economic status, better health, lessened labor and increased efficiency, not to mention relative freedom from pain and absence of worry. The chemist has added millions of dollars to the capital of nations sensible enough to foster his education and to equip him with laboratories and to set him at work in agriculture, manufacturing and commerce. He also has been a life-saver, a life-prolonger, an agent in transforming the outlook of wise farmers, and in rescuing adults and children from the toils of adulterators of foods. Consequently he deserves generous and respectful treatment by his countrymen.

"The practical side of this matter is simple. If the United States, if New England, if Massachusetts, are to be as wise as they need to be in order to compete with rivals like Germany or Japan, or with American states that have amply equipped universities strong in their scientific equipment, then they must give increased attention to the matter of training men for applied chemistry, men who can do for New England's barren soil and manifold industries what chemists in Germany, Switzerland and Japan have done for those not overfertile lands.

"If conditions at Harvard call for not less than $1,000,000 necessary to put its chemical laboratory, with its staff of expert investigators, in a position to do first-grade work under normal conditions, then there are imperative reasons why Harvard's well-to-do friends should respond to an appeal for aid. Nor is the case different with the "Tech," with the State Agricultural College or any institution in New England which includes in its working plan of service the training of chemists for practical aid in agricultural or manufacturing production, or in the conservation of resources, by the protection of health and the protection from disease."

# ORIGINAL PAPERS.

## OIL SHALES OF AMERICA.[1]

By Charles Baskerville and W. A. Hamor.

Received May 10, 1909.

The use of shale as a source of oil by destructive distillation is well known in England, Scotland, France, Germany, New Zealand, and Australia. In America, however, this fact is not so well recognized, although Gesner claimed to have been the first to produce illuminating oil from bituminous materials on this continent. At public lectures delivered in Prince Edward's Island in August, 1846, he burned in lamps the oil obtained by distilling coal.[1] Patents granted to Gesner nine years later[2] passed into the hands of the North American Kerosene Gaslight Company, who manufactured the oil at their works at Newtown Creek, Long Island, and sold it under the name of "kerosene oil."[3] The agents of this Company encountered considerable difficulty in selling their product.

In 1853, the United States Chemical Manufacturing Company began working coal tar for the manufacture of lubricating oil at Waltham, Mass., and in 1857, the Downer Kerosene Oil Company[4] first made mineral oils from Albert coal mined in New Brunswick, Canada. The works of Downer in Boston were erected at a cost of half a million dollars, and at Portland, Maine, he also erected a smaller works for distilling imported coal. About this time, the New Bedford Company, of New Bedford, Mass., commenced the distillation of Boghead coal, imported from Scotland, but later substituted domestic Breckenridge coal and West Virginia coal for the imported material. In 1859, six plants were erected by various companies near Pittsburg, Pa., and one of these (the Lucesco Company) had a distilling capacity of 6000 gallons of crude oil per day. Many of the companies in operation worked under licenses from the Young Company of Scotland.

In 1860, there were nearly sixty coal oil companies in existence in the United States, many of which were of small capacity. Most of them were not more than fairly started when the discovery of petroleum paralyzed the industry, and the owners were threatened with considerable loss, from which some were rescued by converting their oil works into petroleum refineries, which was accomplished with little outlay of time or money.

The following minerals were used for the production of crude oil in the United States:

[1] Taken from a paper read before the New York Section of the Society of Chemical Industry, April 23, 1909.

[1] "A Practical Treatise on Coal, Petroleum, and Other Distilled Oils," 2nd Ed., 1865, p. 9.

[2] U. S. Patent 12612, March 27, 1855.

[3] The North American Kerosene Gaslight Company, which was organized in 1854, first worked under the patents of J. H. and G. W. Austin.

[4] This Company was founded by Samuel Downer, of Boston. The latter first put an oil on the market, using the process of Luther Atwood, which consisted in distilling coal tar (1850). The product was sold under the name "coup oil" and was used for lubrication (Chandler, *J. Soc. Chem. Ind.*, **19**, 612).

| Mineral.[1] | Yield of crude oil in gallons. |
|---|---|
| Albert coal (albertite[2]) | 110 |
| Asphalt rock, New Brunswick | 64 |
| Pictou shale, Nova Scotia | 47 |
| Breckenridge Cannel coal[3] | 130 |
| Erie Railroad coal | 47 |
| Newburg coal | 72 |
| Falling Rock coal | 80 |
| Pittsburgh coal | 49 |
| Kanawha coal | 71 |
| Elk River coal | 60 |
| Cannelton coal | 86 |
| Coshocton coal | 74 |
| Ouachita brown coal | 68[4] |
| Ouachita bitumen | 64 |
| Ritchie County bitumen (Grahamite) | 170 |

Oil shales occur on the Humboldt River, opposite to Elko, Nevada; on the Big Blackfoot River and near Great Falls, Montana; and in the Cholame Valley, north of Parkfield, California. Some of these are of good quality but none has been worked to any extent.

During the year 1859, the North American Kerosene Gaslight Company imported upwards of 20,000 tons of Boghead coal for the supply of their works at Newtown Creek, Long Island, at an average cost of $18.00 per ton. It was found that a ton of this mineral run in common retorts yielded 120 gallons of crude oil per ton, which gave 65 gallons of lamp oil, 7 gallons of paraffin oil, and 12 pounds of paraffin wax. The cost of the oil was estimated at 63 cents per gallon.[5]

The bituminous shales of New Brunswick, or the "Albert shale," first came into prominence through the discovery at the Albert mines of the peculiar mineral albertite.[6] The discovery of albertite was followed by a contention as to its nature, as this involved its ownership.[7] The testimony offered in the trial was of the most discordant character, and it was adjudged that

[1] See Gesner, "A Practical Treatise on Coal, Petroleum, and Other Distilled Oils," 1st Ed., **1861**, 34; and T. Antisell, "The Manufacture of Photogenic, or Hydrocarbon Oils from Coal and Other Bituminous Substances, Capable of Supplying Burning Oils," **1859**.

[2] This material was retorted at the Downer Kerosene Oil Works in South Boston; at the Downer Kerosene Oil Works in Portland, Me.; and at the New Brunswick Oil Company's Works in St. John, N. B. These companies were under contract with the Albert Mining Company from **1860 to 1864**.

[3] This material was mined in Breckenridge County, Kentucky. The crude oil yielded 58 per cent. burning oil and 12 gallons paraffin. For the yield of crude oil of various Kentucky coals, see *Second Report, Geol. Survey Kentucky*, **1856–7**, 211. Breckenridge coal sold at Cloverport, Ky., for $5.00–6.00 per ton.

[4] The crude oil from this brown coal was semi-solid at 80° Fahr. It is said to have yielded 143 pounds of paraffin per ton. The material was mined along the Ouachita River, Ark.

[5] Report of the Committee, North American Kerosene Gaslight Company, New York, **1860**.

[6] See C. T. Jackson, *Proc. Boston Soc. Nat. Hist.*, **3**, 279.

[7] Suit of A. Gesner *vs.* the Halifax Gaslight Co

the material was of the nature of coal.[1] This supposition was soon abandoned, however, and the material was regarded as a highly altered pitch or bitumen.[2] Two analyses of albertite are given here:

| | Wetherill.[3] Per cent. | Gesner.[4] Per cent. |
|---|---|---|
| Carbon | 86.307 | 85.400 |
| Hydrogen | 8.962 | 9.200 |
| Nitrogen | 2.930 | 3.060 |
| Sulphur | traces | a trace |
| Oxygen | 1.971 | 2.220 |
| Ash | 0.100 | 0.120 |
| Total | 100.000 | 100.000 |

Albertite yielded 110 gallons of crude oil per ton, of which 70 per cent. was made into lamp oil and 10 per cent. into heavy oil and paraffin. As might be expected from its low sulphur content, the oils produced from albertite were almost without offensive odor, and the burning oil was admirably adapted for burning in paraffin lamps. Albertite was also used for gas enriching, and, to a limited extent, in the preparation of cements.[5] Between the years 1863 and 1874, 154,800 tons of this mineral were mined, and it is estimated that in all over 200,000 tons were yielded by the veins in Albert County. The high price obtained, from $15.00 to $20.00 per ton, rendered albertite one of the great mineral assets of New Brunswick. The large vein has not been entirely worked out, and several smaller veins have been proved.

The "black band" shales of New Brunswick were distilled at the Caledonia Works, in Albert County, and yielded 63 gallons of crude oil per ton, while poorer beds on the Memramcook River, in Westmoreland County, were found to give only 37 gallons. Numerous leases were taken out in 1865 for operations on the bituminous shales of New Brunswick, and a company in Westmoreland County erected 100 retorts, with the design of subjecting 100 tons per day to distillation.[6] These shales pro-

[1] See C. T. Jackson, "Report on the Albert Coal Mine," Boston, 1851; and R. C. Taylor, "Deposition Respecting the Asphaltum Mine at Hillsborough, N. B.," Philadelphia, 1851. Also Bailey, *Trans. Roy. Soc. Canada*, **7**, 77; Church, *Chem. News*, **6**, 122.

[2] Taylor, *Proc. Am. Phil. Soc.*, **5**, 241; Hitchcock, *Am. J. Sci.* [2], **39**, 267; Peckham, *idem.* [2], **48**, 362; Geinitz, *Sitz. nat. Ges. Isis*, **1871**, 87; Honeyman, *Min. Mag.*, **7**, 77; Blake, *Trans. Am. Inst. Min. Eng.*, **18**, 563; Rutherford, *J. Fed. Can. Min. Inst.*, **3**, 40; and Ells, "The Geology and Mineral Resources of New Brunswick," **1907**, 107.

[3] *Trans. Am. Phil. Soc.*, **1852**, 353.

[4] *Loc. cit.*, p. 23.

[5] Some specimens of wood and brick cemented by a material composed partly of albertite have been in the Museum of the University of New Brunswick for 60 years, and show no visible change in texture or cementing power.

[6] J. W. Dawson, "Acadian Geology," Edinburgh, 1865, 2nd Edition. Ells (*Summary Report, Geol. Surv. Canada*, **1902**, A363) states that works for the extraction of oil from the black shales at

duced 7500 cubic feet of gas per ton (about one-half of the quantity yielded by albertite), and 1230 tons, valued at $3075.00, were exported in 1865.

The Utica shale was distilled in the township of Collingwood, Ontario, in 1859, as a source of oil, and it was learned that similar shales occur in the Devonian formation in Bosanquet, Lambton County, Ontario. In 1871, D. C. Glen exhibited samples of these shales in England.[1]

Over 2000 tons of oil-coal were raised near Pictou, Nova Scotia, in 1859, mostly from Frazer's mine. The following were found to be the yields from the oil-coals worked in Nova Scotia at this time:

| Locality. | Gallons of crude oil per ton. |
|---|---|
| McLennan's Brook | 40 |
| Coal Brook | 53 |
| McCullock's Brook | 77 |

This oil-coal has been described by H. How.[2]

Oil shale has been found more recently at Macadam's Lake, on the north side of East Bay, Cape Breton, Nova Scotia. This shale yields 15–20 gallons of crude oil per ton.

Near Deer Lake, in the east of Newfoundland, occurs a dark gray shale which is highly bituminous in parts.[3] This deposit has never been worked to any extent.

The large body of peculiar black, brown, and gray shales, which occur in Albert and Westmoreland counties, New Brunswick, have long been known under the name of "Albert shale."[4] The mode of occurrence of these heavy oil shales is quite distinct from that of albertite. In the case of the latter, the mineral occurs in the form of true veins, which sometimes follow the lines of stratification of the enclosing shales, but which also frequently traverse them at well defined angles. The oil shales, however, occur as true interstratified beds in the bituminous shale series. As to the geological position of the shales as a whole, it may be remarked that somewhat diverse opinions have been held from time to time by different geologists. In the early days of the investigation of these shales, it was supposed they represented an integral part of the lower carboniferous portion. This conclusion was reached from the presence in certain of the bands of shale of the remains of fossil fishes and plants, which were then supposed to have a lower carboniferous aspect and to definitely fix their horizon. From investigations made in 1876, however, it was found that the shales should stratigraphically be assigned to a lower horizon or be regarded as of Devonian Age, owing to their nonconformability to the true Lower Carboniferous sediments.

The principal areas most readily accessible at the present time, are at Taylorville, Albert Mines, and Baltimore. In all these localities the outcrops have been examined. A detailed description of these would be out of place in this paper, but suffice it to say that in the Taylorville district, although the area of shales exposed is limited, according to the report of the Canadian Department of Mines, four beds of high quality of shale with a total thickness of eleven feet have been uncovered. In the Albert Mines district six bands for a quarter of a mile along the stream, with a total thickness of about twenty-six feet, have been exposed. The shaft of the Albert Mines was sunk to a depth of 1500 feet. It cut numerous beds of oil shale and, in fact, work was discontinued in such deposits. What is known as the Baltimore shales are found for several miles along the north flank of the Caledonia Mountains, going west from Albert Mines, in five bands, with a total thickness of over twenty-two feet. These beds have been explored by two diamond drills and one churn drill through a depth of 900 feet. They were encountered at intervals throughout the borings.

Outcrops of several other beds of this shale have been observed near Rosevale post-office, and it is considered likely that at least two other beds may be found in this area. In fact, a band with a thickness not far from fifteen feet, not opened up, has been measured along the bank of the brook, which cuts it. A "gray shale," with an exposed thickness of about four feet, is found three-quarters of a mile to the west of the above; and four miles beyond; three other bands of brownish shales, the thickness of one being five feet, and all yielding oil, are found. Portions of the original bed of albertite remain in certain parts of the old workings, and recent investigations have disclosed the presence

Baltimore and Taylorville were erected in 1864, and that the industry was carried on for several years. Crude shale from Taylorville was also exported to ports in U. S. and sold for $6.00 per ton.

[1] *Geol. Mag.*, **8**, 88.

[2] *Am. J. Sci.* [2], **30**, 74.

[3] J. P. Howley, "Report to the Newfoundland Government on the Humber Valley," 1893, 16.

[4] R. W. Ells, *Ann. Report Geol. Surv. Canada, n. s.*, **1**, 1885, Report E, 63; *Summary Report Geol. Surv. Canada*, 1902, A 363–69; *Trans. Roy. Soc. Canada*, **12**, 276; "The Geology and Mineral Resources of New Brunswick," 1907, 107; *Trans. Nova Scotian Institute of Sci.*, **11**, part 4, 612; *J. Can. Min. Inst.*, **11**, 12 pp. (adv. reprint); and a forthcoming report which is to appear this summer among the publications of the Department of Mines of Canada.

of other veins of albertite. The immense dumps of shale, aggregating over 100,000 tons, contain large quantities of the mineral. It will be thus observed that the quantity of shale which yields oil on distillation is enormous, if not beyond measure.

A preliminary examination was conducted with a view of ascertaining the laboratory yield of oil and the products from the crude oil obtained from a sample of shale. This shale, which was obtained from the Baltimore locality, had the following physical characteristics: lustre, moderate; fracture, irregular and without natural line of cleavage; cross fracture, angular, partly inclining to conchoidal; and a specific gravity of 1.44. It was solid and compact. It burned with a dense smoky flame, when ignited with a match. The yield of gas saturated with tarry matters was large when a sample was heated to dull redness in a tube closed at one end.

The average composition of the shale was as follows:

| | Per cent. |
|---|---|
| Moisture | 0.35 |
| Volatile matter | 44.77 |
| Fixed carbon | 5.95 |
| Ash { Phosphoric acid 0.30; Trace of chromium; no vanadium. Light brown color | 48.93 |
| | 100.00 |
| Total sulphur | 1.43 |
| Sulphur in coke | 0.20 |
| Nitrogen | 1.96 |

A laboratory retort for obtaining the crude oil was constructed of cylindrical cast-iron, 24 inches long and 4 inches in diameter. This retort was closed at both ends by removable caps, and at one end a 3/4 inch pipe was inserted for leading the vapors to a coil condenser, to which were attached two supplementary glass condensers. The retort was heated in a furnace to a low red heat. No difficulty was experienced in condensing the vapors evolved, as all the condensers were kept packed in ice and the distillation was allowed to proceed slowly. The distillation was made repeatedly with five pound charges. Run-of-mine material gave 55 gallons per ton (2000 pounds) of a crude oil, greenish black in color and somewhat tarry. It had a specific gravity of 0.93. The residue, or spent shale, had the appearance of burned coke. The oil "refined" in the laboratory by variations of the Tervet method[1] gave:

[1] Redwood, "Petroleum and Its Products," **2**, 644; Allen, "Commercial Organic Analysis." 1907. **2**, ii, 39.

| | Per cent. | Gallons per ton. |
|---|---|---|
| Naphtha (0.72) | 9.09 | 6.9 |
| Light oil (0.79) | 16.57 | 12.0 |
| Heavy oil (0.916) | 14.00 | 7.8 |
| Paraffin | 7.54 | 35.0 lbs. |
| Total yield of products | 47.20 | |
| Loss | 52.80 | 280 lbs. |

This preliminary examination, which was not intended to be exhaustive, indicated that the shales were worthy of more extensive investigation; therefore, some forty odd tons of the run-of-mine shale were put through the experimental plant of the Pumpherston Oil Co., Ltd., near Edinburgh, Scotland, in the presence of Dr. R. W. Ells, representing the Canadian Government, and one of us (W. A. H). This commercial test gave 48 U. S. gallons of crude oil (naphtha not recovered) and 77 pounds of ammonium sulphate per long ton.

The crude oil possessed a brownish black color, and had a specific gravity of 0.92, a flash-point of 194° Fahr. and a setting-point of 54° Fahr. It was found to contain 0.62 per cent. sulphur. It had a heating value (by bomb calorimeter method) of 18,474 B. T. U.

The crude oil is probably of a semi-asphaltic base nature. When distilled in an Engler distillation flask at the rate of 2.5 cc. per minute up to 740° Fahr., a ten per cent. residuum, soluble in carbon disulphide, was obtained. This may perhaps be increased by air-blowing. This phase of the investigation is to be pursued further.

A considerable amount of uncondensed gas was produced from the shale during retorting; in fact, this gas served to carry out the retorting. Several samples of the gas were taken at a point between the ammonia scrubber and retort combustion chamber and analyzed, with the following results:

| | Per cent. |
|---|---|
| Carbon dioxide | 29.67 |
| Carbon monoxide | 5.06 |
| Olefines | 1.33 |
| Methane | 11.02 |
| Hydrogen | 52.92 |
| | 100.00 |

Calorific value, 305.1 B. T. U. per cubic foot (N. T. P.).

Sp. Gr., 0.613 (air, 1).

Weight per cubic foot, 0.0492 pound.

On refining, the crude oil gave the following yields per ton of shale[1] (23):

[1] The authors are greatly indebted to Mr. Wm. Fraser, managing director, Mr. James Bryson, works manager, and Mr. E. M. Bailey, chemist, for many courtesies during the investigation at the main works of the Pumpherston Oil Co., Ltd., at Pumpherston, Mid-Calder, Scotland.

| | Brit. gal. | U. S. gal. |
|---|---|---|
| Naphtha | 0.6 | 0.7 |
| Burning oil | 4.3 | 5.1 |
| Gas oil | 5.6 | 6.7 |
| Cleaning oil | 0.8 | 0.9 |
| Lubricating oil | 4.1 | 4.9 |
| Paraffin wax | 1.1 | 1.3 |
| Total | 16.5 | 19.6 |
| Residuum | 1.5 | 1.8 |
| Creosote, tar, pitch, coke, etc. | 22.00 | 26.6 |

The yield of refined products was regarded as satisfactory, considering the low-grade material from which the crude oil was retorted. As mentioned above, the light naphtha was lost during retorting; and, moreover, it was found impossible to extract all the lower melting-point paraffin on a small scale.

An incomplete, but sufficiently extensive chemical survey of the field was carried out to determine its value. The oil was determined by the tube test, such as is used in Scotland in testing a shale before passing it through the retorts on a commercial scale.

The tubes which were employed for the determination of the yield of crude oil from a given sample of shale, were made of 1/5 inch wrought iron tubing, having a diameter of two inches and a length of six feet, and were sealed by a cap at one end. One pound of the shale in pieces about ½ inch square was put into the tube, which was then placed in an oven and heated gradually to a dull-red heat. The tube was inserted in the oven for about a foot of its length, and inclined at a convenient angle. No condenser was used in making these tests, so that the naphtha was lost, but, by controlling the heat properly, the conditions of distillation are nearly identical with those occurring in a modern retort.

The method used for the determination of the yield of ammonium sulphate obtainable from a sample of shale was that known as the Bailey method, and which is used in the laboratories of all crude oil works where Pumpherston retorts are in use. A definite weight of the shale in small pieces (30 mm. in diameter) is heated in a malleable iron tube to bright redness in the presence of a current of steam for 1½ hours, the gases resulting being led into a flask containing 2 *N* sulphuric acid. In this solution, the ammonia is determined as nitrogen by sodium hypobromite in a nitrometer and the yield of ammonium sulphate is calculated therefrom.

Determinations by these methods approximately equal the yields obtained by retorting the shale in a Pumpherston retort.

Oil and Ammonium Sulphate, taken from Different Localities.

| Locality. | Imperial gallons of crude oil per ton. | U. S. gallons of crude oil per ton. | Specific gravity of oil. | Pounds of ammonium sulphate per ton. |
|---|---|---|---|---|
| Shale retorted in Scotland | 40 | 48 | 0.92 | 77 |
| Geo. Irving's | 39 | 47 | 0.895 | 76 |
| Baizley's farm, Baltimore | 54 | 65 | 0.895 | 110 |
| E. Stevens | 49 | 59 | 0.892 | 67 |
| Hayward's Brook, Prosser Brook | 30 | 35 | 0.895 | 75 |
| Adams Farm | 43 | 51 | 0.90 | 93 |
| A. Taylor's Farm, No. 1 | 48 | 58 | 0.91 | 98 |
| A. Taylor's Farm, No. 2 | 37 | 44 | 0.925 | 110 |
| Sample of 85 lbs. run in 1907 | 51 | 61 | 0.91 | 111 |

Oil shales are always of variable character, and it is impossible to procure true average samples of the various seams for examination. However, we have shown by laboratory tests that the oil shales of New Brunswick are not so variable in the yield of crude oil and ammonium sulphate as the shales of Scotland, where it has been clearly demonstrated that shale oil can live against petroleum.

The beds of oil shale in New Brunswick are more extensive than those of any other country, and the by-product obtained on retorting, ammonium sulphate, which was not recovered in the early days, will more than bear the expense of mining and treatment. It is one of the difficulties of a petroleum field that it is almost impossible to estimate the quantity of oil which may exist, and only the successful sinking of wells year by year can show the probable extent of the payable area. The crude oil obtained by retorting New Brunswick oil shale is essentially the same as the petroleum of the mid-continent field, and therefore the same markets are open for it. As an article of commerce, however, it is especially suitable for liquid fuel, and at the present time, as is well known, it has been impossible to secure adequate supplies of liquid fuel for general employment.

College of the City of New York.

## THE MANUFACTURE OF ANHYDROUS CHLORIN FROM MOIST DILUTE GASES AND ITS INDUSTRIAL APPLICATION IN CHLORIN DETINNING.[1]

By Elmer A. Sperry.

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As is well known there are several reactions and operations which produce chlorin, either as a direct or as a secondary product. The uses of this material are also gradually extending and new uses are

[1] Read before the New York Section, American Chemical Society, March 5, 1909.