II.—*On the Action of Old Coal-pit Water upon Iron, in the Pendleton Colliery.*

By Mr. E. W. Binney.

[*Read November* 16*th*, 1852.]

The general use to which iron is now devoted in the erection of buildings, the structure of ships and lighthouses, and in the protection of mines from water, makes every fact in any way connected with its destruction or preservation worthy of being recorded, especially in this Society, where so many valuable communications upon this subject have been read, and so much practical information given to the world.

Cast iron is now used to a great extent for the purpose of "tubbing" water from mine shafts. This process may be briefly described as follows:—In sinking through beds of sand and porous sandstone like those of the lower new red sandstone at Monkwearmouth and other places, or in carrying a shaft through old coal workings down to deeper mines, immense volumes of water are sometimes met with. These are frequently dammed out of the shaft by cylinders of cast iron, put in in segments and firmly wedged, and made water-tight by pieces of wood being driven between them. By these means the water is generally dammed out or pent back, and in the latter case driven into old abandoned workings, which are too often allowed to remain full to save the expense of pumping out. The shaft is thus carried down to great depths without meeting with much difficulty from water.

These dammed-up waters, however, are not only very foul from the mineral matter with which they become charged in the old workings, but they exercise considerable pressure, in some cases reaching to one or two hundred yards of a column, against the sides of the tubbing. Now, should the iron from any cause give way, great loss of life must necessarily ensue; for that material generally gives but little warning of its breaking, and the irruption of water into the pit before the miners could escape, must therefore prove most disastrous, especially in deep collieries, where there are often but two shafts, and those placed close together.

Mr. Robert Mallet, M.I.C.E., &c., in his valuable reports (published in the 8th and 13th volumes of the Transactions of the British Association for the advancement of Science) upon the action of air and water, whether fresh or salt, clear or foul, and of various temperatures, upon cast iron, wrought iron, and steel, gives many instances of the effects of acid solutions and sea and fresh water upon these metals.

The action of sea water and a mixture of salt and fresh waters upon cast iron, by converting it into what has been called plumbago, is well known, and many instances have been recorded of iron guns and shot having been partially converted into that substance. The guns of the Royal George at Spithead may, amongst many others, be mentioned as a case which has lately come before the public. So certainly is this effect produced, that it strongly behoves those who have charge of the lighthouses now so often erected in the sea upon cast iron pillars, carefully and frequently to inspect such structures, for day by day their supports must be weakened by the action of the salt water.

With regard to the effect of sea water upon wrought iron, there appears to be some difference of opinion, for Mr. Mallet* states that he has in his possession a portion of an ancient anchor taken up in the port of Liverpool, the iron that remained of which was of remarkable purity, and which was converted into plumbago of unusual hardness and brilliancy to the depth of half an inch. This plumbago did not heat on

* Vol. vii. Brit. Ass. Rep., p. 259.

exposure. Its specific gravity is 1·773. This fact militates against an observation made by Mr. Hatchett, and repeated by M. Becquerel, that anchors and other objects of forged iron sustain no alteration in sea water but oxidation; from which we must suppose that the contact of iron and plumbago in the cast iron, produces a current which accelerates the action of the latter.

In Mr. Mallet's report before alluded to, he only mentions one case of the effects produced by waters in mines upon cast iron. This was given by one of the most distinguished members of this Society, the late Dr. William Henry, F.R.S., and is printed in vol. v., p. 66, of the *Annals of Philosophy*. It is entitled—"On the conversion of cast iron pipes into a substance bearing some resemblance to plumbago." As this communication bears so much on the subject of this paper, and appears to be but little known, I shall give it entire. He says—

"I was lately requested by a gentleman who resides in the neighbourhood of Newcastle-upon-Tyne, to examine the nature of the change effected in a cast iron pipe, placed in the shaft of a coal mine near that town. In sinking the shaft it was necessary, as sometimes happens, to put down a *curb*, or cylinder, of cast iron, in order to support a bed of quicksand: and into a suitable opening in this cylinder, the cast iron pipe, three inches diameter, was bolted by means of a *flanche* at its extremity. Its use was to allow an exit to the water and gas which issued from the stratum of quicksand.

"The fragment of the pipe with which I was furnished was of a dark grey colour: its inner surface was smooth and black; and its outer surface had a thin ochrey incrustation. The usual fracture of cast iron was exchanged for an earthy one, except near the centre of the mass, where somewhat of the usual texture of cast iron was still visible. It was soft enough to be easily scraped with a knife, and was readily broken by a slight blow of a hammer. Some parts of it left a black trace on writing paper, but destitute of the lustre which the traces of plumbago exhibit.

"The specific gravity of the specimen was 2·008, and, after being soaked an hour or two in water, it became 2·155.

"Twenty grains of the powdered substance was projected upon 200 grains of melted nitre. The combustion was very feeble, compared with that which happens to plumbago under similar circumstances. After washing off the nitre, there remained 14½ grains, which were almost entirely oxide of iron, consisting probably of 11·2 iron, and 3·3 oxygen.

"A small piece of the pipe, weighing 6½ grains, was passed into a glass tube containing diluted sulphuric acid over mercury. The acid acted very slowly: and, in eight days, when its effect seemed to be complete, only half a cubic inch of hydrogen gas was formed. This was only about $\frac{1}{20}$th of what would have been obtained from the same quantity of cast iron.*

"There remained a black and bulky substance, which, when dried and projected on red hot nitre, burnt rather more vividly than the original substance, but still afforded much oxide of iron.

"It was clear, therefore, that a large share of the metallic part of the pipe had been removed; and that what remained was composed of iron, plumbago, and other impurities usually present in cast iron. With the view of ascertaining the cause of the change, I next examined the water from the bed of quicksand, a bottle of which had been sent along with the fragment of pipe.

"The water had a brackish taste, and was of the specific gravity, 1·008. It gave no traces of iron, either with triple prussiate of potash, or succinate of ammonia. I collected the gas from a wine pint of it, but it was lost by accident before being examined. By the usual methods of analysis, a wine pint gave 64 grains of dry salt, composed of—

Muriate of soda	32
——— magnesia	16
——— lime	10
Sulphate of lime	4
Carbonate of lime	2
	64

* A piece of plumbago from Borrowdale, kept eight days in dilute sulphuric acid, had evolved no gas.

"It is most probably to the agency of the muriates of lime and magnesia, that we are to ascribe the removal of the metallic part of the pipe. I have often remarked the effect of solutions of these salts in discharging writing ink from the labels of bottles to which they have been accidentally applied: and I was lately baffled in several attempts to restore the legibility of some of the MSS. of a most accomplished scholar (the late Mr. Tweddell, of Trin. Coll., Cambridge) which had lain some time under sea water, abounding, as is well known, in muriate of magnesia. The texture of the paper was entire, but the iron basis of the ink, as well as the gallic acid, was entirely removed.

"In that copious repository of valuable knowledge, Dr. Priestley's *Experiments and Observations on Air*, some facts are stated that bear an analogy to the one which I have described. Cast iron nails, he found, dissolved very slowly in diluted sulphuric acid; and left a large proportion of black matter which had the original form of the nails. This experiment, he observes, explains what happens to cast iron pipes in pits, the water of which is impregnated with vitriolic acid; for, in time, they become quite soft, or, as it is called, rotten, and may be cut with a knife.

"In Cornwall, I am informed, cast iron pipes are disused in many of the mines; but this is owing to the presence of sulphate of copper in the water, the corroding effects of which render it necessary to substitute pipes of brass or copper.

"The following fact, which was lately observed at the printing works of a friend of mine, belongs to a different class of phenomena, and is, perhaps, to be accounted for by galvanic agency. In order to confine the heat in some cast iron steam pipes, they were placed in a trough or gutter made of bricks, into which powdered charcoal was tightly rammed. At a place contiguous to a joint, formed by bolting two flanches together, a leak had happened, and when the iron pipe was taken up, it was found, in the neighbourhood of the leaky part, to be perfectly soft and rotten. I was not able to obtain an opportunity of examining the nature of the change by an experiment on the altered iron."

The facts which will be brought before you in this communication occurred in the deep pits of the Pendleton colliery, near Manchester. This "winning" was commenced by Mr. Fitzgerald on the 17th day of July, 1837, and the Duchess of Lancaster seam of coal was reached in 1840, at a depth of 464 yards from the surface. About 150 yards of cast tubbing, varying from one-half to three-quarters of an inch in thickness, was put into the shafts down to the distance of 150 yards from the surface; behind this was generally a four and a half inch wall of circular bricks, but near the seams of coal a brick wall of one yard in thickness, both grouted at the back with Ardwick lime and gravel. A portion of the tubbing originally made for a shaft of ten feet in diameter was used in these of eight feet. At the time of the accident there was in the old workings of the four feet mine, and the shaft communicating with them, a vertical column of water of about 600 feet, and at the place where the tubbing gave way, three segments of the ten feet castings were used with one of the eight feet; thus forming an imperfect circle.

The colliery continued working until the first day of August, 1843, when the waters from the old four feet mine workings burst through the tubbing in No. 2 shaft, about 140 yards from the surface, and rushed down the remaining 344 yards with fearful violence, displacing the air from the lower part of the workings, and ultimately filling the latter and the shafts up to within 40 feet of the surface. The dip of the strata in the mine was about one in three; so when the workings were filled to the bottom of the shafts, the air and gases in the mine were pent up in the "rise" part, and kept there by the pressure of a column of water of 1,352 feet.

The accident took place in the night, and Mr. Ray had time, from some warning, to withdraw all the men out of the pits, so that there was no loss of life. Many waggons full of coal were near the pit bottom at the time of the irruption of the waters, and they remained there until the mine was drained. Some of the cast iron wheels and wrought iron axles of these waggons will be mentioned in this communication, and are now exhibited on the table.

On the first day of November, 1844, the pumps for withdrawing the water from the mine were started, and by the second day of February following, the hole where the water had burst into the shaft was reached, and the men commenced to put in the new tubbing. The bottom of the shafts, filled with four yards of dirt, was reached on the 4th day of October, 1846. At the commencement of 1847, the workings were cleared, and the specimens of iron described in this communication brought out of the mine, having been thus buried and immersed about four years and six months.

A description of the specimens will now be given.* These consist of cast and wrought irons. There is no evidence as to their make, either as to the locality where they were made, or whether they are of hot or cold blast manufacture.

First as to the cast iron:—

No. 1 is part of an edge wheel, ten inches in diameter, one inch thick in the centre, formerly belonging to one of the underground waggons. The shape of the wheel is preserved, but the whole substance of the casting has been altered. When first taken out of the pit it was of a brownish black colour, and could be easily cut, like soft clay, with a knife. Since it has been exposed to the air, it has become harder, and is now not so black as it first was. Its fracture is earthy, and not like that of cast iron. The composition of it I am enabled to give through the kindness of my friend, Dr. Robert Angus Smith, F.C.S., who has been at the trouble of analyzing a portion of this specimen. He found it to consist of—

Iron and bases	38·8
Carbon	40
Silica	19·7
Its specific gravity is	2·0133

* These specimens, as well as much valuable information, I owe to the kindness of Mr. Andrew Ray, the late intelligent manager of the Pendleton Colliery.

For the sake of comparison, it may be as well to give an analysis of the Dowlais hot-blast iron, No. 4:*—

Suspended graphite	1·22
Combined carbon	2·13
Phosphorus	0·21
Manganese	0·17
Alumina	0·00
Sulphur	0·00
Silica	1·21
Iron	95·06
	100·00

The average specific gravity of cast iron, according to Karsten, is 7·5.†

It will be at once evident that not only has a great alteration taken place in the specific gravity of the specimen, but that a large proportion of its iron has been removed, and its place occupied by carbon and silica, for the bulk and shape of the specimen still remain the same, although it has lost so much of its weight. The iron appears dispersed through the earthy mass in little globules of a bright colour, when viewed under a lens.

Nos. 2, 3, 4, and 5 are specimens of portions of other edge wheels of cast iron. All of them shew a decomposition from the outside to the inside, varying, in different cases, from a third to half an inch, the middle part of the casting still consisting of metallic iron, surrounded by a brownish black substance resembling plumbago. In every respect as to size, and the use to which they were applied, these specimens are the same as No. 1, which, as before described, is altered throughout its whole mass. Whether the iron varied from the last-named specimen, or they were placed in a different position, and thus subjected to other conditions, there is no evidence to shew.

* Mallet's Report, Vol. xiii. Brit. Ass. Rep., p. 4.

† Vol. v., Gmelin's Hand Book of Chemistry, p. 211.

No. 6 is a most interesting specimen of a portion of cast iron tubbing, of an inch in thickness. One side of it appears to have been built into a wall, or somehow covered with a coat of lime, for it is still coated with whitewash, except a portion near the edge, which has a little yellow ochre upon it. Now where the thin covering of lime remains, the iron on that side shews no signs of decomposition, whilst on the other side, where there is no lime, the iron in the centre of the casting has been eaten away to the depth of one-fourth of an inch.

The effect produced upon the wrought irons:—

No. 7 is a chisel of wrought iron, faced with steel, ten inches in length, by three-quarters of an inch in diameter. The iron is corroded and eaten into so as to shew the threads of which it is composed, in some places, to the depth of two-tenths of an inch. This is most marked where the iron and steel join. The steel itself has scarcely been acted upon at all, and the broken point exhibits a fracture just as if it had only been made a few days.

No. 8 is the outside of a 1½ inch axle, which was attached to one of the waggons to which the cast iron wheels previously described belonged. The thickness of it is about one-third of an inch, and it appears as if it had shelled off from the sounder part of the axle. It has not the black plumbago appearance which the cast iron before noticed exhibits, but shews more of the characters of ordinary rust, produced by oxidization of the metal.

No. 9 is a wrought iron hammer, with a handle of ash fixed in it. This specimen appears to have been acted upon more than any of the other specimens of wrought iron, being in some parts, especially the faces, corroded to the depth of one-third of an inch. The threads of iron and every bend in them are beautifully shewn all over the surface of it.

There was another hammer, with steel face, found in the pit. This was corroded in a similar manner to that last described, but the facings of steel were quite free from injury.

All the wrought iron specimens appear as if they had merely been oxidized, and not converted into plumbago like those of cast iron. This, Hatchett and Becquerel contended, was the case with wrought iron immersed a long time in sea water, and which has been previously alluded to in this paper.

Mr. Ray informs me that neither the wrought nor cast irons heated on first being taken out of the pit and exposed to the air.

Unfortunately no analysis was made of the waters, either at the time of their first breaking into the shaft, or when they were nearly drained out of the mine. These would in all probability be of two descriptions, namely, a small supply of salt water found at the bottom of the mine, containing the chlorides of sodium, magnesium, calcium, and other salts usually found in deep collieries, and the vast body of water which burst into the shaft from the old workings of the four feet mine, extending on the level of the coal four or five miles, where the water had been pent up some years, and, like all such waters, containing an abundance of sulphate of iron and some free sulphuric acid, derived from the decomposition of bisulphide of iron, together with silica and carbonic acid. The pressure of the column of water in the shaft would cause the waters below to be charged with highly condensed air, light carburetted hydrogen, and carbonic acid gases. Waters highly condensed with the latter, both take up considerable amounts of silica, and are known to exercise a destructive action upon iron.

The effect of lime in preserving steel and iron from oxydizing, has been long known and employed by artizans in preserving their tools bright. M. Payen* has presented several memoirs to the Academy of Sciences, on the subject

* Comptes Rendus, Feb. 1837, No. VI.

of local actions on iron, and has added to their explanation the facts he had previously discovered as to the effects of alkaline and saline solutions in retarding or accelerating the corrosive action of water on iron. Sir John Herschel, in a letter in the *Comptes Rendus* for 1836, page 509, recommended an engineer at the Cape of Good Hope to soak some iron pipes with Roman cement, and it produced a good effect in preventing their decomposition.

Mr. Mallet† states that M. Payen's observations as to the power of alkaline waters to protect iron from rust, though seldom applicable, are worthy of further investigation, and an attempt to preserve their rationale; and he then alludes to the circumstance of workmen having been long aware of the fact, and suggests that alkaline solutions might be of considerable use in certain cases, but he makes no mention of coatings of lime on the iron itself.

I have thus given a brief description of the specimens of altered iron, and, so far as I am able, of the circumstances under which such alteration took place. The removal of iron in acid solutions, where the softer portions are first decomposed, is well known, and now generally attributed to the want of homogeneity in its parts, which causes galvanic currents. In waters of the Pendleton colliery, sulphuric, hydro-chloric, and carbonic acids would all be present, and produce their effects upon the iron; but these would, doubtless, be much assisted and increased by the pressure of a vertical column of 1,352 feet of water acting upon the air and gases of the mine. This great pressure on the air and gases (carbonic acid and light carburetted hydrogen) in the mine, would cause the water to be charged with them in a highly condensed state, and thus bring them into a condition peculiarly appropriate for combination.

The cast iron wheels lying in contact with coal, and immersed in water containing acid solutions, would present

† 8th Report of the Brit. Ass., p. 305.

nearly similar conditions to the cast iron pipe with a leak in it, surrounded by charcoal, previously mentioned by Dr. Henry, and a strong galvanic current can be easily supposed to have been generated and the iron removed by this cause; but how the carbon and silica have occupied the place of the iron, I am unable to account for. The waters highly charged with carbonic acid would doubtless take up a large quantity of silica in solution, and as portions of iron were removed, parts of silica might take their places, as it is imagined is the case with fossil woods containing silica. In what manner the carbon was deposited, however, I can give no opinion.

This is a very interesting subject, and requires much further investigation than I can devote to it. The chief object of this communication was to direct the attention of coal masters to the action of old mine waters upon iron, and to recommend them not to place too much trust on metal tubbing alone; and also to point out the protection which lime in the shape of mortar affords to iron under the most severe tests,—for the water that could decompose an inch casting in four and a half years, must be taken as an extreme case. After the facts stated in this paper, no proprietor of a colliery ought to omit placing a bed of hydraulic lime inside the metal tubbing of his shafts, when so simple and cheap a precaution will tend not only to save a great amount of property, but, what is of far greater importance, preserve a number of valuable lives.