

XVIII.—*On the Chemical Composition of a Nodule of Ozokerite found at Kinghornness.* By W. IVISON MACADAM, F.C.S., Lecturer on Chemistry, Edinburgh.

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The nodule to which this paper refers was discovered at Kinghornness during the excavations rendered necessary by the fortifications at present being raised for the defence of the Firth of Forth.

The material was enclosed in a nest or nodule, and was found at a depth of 15 feet from the surface of the ground, and embedded 5 feet in hard trap-rock.

The rock in which the nodule was obtained was sound, there being no crack or fissure observable for several feet round the nest, but at a point some distance below the nodule the section shows a series of small veins or fissures running through the rock in various directions, and averaging  $\frac{3}{4}$  of an inch in breadth. The analysis of the rock gave the following results, calculated to percentages:—

1. On treating the pulverised sample with hydric chloride (HCl), and subjecting the mixture to a prolonged low heat, it was found that 29·73 per cent. of the substance dissolved in the acid. The detailed results of the analysis of this solution are as follows:—

Ferric oxide	(Fe <sub>2</sub> O <sub>3</sub> ),	. 11·45	per cent.
Aluminic oxide	(Al <sub>2</sub> O <sub>3</sub> ),	. 3·63	„
Calcic	(CaO),	. 3·70	„
Magnesian	(MgO),	. 0·37	„
Potassic	(K <sub>2</sub> O),	. }	0·13
Sodic	(Na <sub>2</sub> O),	. }	„
Carbonic anhydride	(CO <sub>2</sub> ),	. 8·17	„
Sulphuric	(SO <sub>3</sub> ),	. 0·21	„
Silica from soluble silicates	(SiO <sub>2</sub> ),	. 2·07	„

Total soluble in acids, . . . 29·73 per cent.

Insoluble in acids, silicates, &c., . 70·27 „

100·00 per cent.

2. The portion insoluble in acids was then fused with a flux and the following results obtained from the after-solution in acid:—

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Ferric oxide	(Fe <sub>2</sub> O <sub>3</sub> ), .	9.92 per cent.
Aluminic oxide	(Al <sub>2</sub> O <sub>3</sub> ), .	5.36 "
Calcic "	(CaO), .	8.17 "
Magnesian "	(MgO), .	5.67 "
Silica from silicates, &c.	(SiO <sub>2</sub> ), .	41.12 "
Total from fused portion, . . .		70.24 per cent.
Soluble in acids, . . .		29.73 "
		<u>99.97 per cent.</u>

The rocks lying next to the trap were also analysed, and gave results as stated below:—

1. Soluble in Hydric Chloride (HCl)—

		No. 2.	No. 3.	No. 4. Same as No. 2, but nearer the surface of ground.
		Rock above trap.	Rock below trap.	
Ferric oxide	(Fe <sub>2</sub> O <sub>3</sub> ),	21.37	31.48	15.78
Aluminic oxide	(Al <sub>2</sub> O <sub>3</sub> ),	4.06	4.59	7.92
Calcic "	(CaO), .	2.83	3.11	2.19
Magnesian "	(MgO),	2.98	4.23	2.47
Potassic "	(K <sub>2</sub> O),	0.98	0.82	1.48
Sodic "	(Na <sub>2</sub> O),			
Carbonic anhydride	(CO <sub>2</sub> ), .	5.19	6.01	4.62
Sulphuric "	(SO <sub>3</sub> ), .	0.32	0.28	1.62
Sulphur	(S), .	0.13	0.16	1.17
Silica from soluble silicates	(SiO <sub>2</sub> ), .	2.08	2.23	3.95
Moisture, . . . . .		3.22	3.41	3.14
Total soluble in acid, . . .		43.16	56.32	44.34
Insoluble in acid, . . . . .		56.84	43.68	55.66
		<u>100.00</u>	<u>100.00</u>	<u>100.00</u>

2. Matter insoluble in Hydric Chloride (HCl), fused with flux and then treated with acid—

		No. 2.	No. 3.	No. 4. Same as No. 2, but nearer the surface of ground.
		Rock above trap.	Rock below trap.	
Ferric oxide	(Fe <sub>2</sub> O <sub>3</sub> ),	5.28	4.84	7.04
Aluminic oxide	(Al <sub>2</sub> O <sub>3</sub> ),	3.48	4.12	7.76
Calcic "	(CaO), .	2.15	1.18	0.78
Magnesian "	(MgO),	1.03	0.28	0.24
Silica from silicates, &c.	(SiO <sub>2</sub> ), .	44.68	33.12	39.72
Total from fused portion, . . .		56.62	43.54	55.54
Soluble in acids, . . . . .		43.16	56.32	44.34
		<u>99.78</u>	<u>99.86</u>	<u>99.88</u>

The nodule when broken consisted of—

1. An outer coating of hard rock ;
2. An inner lining of calcite crystals ; and
3. Centre nodule of bituminous matter.

When first brought to light the calcite crystals were almost black in colour, due to a certain amount of the bituminous matter, but this slowly evaporated, and left the crystals pure white in colour. The analyses of these crystals of calcite yielded the following results :—

	Black Crystals containing Bitumen.	White Crystals.
Calcic carbonate ( $\text{CaCO}_3$ ), . . .	96.76	98.11
Ferrous „ ( $\text{FeCO}_3$ ), . . .	0.19	0.21
Magnesian „ ( $\text{MgCO}_3$ ), . . .	0.31	0.33
Silica ( $\text{SiO}_2$ ), . . .	1.06	1.22
Bituminous matter, . . .	1.68	0.13
	<hr/> 100.00	<hr/> 100.00

The lower veins or fissures were also calcite-lined, and contained within this coating the bituminous matter.

Besides the nodule found at Kinghornness, another nodule of a similar character was obtained on the island of Inchkeith, embedded in solid trap, 10 feet from the surface, and a small spring of water on that island smells and tastes distinctly of paraffin products.

The Kinghornness nodule has a distinct bituminous odour, is a lustrous black, amorphous, soft solid, easily cut with the nail, and pliable between the fingers. The specific gravity is 9.70 (water, 1000), so that the nodule floats upon water. It fuses at 176° Fahr., and becomes solid on cooling. Experiments with the various solvents upon the bituminous material showed that water and ordinary acids had practically no action whatever. Alcohol, both hot and cold, had a very slight solvent power ; but ether dissolved a considerable proportion, giving a brown solution ; and turpentine readily acted upon the substance, yielding a deep brown-black solution. The ethereal liquid had a fine iridescent green colour when viewed by reflected light. The substance of the nodule readily burns when lighted, giving a strongly luminous flame.

The analysis of the contents of the nodule gave as follows :—

Volatile organic matter, . . .	99.98 per cent.
Ash or mineral matter, . . .	0.61 „
	<hr/> 99.99 per cent.

Volatile gaseous matter given off below 212° Fahr., 5.961 per cent.

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When distilled at a bright cherry-red heat, 26·57 grains being used, the results gave—

	Volatile matter, . . .	15·93 grains.
Coke, 10·64 grains	{ Fixed carbon, . . .	10·48 „
	{ Ash (mineral matter), . . .	0·16 „
		<hr/> 26·57 grains.

These results calculated to the percentage give—

	Volatile matter, . . .	59·955 per cent.
Coke, 40·041 per cent.	{ Fixed carbon, . . .	39·431 „
	{ Ash (mineral matter), . . .	0·610 „
		<hr/> 99·996 per cent.

The coke left behind after this treatment was a hard, black, shining, porous mass, and the ash obtained by incinerating it was pure white, and principally consisted of calcic carbonate ( $\text{CaCO}_3$ ) and silica ( $\text{SiO}_2$ ).

The material was afterwards submitted to destructive distillation at a black red heat, when the substance was found to split up into six distinct parts—four distillates, a coke, and a volatile non-condensable gas. In this operation 58·29 grains were used, and yielded—

1st distillate, . . . . .	5·65 grains.
2d „ . . . . .	11·35 „
3d „ . . . . .	21·33 „
4th „ . . . . .	14·72 „
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Total volatile condensable products, . . . . .	53·05 grains.
Coke, . . . . .	2·28 „
Uncondensable gas, . . . . .	2·96 „
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Total, . . . . .	58·29 grains.

Calculated to percentages, the results stand—

1st distillate, . . . . .	9·694 per cent.
2d „ . . . . .	19·471 „
3d „ . . . . .	36·592 „
4th „ . . . . .	25·253 „
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Volatile condensable products, . . . . .	91·010 per cent.
Coke, . . . . .	3·911 „
Uncondensable gas, . . . . .	5·078 „
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	99·999 per cent.

When first heated, the substance fused and frothed, and on the further application of heat gave the first distillate, which was of a grey colour, somewhat mobile, and had a disagreeable odour. The second distillate was black in colour, fully more mobile than the first distillate, and also possessed a most disagreeable odour. The third portion was more mobile than the second, had a yellow colour, and a marked paraffin odour. The fourth distillate was obtained after raising the heat, had a yellow-red colour, was liquid whilst hot, but turned solid on cooling, and had also a paraffin odour. The uncondensable gaseous matter readily burned on the application of a white light, gave a pale non-luminous flame, and possessed all the chemical properties of methane, or marsh-gas ( $\text{CH}_4$ ). The carbon left in the retort, added to the amount of uncondensable gas, gives 8.989 per cent.; and on calculating the incondensable gas into ethylene or olefiant gas ( $\text{C}_2\text{H}_4$ ), the result obtained is 8.886, or nearly the same. These results go far to show that the bituminous-like matter of the nodule consists of a member or members of the olefine (or  $\text{CH}_2$ ) series of organic compounds, a point which is further strengthened by the fact that the carbon and hydrogen in the original substance are contained therein in almost exactly the necessary proportions to form an olefine.

It is probable that the source of the contents of the nodule lies in one of the coal or shale beds abounding in the district, and that a low internal heat has distilled the material from its parent stratum. That the heat was low, or certainly not above a cherry-red, is certain, else the olefine would have been split up into a member of the methane (or  $\text{CH}_4$ ) group of organic substances, accompanied by a deposition of free carbon.