THE OCCURRENCE OF BARIUM COMPOUNDS IN ARTESIAN WELL WATER.

BY JOHN WHITE, F.I.C.

(*Read at the Meeting, January 4, 1899.*)

THE presence of a salt of the metal barium in solution in a natural water in this country is in my experience of very rare and unusual occurrence. I can only find a few instances recorded of the existence of a soluble salt of this metal as a constituent of unartificial waters, and therefore think it desirable to lay before this Society the results of my analyses of some samples of water derived from an artesian well of very great depth at Ilkeston in Derbyshire. I give all the information I have been able to obtain respecting the bore-hole, and exhibit drawings in section of the strata passed through, which are here reproduced (see diagrams 1 and 2). For much of this information I am indebted to Mr. Henry J. Kilford, the Borough Surveyor of Ilkeston, also for the loan of the drawings.

The bore-hole, the surface of which is 160 feet above sea-level, O.D., has been carried to a total depth of 1,801 feet, water being found at 837 feet, and rising to a height of 15 feet above the surface. As only about 180 gallons per hour were obtained at the surface from that depth, the bore was deepened as stated, with the result that the yield remained practically unaltered. A pumping shaft was then sunk round the bore-hole to a depth of about 150 feet, and this is now in course of being deepened to about 300 feet. The steel tubes were removed as the sinking proceeded, and a considerable increase in the volume of water yielded has been the result, great difficulty being experienced at times in plugging up the tube. It was during the removal of a length of tube that the accident happened which caused the admittance to the bore-hole of the abnormal water presently to be described. Mr. Kilford is of opinion that the tubes split somewhere lower down, and by sinking the shaft below the Kilburn coal measures, he expects to be able to "tub out" the abnormal water. The bore-hole was lined with steel tubes to a depth of 1,040 feet.

The diagrams give exact particulars of the nature and thickness of each layer of the strata passed through. By adding together the figures given for the various layers of like material, and grouping them according to their general description and classification, a rough synopsis of the formation is obtained, as shown in the following table :

TABLE I.

Nature of Strata.	Varieties mentioned in Section Diagram.	Total Thickness in feet.
Shale	Black, blue, light blue, dark blue, soft blue, gray, dark, sandy, variegated.	1,100
Sandstone	Brownish mottled, broken, coarse, close-grained, fine, greenish gray, dark gray, hard gray, open gray, reddish, shaley, streaked, variegated, white.	350
Millstone grit	— — — — —	300
Coal	— — — — —	17
Fire clay	— — — — —	16
Miscellaneous	Beryl, blue bind, sandy bind, clay, clunch, ironstone, limestone, spar.	20

Before proceeding further to consider the nature of the strata, I give in the next table the results of my analyses of six samples of water :

A is the water originally yielded by the bore-hole.

B is the abnormal water which gained access to the bore-hole, as is supposed by the splitting of the steel lining tubes.

C is a similar sample, collected about six months later than B.

D is from the pumping shaft, collected since this abnormal water appeared.

E and F are from the pumping shaft, taken about 80 feet below the surface, before the abnormal water was found.

TABLE II.

Results expressed in Parts per 100,000.

	From Bore-hole.			From Pumping Shaft.		
	A.	B.	C.	D.	E.	F.
Total solid matter, dried at 100° C.	59.5	2628.0	2752.0	282.0	62.5	51.0
Loss on ignition	3.0	194.0	198.0	19.0	—	—
Saline residue	56.5	2434.0	2554.0	263.0	—	—
Free and saline ammonia...	0.060	0.875	—	0.120	0.100	0.080
Albuminoid ammonia	0.002	0.004	—	0.006	0.008	0.004
Nitrogen in nitrates and nitrites	0.0	0.0	0.0	0.0	0.055	0.055
Oxygen absorbed in four hours at 80° F.	0.036	0.680	—	—	0.124	0.035
Hardness by soap test :						
Temporary	—	—	—	21.03	13.58	13.26
Permanent	—	—	—	23.22	7.02	7.14
Total	7.71	—	—	44.25	20.60	20.40
Silica	0.0	0.0	1.2	1.0	—	—
Iron oxide, Fe ₂ O ₃	Traces.	4.5	1.6	1.2	Traces.	Traces.
Barium oxide, BaO	1.38	28.36	29.94	2.23	0.0	0.0
Calcium oxide, CaO	2.60	141.64	169.0	15.40	—	—
Magnesium oxide, MgO	Traces.	42.16	39.06	4.82	—	—
Potassium oxide, K ₂ O	0.0	0.0	0.0	0.0	—	—
Sodium oxide, Na ₂ O	—	1080.76	1109.15	114.02	—	—
Heavy metals	Absent.	Absent.	Absent.	Absent.	Absent.	Absent.
Chlorine	17.1	1491.0	1554.9	142.0	10.7	4.8
Sulphuric anhydride, SO ₃	0.0	0.0	0.0	0.0	—	—
Phosphoric anhydride, P ₂ O ₅	0.0	0.0	0.0	0.0	—	—
Total alkalinity, calculated as CaCO ₃ ...	26.5	20.0	19.0	25.0	34.5	34.0
Alkalinity after boiling, calculated as CaCO ₃	21.25	2.0	1.5	2.5	21.5	21.0
Alkalinity after boiling, equivalent to Na ₂ CO ₃	22.52	—	—	—	22.79	22.26
Specific gravity at 60° F. water 1.000	—	1.018	1.019	—	—	—
Appearance in 2-feet tube	Fairly clear ; brownish-green.	Turbid ; brownish-green.	Turbid ; brownish-green.	Turbid and opalescent ; brownish-green.	Rather turbid and opalescent ; brownish-green.	Rather turbid and opalescent ; brownish-green.
Odour	None.	Slight.	Slight.	None.	None.	None.
Taste	None.	Strongly saline.	Strongly saline.	Saline.	None.	None.

These waters are of peculiar and abnormal composition. Samples E and F are of no great interest, and are only included as indicating the kind of water occurring in the neighbourhood of the bore-hole; they are typical examples of water such as is frequently found in or near the coal measures, containing, as these samples do, a comparatively high amount of free ammonia and chlorine, with traces of iron and a considerable quantity of sodium carbonate.

The first four samples contain barium in varying amount, and there is consequently an entire absence of sulphates and phosphates. As compared with the total solid matter present, the proportion of chlorine is relatively exceedingly high, while the lime and magnesia are in each instance very low. There is no evidence of pollution, the free ammonia being doubtless of mineral origin, and organically the waters may be pronounced to be pure.

Sample A was decidedly alkaline from presence of sodium carbonate, a fact which renders the occurrence in the water of barium particularly remarkable, inasmuch as sodium carbonate will precipitate the chloride or other soluble salt of barium at the ordinary temperature and in very dilute solutions. The barium, therefore, must exist as the carbonate, which salt is slightly soluble in water; it is present to the extent of 1.77 parts per 100,000.

This water flowed from the bore-hole at a temperature above normal; at the date of collection the thermometer in the open registered 47° F., but the temperature of the water was 61° F.

Samples B, C, and D all contained barium chloride. B and C closely resemble each other in their phenomenal composition; they contain an amount of barium corresponding respectively to 38.55 and 40.70 parts per 100,000 of barium chloride. With the exception of a water stated by Professor Bedson (*J.S.C.I.*, vol. vi., p. 712) to contain 96.04 grains per gallon of barium chloride, this is the highest amount I have been able to find recorded as occurring in a natural water. The other features of these waters worthy of notice are the extraordinary quantity of common salt in solution, and the comparatively small amounts of lime and magnesia present.

When freshly obtained, samples B and C, upon being briskly shaken at the ordinary temperature, evolved a considerable amount of gas, which I believe mainly consisted of nitrogen.

Sample D appears to consist of some similar water to B or C, diluted to nearly ten times its volume with some other normal water; the solid matter, chlorine, barium chloride, lime and magnesia, are present approximately in about one-tenth the amount in which these constituents occur in samples B and C.

In Table III. I have combined the acids and bases to show what may probably represent the actual salts present in solution in the four waters containing barium. It frequently happens that there is a difference of opinion as to the method to be adopted in combining these acids and bases. I have no wish, therefore, to insist upon the correctness of the view I have taken, but simply to follow the usual custom and state the calculated analyses:

TABLE III.

Results expressed in Parts per 100,000.

Calculated Analysis.	A.	B.	C.	D.
Barium carbonate	1.77			
Calcium carbonate	4.64			
Sodium carbonate	22.52			
Sodium chloride	28.17			
	57.10			
Silica	—	0.0	1.20	1.00
Oxide of iron	—	4.50	1.60	1.20
Barium chloride	—	38.55	40.70	3.03
Calcium chloride	—	258.55	315.08	2.77
Calcium carbonate	—	20.00	19.00	25.00
Magnesium chloride	—	100.13	92.76	11.44
Sodium chloride	—	2039.50	2093.08	215.29
	—	2461.23	2563.42	259.73

The barium was estimated in the water without previous concentration by acidifying with dilute hydrochloric acid, and then precipitating with very dilute sulphuric acid (about 1 in 300) and heating to boiling. The filtrate and washings were subsequently used for the determination of the lime by precipitation with ammonium oxalate in the usual way.

Having proved the absence of all other metals, including potassium, the amount of sodium oxide was ascertained, which was equivalent to the sodium chloride calculated. This was then checked by sulphating the residue from a known quantity of water, igniting and weighing, and comparing the result with the sum of the salts calculated to their respective sulphates. In this way a very fair approximation was obtained.

These waters give, as I will show you, marked precipitates with potassium chromate and dilute sulphuric acid, without previous concentration. I would point out in this connection that it is not advisable, when testing waters for lead, to rely entirely upon the chromate or bichromate of potash test. This should obviously be confirmed by the use of sulphuretted hydrogen, otherwise such waters as these might be pronounced to contain lead.

And now a few words as to the possible origin of the barium salts. There is not very much of a striking character, from a geological point of view, to be discovered by an examination of the diagram of the section of the strata through which the bore-hole passes, and no direct evidence appears to be afforded as to the whereabouts of the barium compounds. Some of the seams are described as containing "spar," but I have been unable to obtain any of this for analysis, and cannot say what is its composition. Nearly one-fifth of the strata is classified under the head of sandstone, and, with millstone grit, this constitutes upwards of one-third of the whole. Clowes (*Chem. News*, 52, p. 194) states that the beds of the new red sandstone near Notting-

ham are permeated by minute crystals of barium sulphate, which acts as a cementing material. Dieulafait is also stated to have shown that all primary rocks contain barium in sufficient quantity to be easily detected. The occurrence, however, of barium sulphate in the strata, although the most likely salt to be present, does not of itself account for the barium carbonate or chloride in these waters. The only explanation that occurs to me is that the barium sulphate in the rock, etc., has by some means, possibly by the action of heat in presence of carbon or carbonaceous material, been reduced to the sulphide, and this salt has then, by coming into close contact with beds of common salt or with some strong solution of brine, been converted into the chloride. This might then react with other water containing sodium carbonate, and so become changed into barium carbonate. It is possible that the carbonate might be directly produced from the sulphide, but the first hypothesis, having regard to the enormous amount of common salt associated with the barium salts, seems to me to be the more probable.

Clowes (*Royal Society Proceedings*, vol. xlv.) gives the results of some analyses of deposits formed in the water-boxes of coal-mines in the neighbourhood of Newcastle-upon-Tyne. These deposits consisted mainly, and in some cases almost entirely, of barium sulphate; they were soft and easily powdered, and appeared to have been produced by a process of rapid precipitation. He is of opinion that these deposits may be formed by the admixture of a water containing barium chloride, such as the one to which I have already referred, communicated by Bedson, with a water containing sulphuric acid or ferrous sulphate, produced by the oxidation of pyrites in the coal measures. The water analysed by Bedson was from a coal-mine near Newcastle-upon-Tyne.

Neither Clowes nor Bedson, as far as I know, have, however, offered any explanation of the origin of the barium chloride in solution in these waters.

Another instance of the occurrence of barium chloride in a natural water is to be found in a spring at Llangammarch, a small village in Breconshire, Central Wales. This spring has been analysed by Dupré and by S. Arch Vasey, of the *Lancet* laboratory. The former found 6·26 and the latter 6·74 and 6·49 grains per gallon of barium chloride, the total mineral matter amounting to 302 grains per gallon. Waters have also been found containing this salt at collieries near Sunderland and near Rotherham, and in a spring water near Shotley Bridge in Durham.

Barium chloride is said to possess valuable medicinal properties, acting chiefly upon the heart. As it is not, however, an official drug of the British Pharmacopœia, it is possible that its therapeutical effects are not yet properly understood. According to toxicological authorities, the minimum authenticated fatal doses recorded are of the carbonate 60 grains, and of the chloride 100 grains. From the results I have laid before you, it does not seem probable that cases of poisoning by the consumption of water containing salts of barium are likely to arise.

DISCUSSION.

The PRESIDENT thought that it might be possible to account for the presence of the soluble barium somewhat less elaborately than in the manner suggested by Mr. White, viz., simply by the action of sodium carbonate, under pressure, on the

barium sulphate. Without pressure, of course, the action of aqueous solutions of alkaline carbonates on barium sulphate was very slight, even when the solutions were boiled with the sulphate. It might be, however, that the original material was barium carbonate (witherite), which would more easily be dissolved. In the red sandstone, strontium occurred as celestine, the sulphate, and as strontianite, the carbonate; and possibly barium also occurred there in the forms of sulphate and carbonate. Anyone who met with either of these waters would at once notice that there was something unusual about it, from the fact that it contained no sulphuric acid.

Mr. HEHNER inquired whether the author had examined the water spectroscopically for the presence of small quantities of strontium as well as barium. In the case of many analyses made by Fresenius it had been demonstrated that both of these metals were often present in water, of course in very small quantities, and not in any way comparable with the cases referred to in the paper.

Dr. RIDEAL remarked that an analysis made by Dr. Dupré of the Breconshire water referred to had been widely circulated for purposes of advertising the water as a specific for cardiac diseases; and, inasmuch as that water only contained six or seven grains of barium per gallon, it would appear that these Ilkeston waters, containing several times that quantity, should have a greater value in such diseases. It would be noted that the absence of alumina was a characteristic feature of all these waters.

Mr. WHITE, in reply, said that the President's suggested explanation did not appear to account for the presence of barium chloride, and he (Mr. White) thought the barium could not exist in the water otherwise than as chloride. It might, however, account for the carbonate present in sample A, which was the original water from the borehole. The only evidence he had upon which to base his conclusion that barium sulphate was the original mineral, was the information contained in the papers of Dr. Clowes. Dr. Clowes had taken much interest in the subject, and it seemed quite clear that, in the neighbourhood referred to, there existed considerable quantities of barium sulphate in the sandstone, which formed about a fifth of the total strata passed through in boring the well; and therefore he (Mr. White) thought it fairer to conclude that barium sulphate, rather than barium carbonate, was present originally, for there was no evidence at all of the occurrence of barium carbonate in the neighbourhood. Some few miles away there was a piece of millstone grit, forced up, probably, by volcanic action, known as the "Hemlock Stone," from its shape and spreading top. Dr. Clowes had published an analysis of this stone, which showed that it contained in some parts a large percentage of barium sulphate. He (Mr. White) could confirm this from his own analysis of portions of the stone. He had not used the spectroscope to prove the absence of strontium, but had tested every precipitate of barium sulphate very carefully, without getting any evidence of the presence of strontium. He had no information as to the solubility of barium carbonate in solutions of alkaline chlorides, but had already, in referring to the President's remarks, stated his reasons for assuming the original presence of barium sulphate, and the way in which he thought the chloride was to be accounted for.