NOTE¹ ON THE CORROSION OF STEAM BOILERS BY THE
SULPHURIC ACID IN THE SOOT DEPOSITED FROM
THE SMOKE UPON THEIR SURFACES.

Translated from the *Annales des Mines*, of 1876, for the JOURNAL OF THE FRANKLIN
INSTITUTE,

By Chief Engineer ISHERWOOD, U. S. Navy.

The Central Commission on Steam Engines had its notice called at the commencement of the year 1875, to the explosions of two steam boilers, one at the pits of Glenons, in the La Machine coal mine (department of the Nièvre); the other at the iron works of Ougrée, in Belgium; both of which are attributed to the deterioration of the metal by the sulphuric acid in the deposits left by the smoke on the iron plates of certain parts of the boilers.

Other facts of the same nature having since come to the knowledge of the Commission, it has thought that by making all the observations it has collected, the subject of a note, to be inserted in the *Annales des Mines et des Ponts et Chaussées*, they would be given the widest publicity, and attract the attention of engineers and manufacturers to the conversion under special circumstances of the sulphurous acid in the smoke from the furnaces of steam boilers into sulphuric acid; and thus direct inquiry to a question that has been but little studied. With this view the two accidents investigated by the Commission will be first described, and then the other observations made on the same subject will be reported.

I. *Explosion of the boiler at the pits of Glenons.*—The explosion at the pits of Glenons occurred under the following circumstances on the 13th of November, 1872: The boiler was cylindrical, with the fire-grate placed immediately beneath it. Below the boiler, and separated from it by a brick vault, was a feed-water heater, whose top nearly touched the vault. This heater was burst wide open at its front nozzle or connection, the rent extending along a horizontal seam, and perpendicularly to the two ends. The original thickness

¹ This Note, and the succeeding one, are the nearly integral reproduction of two Reports presented to the Central Commission on Steam Engines, by Mr. Hanet-Cléry, Engineer-in-Chief of Mines, during the session of February 2d, 1876.

of the metal, which, in the place that first yielded, had been 0.47245 inch, was found reduced to only 0.06693 inch, a thickness quite insufficient to resist a pressure of 85 pounds per square inch, under which the boiler was operated. The thinning of the metal was wholly on the outside, and extended, but in a much less degree, over all the upper portion of the heater. This deterioration, which was relatively rapid, as the boiler dated from 1867 only, was attributed by Mr. Douville, Mining Engineer, to the action of the oxygen and sulphurous acid in the gases of combustion in presence of the water leaked down from the boiler above, which, after percolating through the brick vault, dripped upon the comparatively cold heater,¹ wetting its upper portion and collecting principally along the horizontal seam joining its top and bottom plates, that prevented the water from running off. The smoke deposits on the top of the heater (which the position of the masonry hindered from being cleaned) were thus enabled to imbibe water, and the conditions became most favorable for the oxidation of the metal by the sulphurous acid. Mr. Douville took large scales of the oxide of iron from the corroded parts, and he therein found sulphur, but was not able to determine its state of combination.

II. In proof of this view of the case, the accident which happened at the iron works of Ougrèe, on the 30th of October, 1873, is most conclusive; in fact, the sulphuric acid was found in the smoke deposits, either in the free state, or combined in the sulphate of iron. The following are the circumstances of the explosion, as clearly set forth by the superintendent of that establishment.

The boiler was constructed in 1863, and consisted of three horizontal cylinders, two of which lay beneath the third, and were joined to it by connecting pipes. The two were of equal diameter, and the third was of larger diameter. All three were set with brick flues, and heated by the waste gases from three puddling furnaces. The flues were so arranged that the gases proceeding on entering in one direction, first enveloped simultaneously the entire circumference of one of the small cylinders, and one-half of the lower semi-circumference

¹ That part being at the extreme end where the smoke leaves the heater to enter the chimney, and where the cold feed-water enters the heater, Mr. Douville remarks that the aqueous vapor in the smoke could be condensed there and that the resulting water could add its action to the action of the water of infiltration in producing the oxidation by the sulphuric acid.

of the large cylinder; then returning in the opposite direction they enveloped simultaneously the entire circumference of the remaining small cylinder, and the remaining half of the lower semi-circumference of the large cylinder. There were thus two equal symmetrical and parallel flues, each containing at the centre, one of the small cylinders suspended by its two connecting pipes or nozzles from the large cylinder above; the interior of the three cylinders being in common by means of these nozzles. The top of each flue was formed by half of the lower semi-circumference of the large cylinder, the remaining two sides and the bottom being formed of masonry. The two small cylinders were wholly filled with water, and the large cylinder was half filled, its upper half containing steam only.

The small cylinder in the second flue, and at the end where the hot gases escape into the chimney, burst under conditions having the greatest resemblance to those just described in the case of the exploded feed-water heater at the pits of Glenons. The fracture commenced at, and closely followed, a horizontal seam; thence it continued vertically in two places, one in the solid plate and the other along the riveting of a joint. The thickness of the metal on the edges first torn was reduced to near 0.03937 of an inch. All the upper part of the small cylinder was corroded, the thinning diminishing progressively from the top. The deterioration was entirely on the outside.

Two specimens of the deposits left by the smoke on the injured iron have been analyzed; they gave between 52 and 53 per centum of sulphate of iron. One gave 1.42 per centum of free sulphuric acid, the other gave 12 per centum nearly. The deposits formed on the rest of the boiler also contained sulphuric acid, but in notably less quantity, and no sensible deterioration of the metal had resulted from it.

The action is explained in the following manner: During the working of the furnaces the deposits are thrown down in the pulverulent state, and quite dry; but on the extinction of the fires the external air charged with humidity, fills the flues, and by lengthened contact makes the soot pasty with moisture. The conditions are now most favorable for attacking the iron, and its oxidation by the sulphuric acid commences. The corrosive action then continues, during the whole time the boiler is out of use, on those parts which are not cleaned; while, on the contrary, it is not sensible on the parts from

which the deposits are frequently removed. Now the thin and torn part of the exploded small cylinder was exactly in the first of these cases: it was backed against the vertical wall of masonry, separating the two flues, a place very difficult of access, and consequently examination and cleaning were neglected.

III. Some examples of exterior corrosion in consequence of the condensation of the aqueous vapor in the smoke on the cold parts of boilers, have been pointed out by Mr. Meunier-Dollfus, director of the Alsatian Association on Steam Boilers. (See *Bulletin de la Société Industrielle de Mulhouse*, 1871.) We cite, particularly, the observations made on the boilers in the shops of Mr. Charles Kestner, at Thann.

These boilers were two in number, and each was composed of four horizontal cylinders, one of which was of large diameter, and the remaining three were of small diameter and suspended below it by two connecting nozzles or pipes each. Between these boilers, and imbedded in the same masonry, were six feed-water heaters, arranged in pairs, each pair being on a different level, but in the same vertical plane. The gases of combustion circulated around the entire circumferences of the three small cylinders, then in one direction, beneath a portion of the circumference of the large cylinder, returning in the opposite direction beneath another portion, from which they continued to the feed-water heaters, passing over each pair successively, from high to low. The feed-water, during its passage through the heaters, moved in the reverse direction.

A single boiler was most often in use; it was worked night and day, but with a less rate of combustion during the night.

In an experiment the feed-water was found to enter the lowest pair of heaters with a temperature of 68° Fahr., and to leave them with a temperature not exceeding 86° Fahr.; it left the highest or last pair of heaters with the temperature of 122° Fahr. On the other side the temperature of the smoke, when leaving the lowest or last pair of heaters, did not exceed 302° Fahr. during the day, and 212° during the night. After two years' use, under these conditions, the heaters were injured, and at the end of six years, although the metal was of excellent quality, its thickness was so much reduced that they had to be renewed.

The corrosion was principally on the cold or but little warmed portions of the heaters, and had, for first cause, the sulphurous acid dissolved in the water of condensation deposited from the smoke. It was ascertained that, in presence of the air and of this watery acid, there was first oxidation of the iron and then formation of the sulphate of the oxide of iron.

IV. Some observations on that cause of the destruction of boilers have been made in the Department of the North, by Mr. Cornut, engineer-in-chief of the Association of the Proprietors of Steam Boilers in the North of France, at Lille. He has frequently discovered exterior corrosions, which seemed to him attributable to the smoke, and he found them strictly limited to the portions of plate kept wetted from any cause—leaks, infiltration of water, etc.

V. We will close with the following remarks: The transformation of sulphurous acid into sulphuric acid, by the action of water, or of the vapor of water and of air in presence of a base or of a metal, is not a new fact. For a long time advantage has been taken of this property of sulphurous acid, either for disinfecting the neighborhood of certain metallurgical establishments or for the treatment of particular ores. In illustration of the last, we can cite notably the process of Mr. DeLamine, for the manufacture of the sulphate of alumina, at Ampuis (Belgium), and the treatment of some oxide of copper ore, on the banks of the Rhine.

It would seem that these old applications ought long since to have drawn attention to the possibility of the corrosion of steam boilers by reactions of a similar kind; but nothing was done, and so far as concerns that special problem—if the general fact is now known—there still remain the details for investigation, some of which are not wanting in practical importance.

CONCLUSIONS.

The results of all the preceding observations can be summed up thus:

When the smoke deposits on boiler surfaces distant from the furnace are rendered moist by any accidental cause, the sulphurous acid in the gases of combustion determines the attack upon the metal by the formation of the sulphate of the oxide of iron.

The attack can take place, while the boiler is in use, on such of its metallic surfaces as may be wetted by leakage from the boiler itself, or by water infiltrated through the masonry, or derived from the condensation of the aqueous vapor in the gases of combustion by contact with surfaces relatively cold. It can also be produced while the boiler is out of use, by means of the humidity of the air in the flues.

These different origins of the corrosive action, point out the precautions to be taken for preventing its destructive effects. They are only those which should be adopted for the preservation of any apparatus, viz., careful construction, thorough cleaning, and maintenance in good repair.

ANALYSIS OF THE REPORTS OF THE OPERATIONS OF THE BELGIC ASSOCIATION FOR THE SURVEILLANCE OF STEAM BOILERS, DURING THE YEARS 1873-1874.

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As the reports made of the operations of the Belgic Association for the Surveillance of Steam Boilers contain a very complete investigation of the different causes of the deterioration of boilers, a detailed extract will be interesting, leaving to the Chief Engineer of the Association the responsibility for his observations and opinions.

The association commenced on the 30th of December, 1872, and its operations extend over all Belgium. At the end of 1874, that is to say, in the second year of its existence, the number of boilers under the association rose to 1031; it was 827 at the end of the first year. 485 boilers were examined interiorly during 1873; 278 were in need of repairs, of which 64 required to be immediately taken in hand by reason of the danger they presented. In 1874 the number of boilers examined interiorly was 607. Many of these examinations revealed serious defects, for which 62 boilers were at once repaired.