnesium and calcium chlorides,

<sup>1</sup> *Das Erdöl*, vol. ii, Pl. I, p. 29 (1909). Gives 25 analyses.

which would be driven slowly upward by the rising gas. As the water passed through bodies of shale the adsorption of sodium chloride on clay particles, mentioned by Johnston,<sup>2</sup> might further increase the relative amount of magnesium and calcium chloride, but since potassium salts are adsorbed on clay more than sodium salts<sup>3</sup> the relatively high ratio of potassium to sodium in oil-field waters indicates that adsorption has played a minor rôle in their alteration.

The second and stronger working hypothesis is that the excess chlorine has been added directly as magnesium and calcium chlorides in solutions rising from below. These substances are characteristically high in oil-field waters. Furthermore, it appears that the waters of the Ohio oil fields are converting limestone into dolomite, indicating that the water which accompanied the oil in its invasion of the Trenton limestone was rich in magnesium, as it still remains. Bownocker states that the percentage of magnesium in the limestone increases as one approaches an oil pool, reaching a maximum in the pool itself. Some have suggested that this is merely a question of the relative porosity of dolomite and limestone, but the factor of porosity, although very important, does not explain the whole question. It fails especially to correlate the phenomena with the characteristically high percentage of magnesium in the waters of oil fields, and with the occurrences of secondary dolomite in the coastal fields of Louisiana, Texas, and Mexico. The lenses of dolomite or of dolomitic limestone which cap many of the salt cores of the Gulf coast are clearly secondary deposits which grew within the strata. They were precipitated from the same solutions that deposited the sodium chloride, or at least from solutions which followed the channel made by the plug or core of rock salt. The localized occurrence of dolomite, which is so intimately associated with oil near the coast of the Gulf of Mexico, and in Ohio, Indiana, and Canada, is therefore regarded as the direct or indirect product of solutions rich in magnesium chloride. The bitter brine found in the latter fields is thought to have produced the local dolomitization of the Trenton limestone.

The source of the magnesium and calcium chloride as well as of much sodium chloride may be found theoretically in the emanations from deep-seated basic rocks rich in magnesium, such as the olivine-basalt which is so intimately tied with the occurrence of oil in Mexico, and the peridotite in the dikes of western Kentucky, or the serpentine at Syracuse, N. Y., which are the only igneous rocks known near the northern oil region. Moreover, it is rock of this general character which contains diamonds in South Africa, Arkansas, and other places.

<sup>2</sup> Discussion of paper by J. A. L. Clerc and J. F. Brezeale, *Journal of the Washington Academy of Sciences*, vol. iii, p. 198 (1913).

<sup>3</sup> Clarke: Data of Geochemistry, *Bulletin No. 491, U. S. Geological Survey*, p. 200 (1911).

Stelzner, Bonney and others have proved that the diamonds of the Kimberley district crystallized as an integral part of the magma and that the carbon is of deep-seated origin. In Cuba there is a remarkable series of occurrences of light oil in serpentine. In similar rock Diller has found metallic iron which probably contains carbides. Magnesium-rich magmas therefore are the most probable source of oil (if it be volcanic) and of the accompanying chloride solutions.

The acceptance of the idea that modified volcanic emanations have entered the strata of oil fields simplifies many problems besides that of the relative excess of chlorine. For instance, it furnishes an adequate cause for the localization of the great salt-cores of the Texas, Louisiana, and Chiapas. Harris<sup>4</sup> finds that the salt domes of Texas and Louisiana have a linear arrangement suggestive of long intersecting fissures. He finds that the amount of uplift of the strata is entirely inadequate to account for the amount of space occupied by the salt plugs, some of which have been penetrated by the drill nearly 3,000 ft., without reaching bottom. He concludes, therefore, that the salt cores are not laccolithic or plug-like intrusions into the sediments, squeezed up from a great hypothetical salt bed in some lower formation, but rather that they have grown by crystallization at the places where they now occur and have not undergone much deformation. In other words, they are great cylindrical concretions of salt 1,000 ft. or more across and over 3,000 ft. high. He believes that the salt and the associated hydrocarbons were gathered by meteoric waters which percolated through the sedimentary strata and rose along the intersections of fissures, where the salt was precipitated because of the decrease in temperature and pressure. The decrease in pressure would cause but a negligible precipitation, practically nothing. Temperature is somewhat more effective, but Lindgren<sup>5</sup> says: "As the solubility of salt increases only slightly with increase of temperature (35.69 per cent. at 10° C.; 39.12 per cent. at 100°; 44.90 per cent. at 180°), only the increment could have been precipitated as the temperature of the ascending current was lowered, and hence the quantity of primary salt required by this hypothesis is incredibly large." Let us assume that the solutions cooled as fast as the normal underground heat gradient, or about 21° C. in ascending 2,000 ft. This would precipitate about 2 per cent. of the total salt in a

<sup>4</sup> *Bulletin No. 429, U. S. Geological Survey* (1910). The alignment of the salt domes was first observed by Captain A. F. Lucas: *Rock-Salt in Louisiana, Trans.*, xxix, 463, Fig. 1 (1899). Captain Lucas was also the first to observe the geological relations of the salt cores with reference to the occurrence of oil, which he proved by drilling the famous "Lucas gusher" at Spindletop. Cf. Robert T. Hill: *Journal of the Franklin Institute*, vol. cliv, pp. 143, 225, 263 (Aug.-Oct., 1902). A. F. Lucas: *Science*, vol. xxxv, pp. 961-4 (June 21, 1912). *Economic Geology*, vol. vi, No. 4, p. 380 (June, 1911).

<sup>5</sup> *Mineral Deposits*, p. 288 (1913).

solution saturated at 100°. In other words, the salt cores would represent only about 2 per cent. of the total amount of sodium chloride which had risen in the fissures, the rest having been carried beyond the top of the cores and lost. The salt cores in this country and Mexico number several hundred and their total volume is many cubic miles. The theory of Harris, if not modified, requires a supply of roughly 50 times as many cubic miles of salt.

Yet the "concretionary" theory of Harris has much in its favor, since it meets the mechanical requirements of the problem better than any other. The chemical difficulty can be met if the salt domes have been the *loci* of the escape of solutions carrying a common ion, either of sodium or of chlorine. Analyses of some volcanic waters show an abundance of sodium chloride, and others of sodium sulphate or carbonate, but these do not meet the requirements of the present problem. From the character of the water and from the presence of secondary lenses of dolomite one may infer that the precipitation was produced by the intermingling of concentrated salt solutions with brines rich in magnesium and calcium chloride. The former were probably derived mainly from the sedimentary strata as suggested by Harris, but the latter probably rose from underlying plugs of olivine basalt which failed to reach the surface.

Plugs and dikes of this type of rock are common in the coastal plain of Mexico, where they have about the same relation to the occurrence of oil as do the salt cores in Texas to the north or in Chiapas to the south of them. The chlorine probably escaped from the magma as free chlorine, as hydrochloric acid, and as chlorides of ammonium, calcium, magnesium, and sodium. If the igneous plugs are not too deeply buried beneath the plains it is probable that large quantities of hydrochloric acid passed up through the overlying fractures made by the intrusion of the plug. This is the most effective precipitant of common salt, and in the case of the fields about the Gulf of Mexico, the evidence of volcanic action is so strong as to suggest that hydrochloric acid may have played an important rôle in the precipitation of the salt above the volcanic plugs. Also magnesium and calcium chlorides would be quite effective to precipitate rock salt, and if the ascending igneous emanations passed through many strata before reaching the horizon of the salt cores it is certain that the hydrochloric acid would be all converted into chlorides, largely into the chlorides of calcium and magnesium. For our present argument it is immaterial whether the chlorine ions were attached mainly to hydrogen, to calcium, or to magnesium. According to Nernst's law, any of these probable chlorides would precipitate sodium chloride from a concentrated solution. In this way masses of salt derived from the sediments would be formed

where the sedimentary solutions mixed with the rising solutions of volcanic chlorides, *i.e.*, directly above the deeply buried plugs.

Thus the volcanic hypothesis offers a simple explanation of the salt and dolomite problem of oil fields, and the relative excess of chlorine in the associated water may be regarded as a possible indication of the entrance of volcanic emanations, which in most cases have been greatly modified by their long ascent through the rocks.

#### DISCUSSION

A. F. LUCAS, Washington, D. C.—I have long held the opinion that igneous rock may underlie the salt domes of Louisiana, Texas, and elsewhere, resembling laccoliths, batholiths, or sills, and an unsuccessful attempt to prove this was made at my instance by the drilling of the Knapp well at Belle Isle, La., which passed through over 3,000 ft. of rock salt (the first time to my knowledge that a salt dome has been pierced), then entered into sedimentary, striking first an oil sand giving about one barrel of red paraffine oil, then limestone, calcite, or dolomite (not positively ascertained), until a total depth was reached of about 3,300 ft., when the well was lost by the collapse of the casing.

At the extreme bottom the drill was working on very hard formation, which it could not penetrate, although repeated attempts were made, nor was it possible to secure samples of this rock, which, from its extreme hardness, I surmised to be possibly some igneous rock, or perhaps iron pyrite.

EUGENE COSTE, Toronto, Canada.—I agree entirely with Mr. Washburne's view that the strong salinity of these waters in the oil fields is due to solfataric volcanic emanations; the composition of these waters, not only the large excess of chlorine in them but the excess of magnesium and calcium, differentiates them entirely from sea waters and they can only be compared with magmatic waters. In the Texas and Louisiana oil fields we certainly have the clearest examples of solfataric action which we have in the oil fields of the United States—I mean in the salt domes of Louisiana and Texas, where secondary products, not only of salt in large bodies, but enormous bodies of dolomite, gypsum, and sulphur, have been deposited in vertical chimneys by solfataric hot waters accompanied with hydrocarbons and sulphuretted hydrogen; the salts being impregnated with natural gas, sulphuretted hydrogen, and oil, and the salt waters and the oils being quite hot yet in some cases.

A. C. LANE, Tufts College, Mass.—Mr. Washburne's paper brings forward some interesting points; and his main thesis, that these are derived from within (juvenile), is one well worthy of careful consideration. Does he not, however, assume that the early sea water had a character

too much like that at present? Judging from the average water now received by the ocean, either according to Murray or Clarke, there *must* have been a gradual change in its composition, as Hunt, Goessman and I have pointed out, not only in increasing salinity but in the relative proportions of the different salts.

It would be interesting for him to extend his collections of analyses to a wider range of geological horizons. Those cited are Paleozoic. In a paper on the chemical evolution of the ocean, yet unpublished, I have shown reason to believe that while underground circulation tends to run up the ratio of Na : Cl, the character of truly stagnant water varies with its geological age.

The trouble with following his suggestions and connecting the calcium chloride waters of the Lake Superior mines with the highly calcic magmas of the greenstones associated is that the calcium chloride waters occur just the same in the felsitic conglomerates interbedded and also in far-removed sandstones, *e.g.*, near Whitefish lake and Ontonagon, in the Michigan iron mines, and in the Storm King granite. If we are to look to an earth sweat for these universal waters, then I think it would be better to assume the chloride merely to be slowly diffused from the interior, picking up its bases *en route*. But a serious difficulty there is that we have, for instance, under the oil-field waters referred to by Washburne, the St. Peter sandstone, with a water which is much fresher, apparently cutting off any prospect of a juvenile source, which otherwise I should be delighted to accept.

The objection to Washburne's theory is the fact, if it be a fact, that different geological horizons have different chemical characters, and that if not too much disturbed by circulation they can be recognized thereby.