

THE OCCURRENCE OF CHLORINE IN COAL.

By A. DE WAELE.

(Read at the Meeting, March 3, 1915.)

A CASE of abnormally rapid corrosion of the tubes of an economiser was brought recently to my notice. The brickwork forming the near end of the flue on its way to the chimney-shaft had been removed for purposes of alteration of direction, so that a very thorough examination was possible. The tubes on examination were found to be deeply pitted in places, and at the time held adhering oily-looking yellow drops. Several of the tubes were carefully scraped in order to remove the loose adhering scale and fluid. An examination for sulphuric acid showed the merest trace, but an abundance of ferric chloride was found. It was thus clear that the source of failure was the presence of chlorine in some form in the furnace-gases.

A record having been kept for several years of the varieties of coal used on this and other boiler-furnaces, I was able to obtain and examine samples of the coals as further deliveries came in. At the same time, it was found that without exception the coals used were those which had been mined in the brine districts of the Midlands. It was thus possible that the chlorine might be present either wholly or partly as sodium chloride.

In order to determine this, duplicate determinations of chlorine were made by (1) ignition of the coal in admixture with chlorine-free lime; (2) direct extraction of the powdered coal with water. The former method was carried out by intimately mixing a weighed quantity of the powdered coal with powdered lime in a platinum crucible, and inverting the latter in a larger platinum crucible, this being then filled up to within $\frac{1}{2}$ inch of the top with more lime. The ignition was then performed in a muffle. The contents of the crucibles after ignition were tipped out into a beaker, dissolved in dilute nitric acid, neutralised carefully, and the chlorine titrated in the usual way. No difficulty was found in obtaining lime containing but the faintest trace of chlorine.

The second method was carried out by exhausting the powdered coal with hot water, filtering through asbestos, and directly titrating the filtrate with silver nitrate.

Comparisons of chlorine determinations by the two methods gave the following figures :

| Sample Number. | By Ignition. | By Extraction. |
|----------------|--------------|----------------|
| 1 | 0.253 | 0.251 |
| 2 | 0.241 | 0.240 |
| 3 | 0.210 | 0.212 |
| 4 | 0.220 | 0.220 |
| 5 | 0.018 | 0.019 |
| 6 | 0.344 | 0.346 |

It would thus appear as if the whole of the chlorine found were present as soluble chloride.

This investigation was followed by examination of another boiler-furnace in which nothing but Welsh coal had been used. The furnace in question had been running for over three years, and although I was not able to accord it quite such a close examination as in the case detailed above, the condition of the economiser tubes was very good, no deliquescence being apparent to any degree, whilst the pitting was very slight indeed.

Whilst the coals used on this boiler could not be located as accurately as in the previous case, I was able to obtain samples of the different coals that had been used on this and others of a group of boilers. The results are included in the following table :

| Sample Number. | By Ignition. Cl Per Cent. | By Extraction. Cl Per Cent. |
|----------------|------------------------------|--------------------------------|
| 1 | 0.003 | 0.003 |
| 2 | — | 0.010 |
| 3 | — | 0.010 |
| 4 | — | 0.010 |
| 5 | 0.007 | 0.006 |
| 6 | — | 0.011 |
| 7 | — | 0.032 |
| 8 | 0.004 | 0.007 |
| 9 | 0.011 | 0.012 |
| 10 | — | 0.004 |
| 11 | — | 0.007 |

The above figures afford a good confirmation of the supposition that soluble chloride was the cause of failure in the first of the two cases.

DISCUSSION ON THE TWO PRECEDING PAPERS.

The PRESIDENT remarked that, while in the case of coal apparently the whole of the chlorine was capable of being extracted by water, in the case of the coke only a portion of the chlorine could be obtained in this way. Did this mean that the portion not obtained was protected in some way, as, for example, by tarry or resinous matter, or that it existed in some different form? In the latter case, could the reader of the paper say what the form was?

Dr. LESSING said that, as far as he was aware, nothing was known as to the form of compounds in which chlorine occurred in coke; he thought it highly improbable that in the coking process the chlorine would form insoluble compounds with the organic constituents of the coal. The chlorine in coal, as Mr. de Waele's figures showed, was all soluble, and as a matter of fact the method of extraction with water was practically the only one in use for the numerous daily determinations of chlorine that were made in many coking works. It seemed quite feasible that any chlorides present or being formed in the process of carbonisation would become so embedded in the softened coal that it was difficult to extract them entirely from the finished coke, however finely this was ground, but it was difficult to imagine the formation of any chlorides insoluble in water or acids. The question of the alkalis present in coal was, as Mr. Bridge had mentioned, a very important one, particularly in connection with the action of alkaline chlorides on the refractory materials of gas retorts and coke ovens, and also in connection with the formation of ammonium chloride, which latter, however, had been turned to remunerative account by its extraction from the liquor. He had met with a case somewhat similar to that described by Mr. de Waele, in which producer gas scrubbers were attacked by hydrochloric acid, formed during the oxidation process.

Mr. J. GOLDING said that alkaline chlorides were present in "flue dust," which was now being tried as a source of potash for manurial purposes. He should like to hear whether there was any actual evidence of the chlorine being given off as hydrochloric acid, and also whether magnesia was present in any notable quantity in the coal and coke examined. The latter question was suggested by the recollection of a recent paper before the Society (J. O'Sullivan, ANALYST, 1914, 39, 425), in which it was stated that the loss of chlorine which occurred during the ashing of beer was largely due to the presence of magnesia. He (Mr. Golding) had tried the method of burning with lime and alkalis for the determination of chlorine in cheese, and had found that for this purpose it was not satisfactory; and Miss Cornish and he had devised another method, which they hoped to communicate to the Society shortly.

Mr. J. H. B. JENKINS said that the peculiar formations called "birds'-nests" which sometimes occurred in locomotive fireboxes were ascribed to the volatilisation from the fuel of traces of sodium chloride, which was deposited in some of the cooler places on the crown of the firebox; small particles of silicious matter, mechanically carried over, were caught in the molten sodium chloride and formed sodium silicate. Any action of that kind would presumably result in the formation of hydrochloric

acid, but it appeared unlikely that any material condensation would take place in the tubes, seeing that the temperature of the issuing gases was about 700° or 800° F., and he had never heard of any damage resulting from such a cause. The proportion of total sulphur in coal may be taken as from 1 to 1.5 per cent., and in the combustion it might be expected that some sulphuric acid would be formed. He was interested, therefore, to hear that, in the case of the economiser corroded by contact with flue gases, referred to by Mr. de Waele, there was very little evidence of the action of sulphuric acid.

Mr. J. A. DEWHIRST suggested that the difficulty of extraction with water might be due to the conversion of part of the originally soluble chloride to an insoluble basic form such as the magnesium salt. Personally he did not see why a little acid should not be used in order to extract any such compounds, if the total chloride was desired.

Mr. G. N. HUNTLY said that the presence of chlorides in coal had an obvious bearing on the determination of the ash. Considerable variation was liable to occur in the percentage of ash obtained, according to the temperature at which the coal was burnt; and this might be partially explained by the presence of 0.25 to 1 per cent. of salt.

Dr. COLMAN said that he did not think Mr. Bridge meant to suggest that other methods would not yield a larger proportion of soluble chlorides than he had obtained. The original object having been merely to ascertain what quantity of chlorine might be dissolved from a coke filter-bed, the grinding of the coke was only moderately fine, in order that the conditions of the experiment might be roughly comparable with those of a filter-bed. No doubt if the coke were more finely ground a larger proportion of soluble chlorine would be obtained. But he very much doubted whether, however fine the grinding and however prolonged the treatment with water, anything like the total quantity of chlorine would be dissolved out, though he was not prepared to say what form the insoluble portion assumed. He could see no reason why some of the chlorine should not be converted into double silicates containing chloride, like some of the insoluble minerals of that class; but this, of course, was only hypothesis. He did not, however, think that any of the chlorine was in combination with carbon. Hydrochloric acid was unquestionably present in the products of combustion from coal-containing chlorides. It was well known in ordinary gasworks practice that, when carbonisation was carried out in the absence of air, hydrochloric acid was always present in the hot gas and in the earliest portions of the ammoniacal liquor. It was, he thought, unquestionable that hydrochloric acid had a far more deleterious action than sulphur on copper and iron because, so long as the temperature was sufficiently high to prevent the deposition of water, sulphur dioxide had no very corrosive action, whereas hydrochloric acid, even in the absence of water, acted rapidly. The method of determination adopted was practically that of Eschka for estimation of sulphur, except that quicklime was used instead of magnesia. It probably would not be a suitable method for organic substances containing a large proportion of volatile matter. When monochloroacetanilide was treated by this method, 20.11 per cent. of chlorine was obtained, as

against the theoretical percentage of 20·9, showing that with such a substance the results would be slightly low ; but in the case of a substance in which the chlorine was not readily volatile it might be relied upon to give fairly accurate results, at any rate sufficiently so for the purpose of this investigation.

Mr. DE WAELE said that for making Mond gas, coal containing more than 0·3 per cent. of chlorine would be rejected, owing to the corrosive effect on the scrubber. The presence of sulphur was not considered to be so serious. In the first scrubber the temperature, as Dr. Colman had pointed out, was too high to allow the sulphur to have much effect. In the ammonia scrubber some pitting was bound to occur, as there was here a fairly high concentration of sulphuric acid.

