tory condition for analysis, but it seems probable that the substance has the composition $AgBr_2I$.

The stability of the salt $RbBr_2I$ is quite marked in the absence of moisture.

1.4047 grams $RbBr_2I$ on standing in a desiccator 16 days lost only 3.3 milligrams. On standing 38 days the loss was only 7.1 milligrams.

The effect of atmospheric moisture in accelerating the decomposition of this salt is well shown in the following table :

Time of standing.	Condition of experiment.	Per cent moisture in air.	Weight of salt. Gram.
	Original weight of salt		0.8678
2 days.	In open vessel		0.8655
1 day more.	" desiccator		0.8650
1 " "	" "		0.8649
1 " "	" open vessel		0.8644
1 " "	" " "	69 per cent.	0.8642
1 " "	" " "	69 " "	0.8640
2 days "	" " "	92 " "	0.8632
2 " "	" " "	93 " "	0.8627
4 hours "	" desiccator		0.8626
20 " "	" "		0.8625
5 days "	" "		0.8622
21 " "	" "		0.8582

The addition of a slight quantity of sulphurous acid to the water solution of the salt produces a precipitation of iodine, which is redissolved on further addition of the reagent.

Finally to 10 grams of rubidium iodide dissolved in 6.6 cc. of water was added 4 grams of bromine, one-half of the quantity of bromine used in the preparation of rubidium dibromiodide. From the solution thus obtained only rubidium triiodide crystallized as the first crop.

UNIVERSITY OF GEORGIA,
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ACTION OF WATER OF THE HUBB COAL MINE UPON CAST IRON.

BY FRANK W. DURKEE.

In 1872 the Hubb Coal Mine, in Cape Breton, Nova Scotia, was abandoned. Soon it filled with water; but in the time between December, 1894, and April, 1895, the Dominion Coal

Company (Limited), the present owners of the mine, pumped the water out. Then, it was found, that the cast iron which had formerly been used for purposes of construction within the mine, had, while lying beneath the mine water, through this long period, undergone radical changes. For instance, the cast iron T-rails in the car tracks, while retaining their original size and shape, were no longer strong and fairly tough like cast iron. A man could break them across his knee, or beat them into fragments with a tack hammer. They were soft enough to be easily cut with a knife. A cross-section, prepared by the use of an ordinary saw, was grayish-brown in color. The internal half of the section, however, was lighter in color than the external, and softer in texture. Where the surfaces of the original castings were not covered by films of a reddish-brown ferric oxide, they were grayish-brown like the cross-sections. The transformed cast iron was magnetic, porous, and several times lighter than the same bulk of cast iron. Brought in contact with a piece of white paper it left a mark like that of a lead pencil. In a word, the greater part of the cast iron that was in the Hubb mine at the time it was filled with water, had been changed, by chemical action, into masses looking like graphite and shaped like the original castings. While the changes described above had been going on in the cast iron, the surfaces of wrought iron structures had been deeply corroded by the mine waters, but the iron in the deep-seated portions still remained perfect. Consequently the wrought iron structures in the mine had diminished considerably in size, but internally had not become porous like the cast iron. Steel structures had wasted away but slightly, and were perfect beneath their surfaces. The waters of the Hubb mine attack white cast iron less readily than gray, wrought iron slowly, and steel with much difficulty.

Changes in cast iron, in some ways, not unlike those that have taken place in the Hubb mine, have been described by Deslongchamps,[1] who found that the cast iron cannon balls, which had been taken from the sea off the coast of Normandy, had lost two-thirds of their weight, contained no metallic

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[1] J. chim. Méd., 13, 89.

iron, and were soft enough to be cut with a knife. Berzelius states[1] that some of the cast iron cannon balls, which had been taken from a vessel, sunk fifty years before near Carlscrona, were changed to their very centers into a gray, porous, graphite substance, which, after exposure to the air for fifteen minutes, became hot enough to drive out the adhering moisture. Other cannon balls in the same lot were changed, as above described, only through a part of their diameters. In the opinion of Berzelius and Karsten, these changes have been produced by the action of oxygen and carbon dioxide from the atmosphere, which have been dissolved in the sea water, and they describe the product as a mixture of graphite, ferric oxide, ferrous carbonate, silica, and the carbide of iron, FeC_3. Karsten has also shown that a mixture of graphite, silicon, and the carbide, FeC_3, is produced by treating gray cast iron with a ten per cent. solution of sulphuric acid. Mallet has found[2] that cast iron yielded more readily to the action of impure waters at the mouths of rivers which empty into the sea, than to the action of pure sea water. The chemical changes that take place under the last mentioned conditions, Mallet summarized as follows: $FeO + H_2O$, $Fe_2O_3 + FeO + H_2O$, and $FeCO_3$, are at first produced. These substances are then attacked by H_2S, forming FeS and $6(FeS + FeS_2)$. The sulphides are transformed by the oxygen of the air into $2Fe_2O_3 + SO_3 + 6H_2O$ and $FeSO_4 + 6H_2O$.

It is noticeable, in all the instances hitherto investigated, where cast iron has been transformed by natural means into the product above described, that the transformation has been effected under sea water, or in a mixture of sea water and fresh water, where the conditions are different from those that might be expected to exist in a submerged Nova Scotia coal mine. Consequently, to find by what means the cast iron of the Hubb mine had been changed to a mass resembling graphite, and the chemical character of the new substance, further investigation seemed necessary.

Through the kindness of the Dominion Coal Company

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[1] Gmelin's Handbook, 5, 218.

[2] Action of Air, Water, Etc., upon Cast Iron, Wrought Iron and Steel, British Assoc. Reporter, 1839 and 1841.

(Limited), several pieces of the transformed cast iron, together with pieces of wrought iron and steel, from the submerged mine, have been obtained for use at our laboratory, and, at the same time, six gallons of the mine water. From the center of a piece of transformed cast iron, a sample of the original cast iron has been obtained. In addition to the sample of cast iron just mentioned, four samples of the transformed cast iron have been selected for analysis and numbered I., II., III. and IV. for convenience. No. I. contained nothing but the light colored central part of the transformed cast iron, mentioned in the description of a cross-section of a rail; II., the outer, harder, and darker part of the piece from which I. came; III., the outside of the piece from which the gray cast iron was taken; and IV., the cross-section of a T-rail. The samples were not dried artificially, but were ground in an agate mortar, and transferred at once to glass-stoppered weighing-tubes. Analyses of these samples should disclose much of the chemical character of the transformed cast iron.

The samples have been analyzed and the calculations made by the following methods: Carbon and water have been determined by combustion with lead chromate and oxygen. In the case of the cast iron, the carbon has first been separated by the use of the double chloride of copper and ammonium.

Water mechanically held has been found by heating weighed quantities of the samples in an air-bath at 105° for four hours.

The first step in the determination of silicon and silicon dioxide in the samples, has been to oxidize the remaining silicon to silicon dioxide by fusion with sodium carbonate and potassium nitrate in a platinum crucible. The silicon dioxide resulting, has then been determined in the usual way.

Another weighed portion of the same sample, freed from water by gently heating in a porcelain boat with a small Bunsen flame, has then been transferred to a combustion furnace and treated with chlorine according to Drown's[1] method for the determination of silicon in cast iron. Afterwards the residue in the boat has been removed to a platinum crucible, mixed with sodium carbonate and potassium nitrate, and

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[1] Journal of Institute of Mining Engineers, 7, 346.

fused. On cooling the fused mass has been treated in the usual way for the determination of silicon dioxide. The weight of the silicon dioxide, found in the second determination, subtracted from the weight of the silicon dioxide obtained by fusion before the treatment with chlorine, gives the weight of the silicon dioxide that has been produced by the oxidation of the silicon in the original samples. From the weight of silicon dioxide thus obtained by difference, the weight of silicon in the samples has been calculated. The weight of silicon dioxide, obtained before the treatment with chlorine, minus the weight of the silicon dioxide, found as above by difference, gives the weight of the original silicon dioxide in the samples.

Phosphorus has been determined by the molybdate method with final precipitation as ammonium magnesium phosphate. In sample IV., which contained arsenic, the phosphorus and arsenic have been precipitated together by boiling with molybdate solution, and afterwards weighed together as magnesium pyrophosphate and magnesium pyroarseniate. In a very dilute solution of a separate portion of IV. the arsenic itself has been estimated by the use of Marsh's apparatus and standard arsenical mirrors. The arsenic has then been calculated as arsenical pyrites and magnesium pyroarseniate. The magnesium pyroarseniate subtracted from the magnesium pyrophosphate and magnesium pyroarseniate give the magnesium pyrophosphate obtained from the samples, and this has been calculated as phosphoric anhydride.

Calcium had been determined by the oxalate method; magnesium by the pyrophosphate method; and manganese by Gibbs's pyrophosphate method.

The total amount of sulphur in the samples has been determined in the usual way after fusion with sodium carbonate and potassium nitrate. The sulphur, combined with a metal or metals to form sulphide, has been determined by Blair's[1] modification of Fresenius' method. The sulphur has been calculated as ferrous sulphide. Sulphur, in the sample, above that in combination with metals to form sulphides, has been calculated as sulphur trioxide.

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[1] Blair's Chem. Anal. of Iron, p. 63.

Iron has been determined by Marguerite's potassium permanganate method. Unfortunately, on account of the presence of considerable carbon and iron or less metallic iron in the samples, it has been impossible to determine the part of each sample that is ferric oxide. But this failure seems to be of little importance, since inspection of the samples alone is sufficient to show that ferric oxide is present only in small quantities, and therefore, the oxygen above that necessary to form ferrous oxide can safely be neglected.

Oxygen, above that in combination with silicon to form silicon dioxide, with hydrogen to form water, with sulphur to form sulphur trioxide, with calcium to form calcium oxide, with magnesium to form magnesium oxide, with manganese to form manganese monoxide, and with phosphorus to form phosphoric anhydride, has been determined by difference, after first assuming that the sulphide, found by direct experiment in the samples, was ferrous sulphide, and that the arsenic in IV. was combined with iron to form arsenical pyrites. If this assumption is true, it follows, for there is no carbonate in the samples, that all the oxygen in excess of that mentioned above, neglecting traces of ferric oxide, must be combined with the iron to form ferrous oxide. Therefore, to find what per cent. this oxygen is of the whole substance, it only remains to add together the percentage of each sample, that is, silicon dioxide, silicon, carbon, water, ferrous sulphide, sulphur trioxide, phosphoric anhydride, calcium oxide, magnesium oxide, manganese monoxide, arsenical pyrites, and iron above that combined with sulphur and arsenic, and to subtract the sum from one hundred. The difference, which is the percentage of oxygen in the samples above that already mentioned, has been calculated as ferrous oxide. The percentage of each sample, that is, iron combined with carbon to form carbide, FeC_3, and metallic iron, has been found by subtracting the sum of the percentages of the iron in ferrous sulphide, arsenical pyrites, and ferrous oxide from the total percentage of iron in the sample.

The analytical results below show the composition of the sample of gray cast iron and of I., II., III. and IV. These results have been calculated in per cent., and, in most cases, are averages obtained by duplicate determinations. The specific gravities of the samples, water standard, are first given.

Gray Cast Iron.

Specific gravity 6.9.

Silicon.	Carbon.	Sulphur.	Phosphorus.	Calcium.	Magnesium.	Manganese.	Iron.	Total.
1.74	3.46	0.15	0.38	0.76	0.24	0.63	92.54	99.90

Transformed Cast Iron.

	I.	II.	III.	IV.
Specific gravity.	2.1	2.5	2.5	2.3
Silicon dioxide	17.97	12.25	10.62	27.81
Silicon	0.57	1.67	0.83	
Carbon	18.21	13.33	9.71	15.21
Water mechanically held	3.04	3.53	4.70	3.29
Water combined	5.40	5.21	7.78	4.49
Ferrous sulphide	0.33	0.38	1.25	0.96
Sulphur trioxide	1.41	2.73	3.02	0.75
Phosphoric anhydride	2.34	1.65	1.88	2.36
Calcium oxide	1.36	1.25	0.99	trace
Magnesium oxide	0.36	0.35	0.87	....
Manganese monoxide	0.30	0.30	1.90	1.84
Arsenical pyrites	....	....	....	0.68
Metallic iron + iron in the carbide FeC_3	22.84	23.06	28.55	3.37
Ferrous oxide	25.87	34.29	27.90	39.24
	100.00	100.00	100.00	100.00

On comparing the above results it is noticeable that IV. contains more silicon dioxide and less magnesium and calcium oxides than either I., II. or III. Moreover, it is not equally rich in sulphur trioxide. The thing that distinguishes IV. from the other samples more than anything else, and from the sample of cast iron is the fact that it contains arsenic. The mine water, which covered all four of the samples, contained 0.00005 gram of arsenic per liter. But, since samples I., II. and III. contained no arsenic the arsenic in IV. must have come from the cast iron, out of which IV. was produced, and not from the mine water. The cast iron, whose analysis has been given above, so far as all the analytical results obtained show, may have been the material out of which samples I. and II. have been produced, and, from the method of sampling, is the material out of which III. has been produced; but, for reasons already given, it could not have been the material out of which IV. has been produced. Consequently the analytical results from sample IV. are not strictly comparable with those from the sample of cast iron and I., II. and III. The percentage of carbon seems large in all the samples, with the possible exception of III., even when allowance has been made for the insolubility of carbon and the loss in weight which the original cast iron has sustained. It is not large enough, however, to warrant the conclusion that the percentages of carbon in I., II., and III. have been augmented by deposition of carbon in any of these samples. It will be seen that in the production of I., II., III. and IV., considerable iron must have passed out of the original cast iron, while oxygen and water have been added. A little silicon dioxide and sulphur complete the additions which the original cast iron has received. Therefore, it would appear, from the large amount of oxygen and the comparatively small amount of other substances added, that the transformation had been brought about chiefly by the addition of oxygen. However, since the oxides of iron are insoluble in water, this supposition does not account for the loss of iron which the original castings have sustained. The iron had to be changed into a soluble compound before it could pass out into the surrounding water. An analysis of the mine water ought, therefore, to reveal the nature of this soluble compound of iron and also the solvent of the iron. I am indebted to my assistant, Mr. John W. Edwards, for a partial analysis of the Hubb mine water. The results are below.

	Grams per liter.
Free and combined sulphuric acid	0.4551
Free sulphuric acid	0.0230
Calcium	0.0419
Silicon dioxide	0.0153
Magnesium	0.0222
Chlorine	0.0284
Arsenic	0.00005
Iron, aluminium, and manganese	0.0096

On account of the presence of sulphate of iron and free sulphuric acid in considerable quantities in the mine water, the former must have been the soluble compound of iron and the latter the solvent.

Going back to the formation of the sulphuric acid, the chemical changes in the original castings may be briefly summarized as follows: A part of the iron pyrites in the coal, acted upon by the moist air, has been converted by a well-known reaction into ferrous sulphate, free sulphuric acid, and sulphur. Once formed, the sulphuric acid has found its way into the mine water, which, after a time, has become strongly acidic enough to slowly attack the submerged cast iron. From this chemical action the sulphates of the strong metals in the castings have resulted, together with hydrogen and hydrocarbon. The soluble sulphates dissolved and passed out of the castings into the mine water, and the mixture of silicon, graphite, and the carbide of iron, FeC_3, described by Karsten, must, after a time, have resulted if the mine water had been more strongly acidic. But, instead of a strength of 10 per cent. sulphuric acid, the mine water attained only a strength of 0.0023 per cent. Consequently secondary chemical reaction set in, and the oxygen and carbon dioxide of the air, which the mine water held in solution attacked the cast iron and produced $FeO + H_2O$, $FeO_2 + FeO + H_2O$, and possibly at first a small quantity of $FeCO_3$, as described by Mallet. This reaction accounts for the existence of considerable oxide of iron in the transformed casting. The ferric iron in the compound, $Fe_2O_3 + FeO + H_2O$, could not, however, exist long in the presence of the hydrogen, produced by the action of the metallic iron on the sulphuric acid, as it would be changed to ferrous iron. The reducing action of hydrogen accounts for the almost complete absence of ferric oxide from the transformed cast iron. When taken from the mine the castings contained no carbonate. If any was ever formed, the sulphuric acid solution, after a time, became strong enough to dissolve it, with formation of ferrous sulphate, carbon dioxide and water. It is also very probable that a part of the ferrous oxide has dissolved in the sulphuric acid to form ferrous sulphate and water. Silicon and phosphorus have been gradually oxidized, while the carbon in the cast iron chemically has remained unchanged, except for a slight loss due to the formation of hydrocarbons. Sulphuric acid and atmospheric gases, dissolved in the mine water, are the principal chemical agents that have been instrumental in changing the original castings in the Hubb mine into masses having the appearance of graphite.

TUFTS COLLEGE.

Contributions from the Chemical Laboratory of the Lehigh University.

III.—THE ACTION OF SULPHURIC ACID ON ANISOL.

BY W. B. SHOBER.

Various statements have been made by different investigators concerning the result of the action of sulphuric acid on anisol (methylphenyl ether). Kekulé[1] and Cahours[2] state that when anisol is treated with sulphuric acid, para- and orthoanisolmonosulphonic acids are formed.

Annaheim[3] obtained the para and ortho acids by heating methoxysulphobenzide with sulphuric acid.

Moody[4] treated 50 grams of anisol with an equal volume of sulphuric acid at ordinary temperature. He found that the ether dissolved readily with evolution of heat. On adding the reaction-mixture to water, a portion of the anisol was liberated. This was shaken with a further quantity of sulphuric acid at 80°. The acid solution was neutralized with calcium carbonate, and the calcium salt purified by fractional crystallization. He found but *one* calcium salt. This was converted into the amide (melting-point 108°).[5] The anisol used was obtained from Kahlbaum. Moody dried it over sodium and then carefully distilled it, rejecting the first and last portions. (boiling-point 153°). Franklin[6] treated anisol, obtained by decomposing diazobenzene sulphate with methyl alcohol (boiling-point 152°–154°), with three times its weight of ordinary concentrated sulphuric acid. In one case the mixture was heated on a water-bath for two hours, in another for one hour at 80°.

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[1] Ztschr. Chem., 1869, 201.

[2] Ann. Chem. (Liebig), 52, 333.

[3] *Ibid.*, 172, 47.

[4] Proc. Chem. Soc., 1892-93. 90.

[5] This melting-point is apparently too low. In this and a previous investigation, I have determined the melting-point of paramethoxybenzenesulphonamide repeatedly. Under all conditions it has melted at 112°-113°. Franklin gives the melting-point as 112°.

[6] Dissertation, 1894.