THIRTY-EIGHTH ANNUAL REPORT

OF

THE LOCAL GOVERNMENT BOARD,

1908–09.

SUPPLEMENT

IN CONTINUATION OF THE

REPORT OF THE MEDICAL OFFICER

For 1908-09.

ON THE NATURE, USES, AND MANUFACTURE

OF

FERRO-SILICON,

WITH SPECIAL REFERENCE TO POSSIBLE DANGER ARISING FROM ITS TRANSPORT AND STORAGE.

Presented to both Houses of Parliament by Command of His Majesty.

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LOCAL GOVERNMENT BOARD (THIRTY-EIGHTH ANNUAL REPORT).

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IN CONTINUATION OF THE

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For 1908-09,

CONTAINING

REPORTS AND PAPERS ON THE NATURE, USES AND MANUFACTURE

OF

FERRO-SILICON,

WITH SPECIAL REFERENCE TO POSSIBLE DANGER ARISING FROM ITS TRANSPORT AND STORAGE,

BY

S. MONCKTON COPEMAN, M.D., F.R.S.,
Medical Inspector of the Local Government Board,

SAMUEL R. BENNETT, M.A.,
One of H.M. Inspectors of Factories,

AND

H. WILSON HAKE, Ph.D., F.I.C.

WITH AN INTRODUCTION

BY THE

MEDICAL OFFICER OF THE LOCAL GOVERNMENT BOARD.

Presented to both Houses of Parliament by Command of His Majesty.

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REPORT ON FERRO-SILICON.

TO THE RIGHT HON. JOHN BURNS, M.P., PRESIDENT OF THE LOCAL GOVERNMENT BOARD.

SIR,

THE possibility of danger to life from the transport of ferro-silicon had already received official attention in this country through a " Notice to Shipowners, Shipmasters, and Shippers " issued by the Board of Trade in September, 1907 (see page 101), but the magnitude of the risks involved in the treatment of this material and the need for more stringent regulations was strikingly demonstrated by the death of five Russian immigrants on board the s.s. " Ashton," in December, 1908, during this ship's voyage from Antwerp to Grimsby. Inquiries made on behalf of the Local Government Board into this occurrence brought to light a number of previous accidents in connection with the transport of ferro-silicon, and after conference with the Home Office and the Board of Trade, the full investigation of the subject was entrusted to Dr. Copeman, with whom subsequently Mr. S. R. Bennett, M.A., one of H.M. Inspectors of Factories, and Dr. Wilson Hake, F.I.C., Lecturer on Chemistry at Westminster Hospital, collaborated.

The details of all the accidents known to have occurred from the handling or transport of ferro-silicon are set out on pp. 11-26 of Dr. Copeman's report. Among these must be mentioned the occurrence on more than one occasion of explosions during the transport or handling of consignments in closed packages in which the ferro-silicon contained about 54 or 55 per cent. of silicon. But more important and much more frequent than these are the well-authenticated cases of serious illness and death caused by the gases evolved from certain cargoes of ferro-silicon. Thus in January, 1905, during a voyage from Antwerp to New York fifty steerage passengers were made seriously ill, and eleven of them died from this cause. In October, 1905, two children died on a canal boat between Hull and Keadby, and their father and mother suffered severely, though they ultimately recovered; and in March, 1906, from the same cause, two children died on a Rhine boat. In September, 1907, the Board of Trade issued a memorandum received from the Home Office as to the circumstances under which five passengers died on a Swedish steamship as the result of poisonous gases given off from ferro-silicon. A further considerable number of persons were also taken ill, but recovered after they had gone on deck. One of the persons who died was a Russian revolutionist, and it was erroneously supposed at the time that a treacherous crime had been committed. In May, 1908, from the same cause, nearly all the crew and passengers of a steamship voyaging from Stockholm to St. Petersburg were taken ill, and two died.

In October, 1908, a consignment of ferro-silicon was discharged from a vessel coming from Antwerp on to a barge for transport to Sheffield. All three persons in charge of the barge were taken ill, two dying. The symptoms, as in some of the other accidents from ferro-silicon, were ascribed to gastro-enteritis from ptomaine poisoning. Accidents of a similar but less serious character are known to have occurred on other barges, and the recent accident on board the s.s. "Ashton" led to the present extensive investigation of the subject. The deaths on this ship had been suspected to be due to cholera, and on this supposition post-mortem material was sent to the Board, whose bacteriologist negatived the presence of cholera. A relative of the victims in the above canal case appears to have first suggested, in a letter to the medical officer of health of Grimsby, the possibility that the deaths might be due to the same cause as those on the barge, the cargo of which consisted mainly of ferro-silicon.

A very full account of the functions of ferro-silicon in steel manufacture, of its manufacture, of its composition and structure, and of chemical investigations regarding it, is given in Dr. Copeman's report, and in the sections of the report contributed by Mr. Bennett and Dr. Hake.

Ferro-silicon is an alloy or eutectic mixture of iron and silicon, of which the low-grade variety, containing not more than 15 per cent. of silicon is made in blast furnaces to a considerable extent in this country; while the high-grade class, containing from 25 to 95 per cent. of silicon can only be made at the very high temperature of the electric furnace. The latter variety is imported from parts of France, and to a less extent from Austria, Scandinavia, &c., where ample electrical energy is derivable at a low cost from water power. About 4,000 tons of this material are said to be imported annually into England, and as serious inconvenience to steel manufacturers is being caused by the refusal of shipping firms to carry it, there is great need for regulations permitting its transport under defined conditions which will obviate accident.

The electrically produced or high-grade ferro-silicon has in recent years displaced in large measure the blast furnace variety in the manufacture of the better qualities of steel, and as an outcome of this change the dangers of noxious fumes from the high-grade variety have gradually been realised. Manufacturers and chemists in the light of their special experience have come to the conclusion that it is solely or chiefly the 50 per cent. variety of the high-grade material which is thus dangerous (see page 107). In connection with some of the results of the present official investigation, reference may be made on this point to the table as to analysis of 64 samples of ferro-silicon which faces page 86. These samples were collected by Dr. Copeman, or sent by manufacturers at his request, as representing the different ferro-silicons in actual use. The following is a summary of the variety of samples examined :—

Under 30 per cent.	13 samples.
30-39 ,, ,, ...	3 ,,
40-44 ,, ,, ...	2 ,,
45-49 ,, ,, ...	11 ,,
50 ,, ,, ...	16 ,,
51-54 ,, ,, ...	4 ,,
55-59 ,, ,, ...	0 ,,
60-64 ,, ,, ...	3 ,,
65-69 ,, ,, ...	0 ,,
70-74 ,, ,, ...	2 ,,
75-79 ,, ,, ...	4 ,,
80-84 ,, ,, ...	1 ,,
85-89 ,, ,, ...	0 ,,
90-94 ,, ,, ...	4 ,,
95 and upwards	1 ,,

Evidently most of the high-grade samples contain somewhere about 50 per cent. of silicon, and it would not be surprising therefore, even on the supposition of equal distribution of risk among all varieties of high-grade ferro-silicon, if accidents had been recorded chiefly in connection with the use of ferro-silicon which ranged in composition near 50 per cent. of silicon. It should be added that some of the firms have recognised the importance of porosity and liability to disintegrate as factors in the ready evolution of poisonous fumes of phosphoretted hydrogen, and the French Commission draw attention to the safety of compact alloys (see page 60 of this report). Whether the excess of incidence of accidents in connection with the transport of ferro-silicon, the silicon of which is about 50 per cent., is due to the greater use of this variety, or to its special liability to give off poisonous fumes, remains to be seen.

The above conclusion as to the special danger associated with the use of ferro-silicon having a 50 per cent. content of silicon, is varied in the report of the Commercial Commission appointed by the Chambre Syndicale des Forces Hydrauliques, &c., which is given on page 58. This report states that the dangerous grades are now known to be those ranging from 30 to 40 per cent. and from 47 to 65 per cent. of silicon, and the intention is announced of ceasing to manufacture ferro-silicon containing silicon within these limits. The omission of 40 to 47 per cent. from the list of dangerous percentages is somewhat remarkable in view of the absence from this report of any evidence that ferro-silicons of these percentages had been examined and found not to evolve poisonous gases. In Dr. Hake's experiments, as will be seen later, all of the seven samples of ferro-silicon containing 40-47 percentage of silicon were found, in the laboratory and when powdered, to evolve poisonous gases to a dangerous extent; but in conjunction with these results it is to be noted that Dr. Hake's table facing p. 76 of this report shows that no spontaneous disintegration had occurred in his six samples containing 42, 43, and 45 per cent. of silicon, though the two 46 per cent. samples showed some tendency to disintegrate.

The present investigation by Dr. Copeman and his collaborators was already in progress before a copy of the report of the French Commission was received. The results of Mr. Bennett's investigation of the composition and structure of ferro-silicon are given on pp. 90-96. They indicate the greater porosity and liability to disintegration of the middle percentages of ferro-silicon. This is also mentioned from different points of view in Dr. Copeman's report and in Dr. Hake's contribution on pages 68-90. Dr. Hake classifies ferro-silicons into those not liable to spontaneous disintegration at the two ends of the scale, and those intermediate percentages of which an uncertain proportion manifest this tendency. This rule undoubtedly holds good for the intermediate percentages, though it is very doubtful at what exact percentage, if any, it begins and ends. If more extended experience and experimentation on the higher and lower percentage varieties of high-grade ferro-silicon confirm the fact that this rule may be accepted, an important preliminary sorting of ferro-silicons will be able to be made, and it may prove possible to consider whether the regulations suggested on page 114, may not be relaxed for the higher and lower percentages of high-grade ferro-silicon. Dr. Copeman has properly refrained from such a limitation of suggested regulations, while recommending that each barrel or other parcel of ferro-silicon shall have marked on it in bold letters its certified percentage grade. The need for regulation is shown by the following summary of some of Dr. Hake's results. Of the 61 total samples (omitting several supplied in powder), in 28 Dr. Hake estimated, by new methods described by him on pages 80-86, the volume of poisonous gases evolved by action of moist air, the amounts being approximately expressed in cubic feet per ton. Below, these are classified according to the percentage of silicon in each sample analysed :—

Samples arranged according to percentage amount of Ferro-silicon.		*Total number of samples analysed.*	Number of samples from which no poisonous gases were evolved.	Number of samples from which poisonous gases were evolved. (Extreme variations in volume of gas evolved are given in brackets.)
Group.	*As represented by Samples containing from—*			
under 30 °/∘	10–29 °/∘	3	2	1 (*0·26*)
30–39 °/∘	30–35 °/∘	1	0	1 (*0·13*)
40–49 °/∘	42–49 °/∘	9	0	9 (*2·1* to *16·4*)
50–59 °/∘	50–52 °/∘	8	0	8 (*2·4* to *15·8*)
60–69 °/∘	60–62 °/∘	1	0	1 (*1·0*)
70 °/∘ and over	70–96 °/∘	6	0	6 (*2·1* to *5·7*)
		28	2	26

The original table should be studied for exact details. Thus in the 40-49 per cent. group the highest evolution of gas was in a 42 per cent. sample (16·4); the 50-59 per cent. group was represented by samples containing 50 to 52 per cent., and the highest evolution of gas in this group was 15·8 in a 52 per cent. sample. Again, in the 60-69 per cent. group one sample was analysed, and in the last group no sample examined gave off more than 5·7 cubic feet of poisonous gas per ton, although all the six specimens examined in this group evolved a certain amount of gas. It is evident, therefore, that at present, unless or until sharp lines can be drawn between the different amounts of gas evolved under similar circumstances, it is impracticable with certainty to distinguish among any of the higher percentage varieties of ferro-silicon between safety and danger. The degree of porosity of ferro-silicon and its liability to disintegration form, however, important preliminary tests which, when their incidence is determined on a larger scale may, in conjunction with chemical analysis, permit of limits of safety being more exactly stated.

Attention may be drawn to the suggestion made by several observers, including Mr. Bennett, that liability to spontaneous disintegration with evolution of poisonous gases is not improbably related to the amount of aluminium present in the ferro-silicon. So far it would appear that this relationship has only been investigated for 50 per cent. grades.

The recommendations suggested by Dr. Copeman on pages 114-115 will, if adopted, probably prevent the occurrence of future accidents in the transport of ferro-silicon. They comprise the need for ascertaining that the ferro-silicon has been broken into pieces of the size in which it is usually sold, some time before being taken on board ship; the marking in bold letters of the certified percentage grade of each consignment on the barrel or other receptacle, and of the date of manufacture; the prohibition of conveyance of ferro-silicon on passenger vessels; and the adoption of certain precautions during transport in cargo boats.

I am, Sir,

Your obedient servant,

ARTHUR NEWSHOLME.

REPORT.

PRELIMINARY REMARKS.

On December 15th, 1908, the Board received a telegram from Dr. Simpson, Medical Officer of Health for Grimsby, stating that on arrival of the s.s. "Ashton," from Antwerp, on the previous day, five Russian immigrants, who had taken passage in this ship, were found to have died during the voyage.

From information subsequently received from Dr. Simpson by letter, and from the evidence at the coroner's inquest, it appeared that the voyage, of some twenty-four hours' duration, had been a stormy one; and that, in consequence the hatches over the fore between-deck accommodation occupied by the five alien travellers (two men aged 35 and 32; two women aged 19 and 15; and a boy aged 11 years), had been battened down and covered with tarpaulins; and both port-holes and ventilators had been closed. Bulk-heads shut off the fore-part from the remainder of the ship.

The ship carried a cargo of *Ferro-Silicon* stored in the hold immediately under the emigrant quarters. This (about 9 tons in amount) was packed in rough barrels, and had apparently become more or less saturated with moisture during the voyage.

Without here setting out details of the post-mortem and chemical examinations made in connection with the enquiry, it may be stated that the conclusion was arrived at that "the deceased persons were poisoned by the inhalation of poisonous gases evolved from the ferro-silicon stored in the lower holds, beneath the compartment which they occupied."

Previous to this occurrence, reports had reached this Board, the Board of Trade and the Home Office, of the occurrence of deaths under somewhat similar circumstances on at least one other sea-going vessel, as well as on canal-boats plying on the water-ways between Sheffield and the Humber ports. Of these occurrences the earliest, and the only one which need be referred to at present, was the subject of a coroner's inquest at Keadby, Lincs., in November, 1905. The coroner subsequently reported the circumstances of this case to the Board of Trade, involving, as he said, the death of two young children on a canal boat at Keadby, as the result of poisoning by the fumes of ferro-silicon, which, stored in barrels, had formed part of the cargo of the boat.

The subsequent report of the death of all the steerage passengers on board the s.s. "Ashton," in December last, directed attention still more forcibly to the dangers associated with the transport of this material, and accordingly, as the result of conferences between this Board, the Board of Trade, and the Home

Office, it was decided that enquiry should be made into the whole subject of the manufacture, uses, and possible dangers, of ferro-silicon; and I was instructed to undertake the investigation.

For the purposes of my investigation, I visited Sheffield, Rotherham, Hull, and Grimsby, during the month of February, 1909, while, later on, I also visited Liverpool and Manchester, to which ports varying quantities of ferro-silicon are shipped; and Wednesfield, where experimental plant for its manufacture by the British Coalite Company was being installed. Ten days were spent in Sheffield, where, with the assistance of Mr. S. R. Bennett, His Majesty's Inspector of Factories, the benefit of whose local and technical knowledge was placed at my disposal by the Home Office, detailed enquiry was made as to the extent to which ferro-silicon (an essential ingredient as I found, in the making of high-class steel castings), was used by the various firms having their head-quarters in that town and its vicinity. All the firms thus approached, when they realized that the enquiry was being instituted with the dual object of assisting trade and minimizing possible danger, afforded me every assistance in their power, and supplied me with details as to:—

1. The amount of ferro-silicon used by them during the past five years, with the percentage grade of each lot purchased.
2. The name and address of the agent through whom purchased; and, where possible,
3. The name and address of the manufacturer.

I also placed myself in communication with the local agents for the sale of ferro-silicon and other ferro-alloys, and with the various railway and canal companies by whom I found that the material had been transported.

With representatives of these companies, among whom Messrs. Wilsons, of Hull, may be specially mentioned, I subsequently arranged conferences, with the object of obtaining information as to the amount of ferro-silicon handled by them, and the nature of the precautions, if any, which their employées were instructed to observe in the handling, transport, and storage of this substance. In several instances where printed notices had been issued, I obtained copies, reprints of which will be found appended to this report.

With Mr. Llewellyn, the Canal Boats Inspector to this Board, I also visited a number of the Canal "keels," in dock at Sheffield, from the "captains" of which I obtained particulars of certain cases of illness and even of death, apparently due to the fumes of ferro-silicon, carried on these cargo boats. Several of these men had taken considerable trouble to find out the true nature of cargoes which they believed had been productive of illness, and where, with the object presumably of obtaining lower freight rates, what eventually turned out to be ferro-silicon had been consigned under such names as "Scrap-iron." "Iron-waste," &c.

Ferro-silicon is a metallic looking, physico-chemical alloy of iron and silicon, which is largely employed in the manufacture of steel. It may be divided into two distinct classes:—

(*a.*) *Low-Grade*, containing not more than 15 per cent. of Silicon. This is made in blast-furnaces, and to a considerable extent, is produced in this country.

(*b.*) *High-Grade*, containing from 25 per cent. upwards to as much as 90 or even 95 per cent. of silicon. This can only be made at the extremely high temperature obtainable in the electric furnace.

High-Grade Ferro-Silicon, as I learnt from the chief agents for its sale, *is not at present being produced, commercially, in this country*, presumably on account of the difficulty of obtaining sufficiently cheap electric power to enable manufacturers to compete with foreign firms.

It would appear that the greater quantity of the electrically produced ferro-silicon imported to this country is manufactured at various localities in the South of France, more particularly in the Provinces of Savoie, Haute-Savoie, and Isere (Ugine and Livet may be mentioned), where the "harnessing" of waterfalls from off-shoots of the Mont Blanc range of mountains affords a means of obtaining abundant electrical energy at a minimal cost. In Scandinavia also, and in Austria and Italy, high-grade ferro-silicon is produced under similar conditions.

Ferro-silicon, of which about 4,000 tons are imported annually into England from France and other countries, forms an essential ingredient as regards its silicon content in the manufacture of certain grades of steel, to which it is added in small quantities while the metal is in a molten condition.

Discussion of the manufacturing requirements necessitating the use of ferro-silicon in steel-works will be dealt with at a later stage of this report.

From Colonel Vickers, the Chairman of Directors of Messrs. Vickers, Son, and Maxim, Limited, I learnt that the low-grade, or "blast-furnace" variety of ferro-silicon has been employed for a very considerable time past; but that within the last ten years or so, although still used in considerable quantities, it has gradually been replaced by the electrically produced material in the manufacture of the better qualities of steel, notwithstanding the fact that this high-grade electrically produced material is much more expensive. The cost is calculated on the percentage of silicon in the alloy. The governing reason for the increasing use of the high-grade product is that if "blast-furnace" ferro-silicon is employed in those cases where a fairly high percentage of silicon is necessary, the concomitant addition of the large amount of iron combined with it exerts a prejudical cooling effect on the bath of metal to which it is added. On the other hand, curiously enough, the addition of high-grade ferro-silicon has precisely the opposite effect, causing a considerable increase in the temperature of the molten mass with which it is incorporated.

From what has been said it will be obvious that any obstacle to the obtaining of high-grade ferro-silicon in the requisite quantities would be fatal to the interests of the steel trade in this country; in which connection the fact has to be faced that, within the last few months, all the important shipping companies trading to East Coast Ports have entered into an agreement *not to carry ferro-silicon under any conditions.*

But, so far as our knowledge at present extends, while high-grade electrically produced ferro-silicon is apt on occasion to be productive of grave danger, no evidence exists that the low-grade " blast-furnace " variety, which indeed is practically only siliceous pig-iron, *i.e.*, pig-iron containing a somewhat larger proportion of silicon than usual, possesses any such objectionable properties.

The possible dangers to be anticipated from high-grade ferro-silicon are threefold. I have already referred to instances such as the case of the s.s. " Ashton," in which death has resulted from exposure to the fumes of ferro-silicon, such fatal consequences being due to the evolution of phosphoretted and arseniuretted hydrogen which occurs when ferro-silicon, of certain percentages especially, comes in contact with water or moist air. But these gases may also be gradually evolved, in absence of moisture; so that if the material, as formerly was not infrequently the case, especially with the 50 per cent. grade, is stored in " hermetically sealed " iron drums the gradual accumulation of these gases, aided possibly by the heat generated by friction, has caused violent explosions, such as took place at Liverpool in January, 1904, a detailed account of which will be found on p. 13 of this Report. Moreover, the phosphoretted hydrogen evolved from ferro-silicon is apparently capable under certain conditions, of spontaneous combustion; an instance of which was reported to me as having occurred recently at Sheffield.

In the course of my investigations I found, at Sheffield and elsewhere, a somewhat general impression that the 50 per cent. grade of ferro-silicon is the only variety likely to prove dangerous. In a letter which appeared in the "Times" Engineering Supplement for January 27th, 1909, Mr. Watson Gray, F.I.C., definitely states that—

" It is only the 50 per cent. variety which has up to the present " caused trouble. Ferro-silicon made in the blast furnace " . . . . is quite safe to carry, as is the electrically-made alloy " containing up to, say, 40 per cent. silicon, and *also the alloy " containing above, say* 60 *per cent. silicon up to* 99 *per cent.;* " the only quality which need be looked upon with suspicion " being that containing between say, 40 and 60 per cent. silicon, " and even then only when it is made at certain works."

As the result, however, of certain preliminary experiments carried out by Dr. Wilson Hake, Lecturer on Chemistry and Toxicology at Westminster Hospital, it became obvious that Mr.

Gray's dictum could not unreservedly be accepted, as evidence was obtained of specially copious evolution of phosphoretted hydrogen, on addition of water to a small quantity (previously powdered in a mortar) of a sample of ferro-silicon stated to contain over 70 per cent. which had been handed to me from bulk by a metallurgist to one of the Sheffield steel-works.

But, as will appear from Dr. Hake's detailed report on p. 68, *et seq.*, other factors than the actual amount of poisonous gases capable of being evolved, under these conditions, require to be taken into account in judging as to the possibly dangerous qualities of any particular sample of ferro-silicon.

A point that specially impressed itself upon me during my investigations at Sheffield was that no first-hand knowledge of the chemistry or precise methods of manufacture of high-grade (electrical) ferro-silicon appeared to be available.

For instance neither from the Professor of Metallurgy at the University, Professor Arnold, nor from any of the chemists or metallurgists to the various firms I visited was I able to learn the name of the inventor of this special electrical alloy; who first used it in the manufacture of steel, or the precise nature of the gases given off by it under certain conditions, or the approximate date of its introduction into this country. As a result of our conferences on the subject, at Sheffield, Profesor Arnold undertook to arrange for an investigation, in his laboratory, on the subject of the gases evolved from ferro-silicon.. He writes, however, under date, July 25th, 1909, as follows:—

"With reference to ferro-silicon, I much regret that we have not had time to get out any quantitative results of the phosphoretted and arseniuretted hydrogen undoubtedly present.

"Some microscopical work was done by my demonstrator, ... the net result was to show the presence of cavities in the metal which no doubt will be full of injurious gases under pressure."

The use of ferro-silicon indeed would seem, in certain respects, to be largely empirical, and except that, as previously stated, the electrically produced material is preferred, where extra expense is immaterial, to "blast-furnace" fero-silicon, mainly because of the less quantity of iron contained in the higher grades, I was unable to obtain any information as to why, under any particular circumstances, one silicon percentage should be preferred to another, although the 50 per cent. grade seemed to find most favour. And indeed it was suggested to me that the supposed dangers incidental to the 50 per cent. variety might be avoided by employing a mixture consisting of 40 per cent. and 60 per cent. in equal quantities.

But in the light of the investigations carried out by Dr. Hake, to which reference has been made above, it will be obvious that the admixture of ferro-silicon of percentages slightly on either side of what is regarded by Mr. Gray and others as the specially dangerous grade, would not necessarily afford solution of the difficulty.

Especially is this caution necessary since the results of examination of samples carried out by Dr. Hake have demonstrated the fact that various brands may differ from one another considerably in their potentiality for danger. But the evolution of phosphoretted (and to a less extent also of arseniuretted) hydrogen, under the influence of moisture, must be regarded as evidence of the presence of impurities, in no way essential to the useful employment of the alloy in which they occur. It would, therefore, appear probable that the greater the care exercised in the choice of the raw materials, and in the supervision of the smelting process, the purer will be the resulting product, and consequently the freer from those adventitious chemical compounds—phosphides and arsenides—on which, in presence of moisture especially, its dangerous properties depend. Nevertheless, however great the care exercised, no firm has apparently, as yet, succeeded in manufacturing ferro-silicon of grades ranging around 50 per cent. which are free from potentiality of danger as regards evolution of phosphoretted hydrogen under appropriate circumstances.

Shippers and others naturally object to handle dangerous goods unnecessarily; and especially to run the risk of doing so unawares, owing to the merchandise being consigned, as not unfrequently, in the past, has been the case, under a false designation. For these reasons, and especially in view of recent accidents, the Board of Trade have received numerous requests to formulate and publish regulations for safeguarding, so far as possible, the transport and storage of ferro-silicon.

But before any such steps could be taken it was, of course, essential that full information as to the methods of manufacture of high-grade, electrically produced, ferro-silicon should be obtained. At an early stage of my investigation, however, it became obvious that this knowledge could only be gained by visits to certain of the localities on the continent, where ferro-silicon, of high silicon content, is manufactured in the electric furnace. And it was hoped that the outcome of such extended investigation might possibly demonstrate the practicability of manufacturing a product almost, if not quite, free from admixture with undesirable constituents.

Pending completion of my investigations abroad the Board of Trade, after conferences with representatives of this Board, and of the Factory Department of the Home Office, issued, in March, 1909, a notification to shippers and others, to the effect that, upon the information at present available the Board of Trade are of opinion that no objection need be raised to the shipment of low-grade ferro-silicon made in a blast furnace, as, after inquiry, no facts have been ascertained indicating that this particular alloy is dangerous. Each consignment, however, must be accompanied by a certificate from the maker or shipper to the effect that it is low-grade ferro-silicon, made in a blast furnace, and containing not more than 15 per cent. of silicon.

Suggestions for a series of regulations dealing with the transport and storage of high-grade, electrically produced, ferro-silicon, will be found appended to this report.

At an early stage of my investigations it became apparent that the services of a skilled chemist were necessary in order adequately to cope with many of the problems involved. Accordingly application was made to the Treasury, and their sanction obtained to the employment of Dr. H. Wilson Hake, F.I.C., of Westminster Hospital Medical School, "to assist in defining the nature and extent of the danger from ferro-silicon."

The special investigation, thus rendered possible, has, throughout its progress, been the subject of frequent conferences between us, although to Dr. Hake alone belongs the credit for the actual chemical work, the originality and interest of which will be evident on reading his contribution to this report.

Thanks also to the kindness of Dr. B. A. Whitelegge, C.B., of the Home Office, short temporary leave of absence from official duties was afforded to Mr. Samuel R. Bennett, M.A., one of His Majesty's Inspectors of Factories, stationed at Sheffield, in order that he might undertake investigation of certain points connected with the structure and composition of ferro-silicon. His work, which has afforded results of much interest, is also incorporated in a special section of this report.

As previously stated, Mr. Bennett also afforded me invaluable assistance in connection with my local investigations at Sheffield.

FUNCTIONS OF FERRO-SILICON IN STEEL MANUFACTURE.

The extent of addition of silicon to steel during manufacture is primarily dependent on the nature of the finished product required. Generally speaking, the presence of silicon in small amount has a hardening effect on iron, similar to—but to a much less extent than is the case with carbon. As the amount of silicon in cast-iron castings is increased the crushing strength rapidly rises to a maximum with 0·85 per cent.; after which by further addition of silicon it as quickly diminishes, until beyond 2·5 per cent. distinctly deleterious effects result. Also the tensile strength reaches a maximum for about 1·8 per cent. of silicon, and quickly falls off as the percentage of silicon rises.

But of greater importance than the hardening effect is the property of silicon of transforming combined carbon into the graphite condition, and thus producing a softening effect. Advantage is taken of this peculiarity in almost all processes of iron manufacture.

The functions of silicon in the manufacture of, and its effects on the physical properties of, steel, may be classified as follows:—

(*a.*) Silicon in being oxidised in the furnace or converter acts as a metallurgical fuel.

(*b.*) Owing to the heat produced it will cause molten steel to remain fluid for a long time, and so enable thin and intricate castings to be made.

(*c.*) It acts as a reducing agent or otherwise to prevent the formation of blowholes in castings.

(*d.*) It is used as an admixture in steel to produce certain important physical properties in the highest degree.

These functions may be dealt with separately here, without entering on the details of actual manufacture.

(*a.*) In the ordinary or *acid* Bessemer process the chief source of heat in the converter is that resulting from the oxidation of the silicon. Consequently the silicon content of the "pig" used must be kept within narrow limits, because if there be more than about 3 per cent. of silicon in the "pig," the "blow" will become too hot and the steel will be of inferior quality. Also the carbon, which is not oxidised out until after the silicon, may at very high temperatures, reduce the silica already formed. And as the "blow" is finished when the oxidation of the carbon is completed, some silicon might yet remain unoxidised and objectionable excess of silicon in the steel would result. On the other hand, if there be not sufficient silicon in the "pig," the "blow" will be too cold, and there may be solidification of the external layer of metal in the converter—a result to be avoided at all hazards.

The calorific value of silicon is approximately 14,000 British Thermal Units; that is to say, almost as great as that of carbon in being oxidised to CO_2, and nearly 3½ times the heat of formation of CO. So that the value of silicon in effecting a saving of fuel in Bessemer practice is easily understood; it is equivalent to about 10 cwt. of coal for a ten ton "heat" of less than twenty minutes duration.

The silicon appears in the slag as silicate of iron, so that the greater the amount of silicon present the more is the waste of iron in the slag. It may be necessary to add ferro-silicon in the ladle, if a special quality of steel is desired, as from 0·2 or 0·3 per cent. of silicon raises the tensile strength of mild steel slightly, though it diminishes the ductility unless the percentage of carbon is very low. Occasionally, however, the ferro-silicon is run in from the spiegel cupola or added directly at the end of the "blow."

In the *basic* Bessemer process the exothermic re-actions of silicon are not so important, because the amount of silicon in basic "pig" is much lower than in ordinary Bessemer "pig," and the temperature does not rise so quickly at the beginning of the "blow," when the silicon is oxidised out. In fact, if there be a high percentage of silicon in the "pig," the "blow" is protracted, and a large quantity of lime is necessary to combine with the silica formed in order to allow of the removal of phosphorus.

In the open-hearth processes the temperatures realised are not usually so high as those obtainable in the Bessemer practice, consequently the calorific value of silicon is not considered to the same extent, but, as the silicon is almost completely eliminated in the slag, the use of a silicon alloy is almost a necessity. For, as Professor Turner, of Birmingham, has pointed out, the presence of silicon is necessary in steel if its important physical properties are to be realised to the utmost. In basic open-hearth working the silicon alloy is usually added in the ladle, so that, in order not to unduly chill the metal, the higher grades of ferro-silicon are used, a smaller quantity sufficing to procure the desired percentage of silicon and to prevent formation of blow-holes. In the acid open-hearth furnace ferro-silicon is put into the furnace just before tapping, or is added to the ladle.

(*b.*) It has been found of great advantage to have a fairly high percentage of silicon where steels at a high temperature are necessary for thin and intricate castings.

(*c.*) What is perhaps the principal reason for the use of ferro-silicon depends on the fact that silicon, in common with some metals, has the property of preventing molten steel becoming too "fiery," or frothing, during casting. The method by which addition of silicon diminishes the extrusion of gases from molten steel in the act of solidifying is not clearly established. The general opinion is that silicon (in steel) having a great affinity for oxygen decomposes any iron or other oxides that may be present. For this reason ferro-silicon and silico-spiegel act similarly to rich spiegel-eisen or ferro-manganese which, on occasion, are employed for this purpose.

(*d.*) The high tensile strength conferred by low percentages of silicon—say, 0·8 or 0·9 per cent.—with 0·7 per cent. of carbon and 0·4 per cent. of manganese—has also resulted in the use of silicon steels for motor-car construction, *e.g.*, in the manufacture of springs. Also for the cast-iron grids used for electrical resistances a comparatively large percentage of silicon is advantageous.

Analysis of Ferro-Silicon.

The following specimen analyses of ferro-silicon were forwarded by Mr. Bennett:—

	Electrically made.					Blast Furnace.
	60 per cent. analysed by Watson Gray.	50 per cent. from cask in Liverpool explosion.	50 per cent. Lump from same cask; gases removed before analysis.	50 per cent. "safe," as used by Cammell Laird & Co., obtained from Birch & Co.	30 per cent. from Everitt & Co., Liverpool.	12 per cent.
Si ...	59·40	53·80	55·08	52·00	30·07	11·5
Fe ...	36·85	41·27	41·70	45·00	65·00	diff.
Mn ...	0·08	0·10	0·06	0·20	0·58	2·25
Al ...	2·73	3·47	2·67	—	—	—
Ca ...	0·14	0·10	0·07	—	—	—
Mg ...	0·17	0·06	0·05	—	—	—
C ...	0·218	0·49	0·15	0·30	0·44	1·40
S ...	trace	0·01	trace	trace	trace	0·05
P ...	0·056	0·069	0·014	0·05	0·041	0·06
Lime ...	—	0·56	nil	—	—	—
As ...	trace	trace	trace	trace	trace	0·06

For comparison with these I set out a number of further analyses of ferro-silicon, of different percentages, published by various firms engaged in the manufacture, or sale (as agents), of this substance.

Analyses of Consignments of Ferro-Silicon imported by Messrs. Geo. S. Blackwell, Sons & Co., Ltd., Liverpool.

"An important point of our ferro-silicons is that they are all solid, whereas the 50 per cent. grade of most makers disintegrates and falls to a coarse powder. We give as follows complete analyses of the grades we currently supply:—"

—	25/35 per cent.	50 per cent.	75 per cent.	95 per cent.
Silicon	32·70	48·70	75·80	94·80
Iron	65·50	50·84	23·97	4·99
Aluminium	·13	·17	·08	·10
Manganese	·31	·13	·11	·08
Sulphur	·04	·03	·02	·02
Phosphorus	·05	·04	·02	·01
Carbon	·27	·09	·00	·00

Analyses of Alloys produced in the Electric Furnace and manufactured by the Société Anonyme Électrometallurgique, Procédés Paul Girod.

Ferro-Silicon.

—	30 per cent.	50 per cent.	75 per cent.	90 per cent.
Silicon	32·50	49·80	78·13	88·26
Iron	66·26	49·39	21·51	11·23
Manganese	·28	·11	·06	·08
Aluminium	·51	·40	·17	·12
Calcium	·12	·085	traces	·08
Carbon	·26	·13	·09	·07
Sulphur	·02	·04	·001	·010
Phosphorus	·028	·024	·007	·009

Analyses of Ferro-Silicon manufactured by the Société Electro-Chimie de Bozel.

9th March, 1908.

	Per Cent.
Silicon	55·20
Iron	42·60
Aluminium	0·80
Calcium	0·30
Manganese	traces
Phosphorus	0·044
Sulphur	0·065

14th April, 1908.

	Per Cent.
Silicon	52·00
Iron	44·60
Aluminium	1·35
Calcium	0·38
Manganese	traces
Phosphorus	0·034
Sulphur	0·068

ACCIDENTS, FATAL AND OTHERWISE, WHICH ARE KNOWN TO HAVE OCCURRED IN CONNECTION WITH THE TRANSPORT AND STORAGE OF FERRO-SILICON.

So far as I am aware the earliest record, in point of date, of danger incidental to the handling of high-grade ferro-silicon, manufactured in the electric furnace, is contained in a paper read before the Iron and Steel Institute early in the year 1904, by the late Dr. Dupré, F.R.S., at that time Chemical Adviser to the Explosives Department of the Home Office, and Captain Lloyd, R.A., His Majesty's Inspector of Explosives.

This paper deals with the circumstances attending a series of explosions which occurred in connection with a consignment of this material from the Cunard Company's s.s. "Veria," at the Alexandra Dock, Liverpool.

Dupré and Lloyd state that the vessel, which had brought a cargo from Trieste, was discharged on 17th December, 1903, and owing, as they learnt, to a fire having occurred on the vessel, the ferro-silicon was detained on the quay until the 12th January, when Messrs. Beck and Co., of Liverpool, removed the forty-eight iron drums in which the alloy was contained to a warehouse in Dacre-street, Bootle.

While in course of removal thither, on a lorry, the attention of an Inspector of the Explosives Department of the Liverpool Police was drawn to them owing to a strong smell of what appeared to him to be acetylene gas. Shortly after, while a drum was being rolled from the truck on to the concrete floor of the warehouse, a violent explosion ensued, accompanied by a flash of flame. The drums were then removed to an open yard, and during this removal a second drum exploded.

By direction of the Fire Salvage Association the ferro-silicon was removed to a fire-proof warehouse, where it was repacked into wooden barrels, in the ends of which holes were bored in order to prevent accumulation of inflammable gases.

Notwithstanding these measures, however, a further explosion occurred on 21st January while a porter employed by the Liverpool Warehousing Company, who was engaged in weighing some of the barrels, was in the act of removing one from the machine. The barrel itself was shattered and the man, who was flung to a distance of seven or eight yards, was so severely injured as to necessitate his removal to the infirmary.

The authors of the paper in question attribute the explosions to the evolution of an inflammable gas consisting, in far greater part at any rate, of phosphoretted hydrogen, a conclusion also arrived at by Mr. Watson Gray, who read a note dealing with the subject, at a meeting of the Faraday Society in February, 1904. In addition, however, to phosphoretted hydrogen, Mr. Gray stated that he also found small amounts of acetylene and arseniuretted hydrogen among the gases generated in the casks.

He also obtained samples of the ferro-silicon, the composition of which, on analysis, he found to be as follows:—

	Per Cent.
Silicon	59·40
Iron	36·85
Manganese	0·08
Aluminium	2·73
Calcium	0·14
Magnesium	0·17
Carbon	0·218
Sulphur	trace
Phosphorus	0·056

Two subsequent analyses made by Mr. Gray gave the silicon content of these particular samples as 53·80 and 55·08 respectively. Mr. Gray further stated in his note, that he had not previously heard of ferro-silicon exploding, although he had been practically acquainted with the material from the experimental stages up to the date of his communication.

As Dr. Dupré and Captain Lloyd pertinently express themselves in the concluding paragraph of their paper, "although "the accident now under consideration was not attended with "any very grave results, the possibility of an explosion on a far "larger scale must not be lost sight of. It is important, there- "fore, that all those who have to store or handle this substance "should be fully alive to the possible dangers attaching to it, "and by keeping it in a dry and thoroughly well-ventilated "place, prevent the accumulation of inflammable gas as far as "possible."

In the course of investigations at Sheffield during the present year, I learnt from Mr. Johns, the metallurgical expert at the works of Messrs. Vickers, Maxim and Company, Limited, that when that firm first purchased a 50 per cent. grade of ferro-silicon it was supplied in iron drums, which had not been the case with consignments of this material previously purchased. Explosions frequently ensued on these drums being opened with a crow-bar, this, in fact, having occurred with about half the total number of drums opened. The explosions, however, were not usually violent in character, and in no instance had a workman been seriously injured. The foreman of the particular department of the works concerned stated that no ferro-silicon in drums had been received for at least five years past.

As illustrating a further possible source of danger from certain grades of ferro-silicon, it was also stated that, on one occasion about a year ago, a barrel of 50 per cent. grade had taken fire, apparently spontaneously, shortly after having been removed from stores.

On the s.s. "Vaderland" during a voyage from Antwerp to New York, in January, 1905, of the steerage passengers lodged in the forward compartment of the vessel, over a hold in which a cargo of ferro-silicon was stored, fifty were made seriously ill by fumes given off from this substance. Of these, eleven died on the voyage, of whom nine were buried at sea, while two corpses were landed at New York.

The authorities became seriously alarmed, and although the medical officer on board certified the deaths as due to pneumonia, the steamer and its passengers were quarantined on suspicion of the vessel being infected by plague. As the result of official enquiry at the time, the deaths were attributed to "unknown causes," but subsequent fuller enquiry resulted in the conclusion that the cause of the sickness and deaths of so many of the steerage passengers was due to fumes given off by the cargo of ferro-silicon.

In March, 1906, two young children aged respectively 4½ years and 2½ years, died on the Rhine boat "Caroline," of Mannheim, the cargo of which, in addition to bales of paper, wine, and soap, consisted of 750 cwt. of electrically produced ferro-silicon, which was in course of transit from a manufactory in Switzerland to Essen. Of three cabins on the vessel the one occupied by these children and their parents was situated immediately over the hold in which the ferro-silicon was stored. In this cabin it had been found necessary to light the stoves, and as only an ordinary wooden deck separated the cabin from the cargo, it would seem probable that the lighted stove, by creating an up-draught had drawn gases from the hold into the cabin. Immediately after departure from Mannheim the children were attacked with giddiness, nausea, and actual vomiting, in consequence of which they were kept in bed. As they got worse rather than better a medical man was called in to see them on arrival at Duisberg, who attributed their illness to food-poisoning. On the following day the children both died, as also did a canary kept in a cage in the same cabin. The occurrence was investigated by P. Lehnkering,* of Duisberg, who states that he, at once, diagnosed the causes of these fatalities. He adds that the parents of these children although spending most of the night on deck, in the open air, also suffered from headache and giddiness.

In his paper Lehnkering also briefly refers to four other instances, coming under his observation, in which one or more deaths occurred on boats plying on the Rhine, and which in each instance, as the result of careful investigation, were found to have been caused by emanations from consignments of ferro-silicon among the cargo.

On October 21st, 1905, Dr. J. F. Robertson, of Althorpe, was called to the Keadby canal to see two children aged three and four years respectively, who were lying ill on board a "keel" (canal boat), named the "Emily." Dr. Robertson states, in a letter to the British Medical Journal of May 15th, 1909, that on arrival he found one child was already dead, while the other was lying in an unconscious state covered with a cold, clammy sweat, the pulse being hardly perceptible, the breathing slow and light,

* Phosphorwasserstoffvergiftung durch im electrischen ofen hergestelltes Ferro-Silicium, von P. Lehnkering (Duisberg). Zeitschr. f. Untersuchung d. Natur- u. Genussmittel. 12. Band. 15. Juli, 1906, pp. 132–135.

and the pupils somewhat dilated. On examining the chest, crepitations were heard all over; nothing else abnormal was found, but the child died soon afterwards.

The father and mother were both suffering from abdominal pain, sickness, and diarrhœa. They stated that the day after leaving Hull, while coming up the Trent to Keadby all the family suffered from a feeling of sickness and dizziness with pain in the body on getting up in the morning, which passed off during the day, for the greater portion of which they were on deck. But towards evening the children again became sick and diarrhœa recommenced. Their mother, who stayed down below with them was also attacked with dizziness, sickness, and pain in the body which became worse when she got out of bed to attend to the children.

On the second and third days there was a repetition of the symptoms, but aggravated in character, the effects by the third day being so pronounced in the case of the two little children that they were utterly unable to get up from bed, and soon lapsed into the condition in which they were found by Dr. Robertson on his arrival. A peculiar and very pronounced smell was noticeable in the cabin.

As Dr. Robertson was unable to certify the cause of death an inquest was held at the Friendship Inn, Keadby, by Mr. Gamble, of Gainsborough, the coroner for the district, and a *post-mortem examination* was ordered. But no further information was thereby obtained regarding the cause of death, the only positive fact observed being some congestion of the lungs. Consequently the inquest was adjourned, and portions of the viscera together with samples of food of which the family had recently partaken and of the cargo were sent to an analyst at Sheffield, who subsequently reported that no evidence of poison could be found in the viscera, but that the sample of the cargo proved to be ferro-silicon, containing 7 per cent. of calcium carbide, a substance which "on exposure to the moisture of the atmosphere, would "lead to the evolution of acetylene gas, which is the probable "cause of the odour noticed." The analytical report added, however, that it had proved impossible by chemical means to detect the presence of this gas.

The jury returned a verdict to the effect that the cause of death was narcotic poisoning, caused by the fumes from the ferro-silicon. The cargo of the boat was found to consist of five tons of this substance packed in boxes, as well as a considerable quantity of iron. The further fact came out in the evidence, that as the atmospheric conditions were dull and damp, sails had been fixed down over the hold in order to protect the cargo from rains.

The coroner subsequently wrote to the Board of Trade, at the request of the jury, as he said, "to draw attention to the fact "that two children, both under six years of age, had died on "board a 'keel,' at Keadby, Lincs, as the result of poisoning by "the fumes of ferro-silicon, which had formed part of the cargo "of the keel." Mr. Gamble further stated that the jury were of opinion that children should not be allowed on vessels where ferro-silicon formed part of the cargo.

In September, 1907, the Board of Trade issued a memorandum, received from the Home Office, in which occurs the statement that Professor Cronquist, of Stockholm, who had been instructed to investigate the cause of the death of four passengers on board a Swedish steamship, the "Olaf Wyjk," "confirms the view that "their deaths must be attributed to the gases given off by ferro-silicon contained in the hold under the cabins."

A full and most interesting account of an investigation of this occurrence has recently been published by MM. G. Bruylants and H. Druyts, of Antwerp,* of which an abstract appeared in the British Medical Journal for July 3rd, 1909. From these sources the following details are compiled.

The "Olaf-Wyjk" arrived at Antwerp on the evening of February 12th, 1907, from Gothenburg, whence the steamer had sailed on February 9th, having on board six passengers. Stowed in the hold of the vessel immediately beneath the cabins occupied by the passengers was carried a cargo of fifteen tons of ferro-silicon, packed in wooden casks bound with iron hoops. The steamer left Gothenburg on a Saturday, and on Monday morning four of the passengers were found to be dead.

The captain, the stewardess, and some of the crew, together with the two other passengers were also taken ill, but recovered, owing apparently to their having been able to escape into the fresh air on deck.

The authors ingeniously trace the effect of gradually increasing roughness of the sea on the evolution of poisonous gases from the cargo, and the effect produced on the passengers and crew by these circumstances in conjunction. Thus, on the first day of the voyage (Saturday), the sea was calm, so that the cabin windows were left open. No one was inconvenienced. In the evening the sea became rough, in consequence more gas was evolved, and although the port-holes were still left open all the passengers suffered more or less, two of them vomiting several times during the night.

On Sunday the steamer encountered a gale which rendered it impossible for the passengers to remain on deck. They shortly were attacked with nausea, vomiting, and intense abdominal pains, followed by loss of consciousness developing into coma. It was noticed that throughout the whole forepart of the vessel, where the cabins were situated, there was an irritating, unsupportable smell, which the sailors attributed to lucifer matches among the cargo. Towards evening the captain, whose cabin was near those of the passengers, was so unwell that he gave up command of the ship to the mate, but, in order to escape the smell, fortunately for himself, he managed to return on deck, and eventually after some conversation with the mate he retired to that officer's cabin which was situated at a distant part of the vessel from his own. Two of the passengers also left their cabins and, although very weak, succeeded in getting on deck. These two survived, whereas, when visited by the captain at 8 a.m. on the Monday morning, three (one of whom it appeared

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* Bulletin de l'Acadamie Royale de Médicine de Belgique. IVe série Tome xxii. (Séance du Janvier, 1909, p. 26 *et seq.*)

had closed the porthole in his cabin) were found to be dead; the fourth was alive but unconscious, and although at once removed on deck all attempts at resuscitation proved unavailing.

The autopsy of the four victims was made five days after death, on February 16th, by Drs. Van Rever and Bailleux, whose report may be briefly summarized as follows:—

1. The four bodies were in a good state of preservation.
2. There were practically no external signs of decomposition, but the surface of the bodies was reddened.
3. In all the blood was found to be fluid and rose-coloured; congestion of the brain and lungs and of the liver and of the alimentary canal was present, and the left cavity of the heart was distended with blood.

Suspicion of poisoning having naturally arisen, the authors of the paper were instructed to carry out toxicological examinations of certain of the abdominal viscera. Search was made both for alkaloidal and mineral poisons, but beyond slight indications of the presence of arsenic no poison was detected. The blood was examined for various gases, including carbon monoxide, sulphuretted hydrogen, acetylene, and phosphoretted hydrogen, but with negative results.

As regards examination of the cargo, it was found that, in addition to the ferro-silicon previously referred to, there were several cases of matches, the greater portion of which, however, were found to be safety matches although some ordinary matches made with yellow phosphorus were also included in the consignment. Elaborate tests on these failed, however, to demonstrate the evolution from them of more than traces of phosphoretted hydrogen.

The ferro-silicon on board was in small fragments about the size of a hazel-nut. It had a grey metallic appearance and was hard and brittle. Numerous experiments were made with it, of which details are given in the original paper. When powdered and moistened a peculiar alliaceous odour was noticed, and both phosphoretted and arseniuretted hydrogen were found to be evolved.

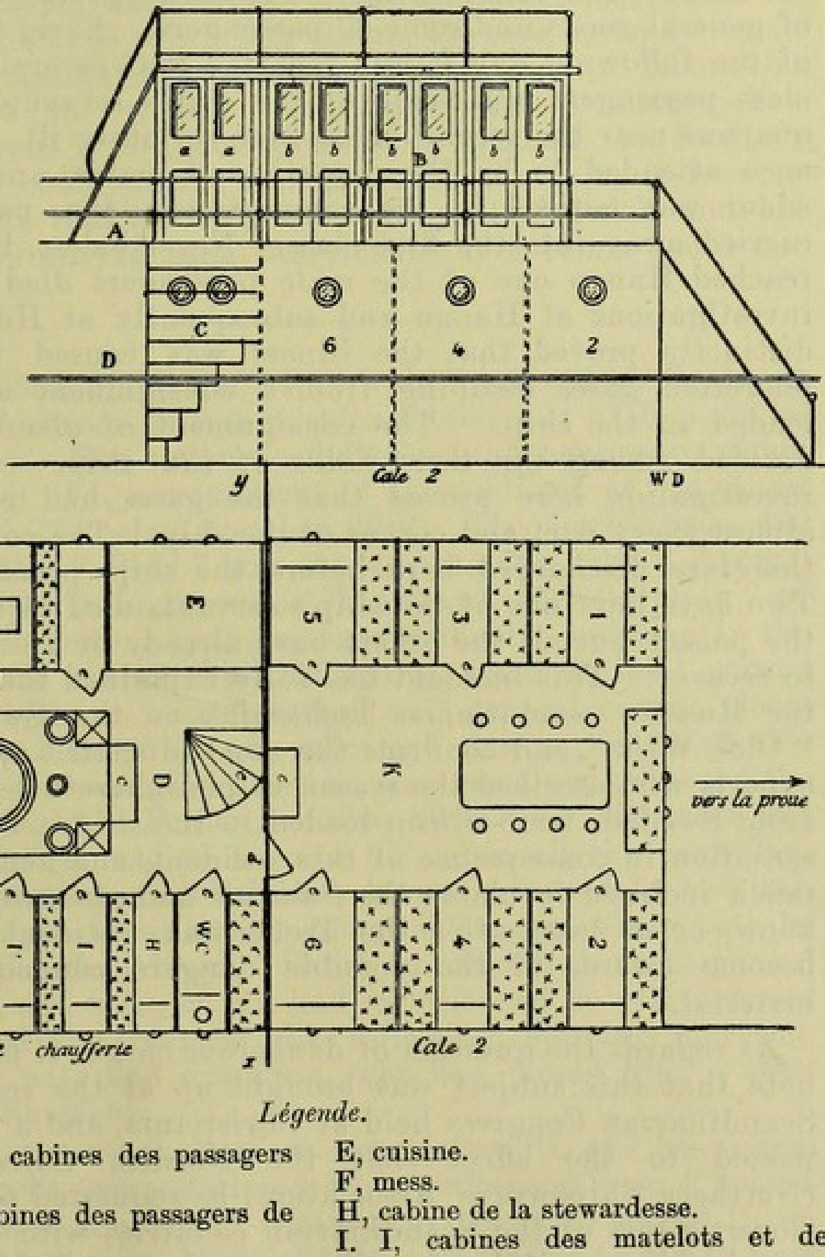
The authors procured a drum of ferro-silicon of similar grade (50 per cent.) from the factory, on making a small opening in which and exposing a paper moistened with silver nitrate in front of the opening, the paper was blackened. A second hole was then made in the drum and a current of air passed through. The outcoming current of air when led into silver nitrate solution was found to cause an abuntant precipitate. Gradually, however, the reaction became less marked, but at once increased again when the drum was shaken. They thus demonstrate that the violent shaking of the cargo caused by the turbulence of the sea, aided by the dampness of the air of the hold, which was readily able to affect the contents of the casks, supplied the needful conditions for continued evolution of poisonous gases from the ferro-silicon.

As the mean of several experiments Drs. Bruylants and Druyts concluded that a ton of ferro-silicon of 50 per cent. silicon-content, disengaged 245 grammes or 161 litres of phosphoretted hydrogen, and 25 grammes or 7 litres of arseniuretted hydrogen, which for the whole cargo of fifteen tons would equal 2,415 litres and 108 litres respectively of these gases.

From these data they formulate the general conclusion that the ferro-silicon on board the "Olaf-Wyjk" was capable of evolving nearly 2,500 litres of a gaseous mixture consisting of 95 per cent. phosphoretted hydrogen and 5 per cent. arseniuretted hydrogen. In reference to this calculation it may be mentioned that the continued breathing of an atmosphere containing either of these gases to the extent of 0·025 per cent. only is stated to be sufficient to cause death in the human subject.

PLAN OF THE S.S. "OLAF WYJK"

Copied from the paper by G. Bruylants and H. Druyts.



Légende.

Nos. 1, 3 et 5, cabines des passagers de 2[e] classe.
Nos. 2 et 4, cabines des passagers de 1[re] classe.
No. 6, cabine du capitaine.
A, entrée du fumoir.
B, fumoir.
C, escalier qui mène au fumoir.
D, antichambre.
E, cuisine.
F, mess.
H, cabine de la stewardesse.
I. I, cabines des matelots et des machinistes.
J, cabine du second officer.
xy, cloison en fer qui sépare la cale No. 2 de la machinerie de la chaufferie.

In May, 1908, on the s.s. "Uleaborg," during a voyage from Stockholm to St. Petersburg, practically all the crew and second class passengers were taken ill, while two deaths occurred. The circumstances are related in a communication from the Finska Ångfartygs Aktiebolaget, of Helsingfors, the owners of the vessel, in a publication entitled "The Baltic and White Sea Conference," for July, 1908. The terms of their letter are as follows:—

"The recent sad occurrence on one of our passenger boats from Stockholm to Finland is of such importance that we consider you should be acquainted with the circumstances, as it, doubtless, can be of use to many shipowners.

"The s.s. "Uleaborg" on the 9th May sailed from Stockholm for Hango, Helsingfors, and St. Petersburg, having a full cargo of general goods and some 40 passengers. Early in the morning of the following day it was reported that several of the second class passengers and some of the ship's servants, having their quarters near the second class, were seriously ill. They were at once attended to by the captain and mates, and as a strange odour was noticed in the compartment the passengers were carried away into the first class. Nevertheless, before the boat reached Hango one of the male passengers died. Immediate investigations at Hango and subsequently at Helsingfors have distinctly proved that the illness was caused through phosphoretted gases escaping from a consignment of ferro-silicon loaded in the ship. The consignment of about 45 tons was divided among the three holds of the ship. The chemical investigation here proved that the gases had penetrated into almost every part and corner of the ship. The consignment was therefore discharged here before the ship proceeded further. Two days later one of the ship's servants died in consequence of the poison, but all the others have already or are fully expected to recover. This incident has fully explained the accident with the Russian revolutionist Tscherniak on the Swedish steamer "Olof Wijk," and confirms the much disputed opinion of those experts who ascribed the reason to phosphoretted gases escaping from Swedish ferro-silicon loaded in the ship. There is a great sensation in consequence of this accident, and general opinion is much inclined to blame the Swedish manufacturers who should know, or at least after the Tscherniak incident should have become aware, of the possible dangers connected with this material."

As regards the question of dangerous cargos it is interesting to note that this subject was brought up at the recent Maritime Scandinavian Congress held at Christiania, and a resolution was passed to the effect that the Nordisk Skibsrederforening (Northern Shipowners' Association) be requested to approach the Governments of the Scandinavian countries with a view of considering the question of calling a conference for the framing of international rules concerning measures for the safe transport of dangerous cargos.

The reference to the Russian revolutionist Tscherniak, in this letter, refers to the fact that prior to the elucidation by Professor Cronquist and other observers of the cause of the fatalities on board the "Olaf Wijk," already referred to, a suggestion obtained currency to the effect that these deaths had resulted from the intentional use of poison with a view to the assassination of Tscherniak, who was a passenger on board. The Russian Government had previously demanded his extradition from Sweden, where he had obtained temporary asylum, and although the Swedish Government found themselves unable to comply to this extent, Tscherniak was ordered to leave the country forthwith. He took passage therefore in the "Olaf Wijk" for Antwerp, and on the following day was found dead in his cabin, as was also the case with three other passengers, one of French and two of Swedish nationality. The tragic circumstances of the death, of which, as previously stated, the true cause for some time baffled investigation, led to a violent outcry from the Socialist leaders in Sweden, who charged the Russian police with a treacherous crime, and practically accused the Swedish Government of connivance. Subsequently, however, it became abundantly clear that the suggestion as to Tscherniak and his fellow travellers having been the victims of a crime could not be sustained.

On October 28th, 1908, the s.s. "Nidd" arrived at Goole, at 9 p.m. from Antwerp, which port had been left at 6 p.m. on the previous day. She commenced discharging her cargo, which consisted in part of a consignment of ferro-silicon, at 6 a.m. on the morning of Thursday, October 29th. The ferro-silicon discharged from the "Nidd" was loaded into the keel "Harry," William Bamfield (also known as Hamshaw), the "captain" of the keel, and the mate, a grandson of Bamfield's, assisting in the operation. There was no "bill of lading," and on the "permit note" the consignment was described as "general cargo: Goole to Sheffield," and Bamfield was informed that a portion of this consisted of steel "scrap." The two men remained on board the keel until the night of Friday, October 30th, when the mate was taken so ill that he had to keep to his cabin all the next day. On Saturday evening, October 31st, he was removed to hospital, but the same night he was taken home to Thorne, where both he and Captain Bamfield lived. Bamfield, who had accompanied him to Thorne, and who, so far, had experienced no symptoms of illness, rejoined the keel on the following Monday morning, when with his wife and grandson, who had joined him, a start was made for Sheffield.

On the way, however, all three were taken ill, and on arrival at Tinsley, Yorks, were declared to be suffering from "gastro-enteritis" by a medical man who was called in to attend them. Dr. Lewis Wetherbe, the Medical Officer of Health to the Rotherham Rural District Council, who saw the Bamfields in consultation with the medical man attending them, states that he agreed in this opinion, considering them to be suffering from ptomaine poisoning. Bamfield died on November 6th and his grandson on the previous day. Mrs. Bamfield eventually recovered.

At the inquest, the jury brought in a verdict, in accordance with the medical evidence, to the effect that the deaths were due to ptomaine poisoning "from eating pork," which was stated to have been eaten by the occupants of the boat shortly before the onset of their fatal illness. As a matter of fact, however, it subsequently appeared that one of the deceased, at any rate, had not eaten any pork, while several other persons who were found to have consumed portions of the carcase of the particular pig in question, which was reared by Bamfield himself, experienced no ill-effects.

The cargo of the "Harry" consisted of flour and sugar in bags, cases of toys, and 91 casks of ferro-silicon, described as steel "scrap." Bamfield had himself noticed what he described as a nasty smell from the part of the hold in which these casks were stored, and possibly for this reason his step-son, Hodgson by name, who was present at the inquest, came to suspect this material as having been concerned in causing the death of Bamfield and his grandson, and the serious illness of Mrs. Bamfield. In a letter from Hodgson, a copy of which has been supplied to me by the Board of Trade, he states that after the inquest two of his brothers took the boat on to Sheffield, where the cargo was discharged, and that when the casks of "scrap" were reached he took about 2 lbs. of the material out of one of the casks, in the presence of several other men, with the intention of having it analysed. On the following day with one of his brothers he went to the transport office for the freight and told Mr. Thornton, the manager for the Goole and Sheffield Transport Company, of his suspicions, and learnt from that gentleman that the so-called "scrap" was really ferro-silicon. Mrs. Bamfield in a letter dated from Thorne, near Doncaster, on December 17th, 1908, stated that the sample of "scrap" had been forwarded "to the analyst at the Chemical Research "Association, Watergate House, Adelphi, and poison was found "in the shape of phosphoretted hydrogen, phosphides, and arsenic." She goes on to say: "It has occurred to me since "reading of the poisoning at Grimsby that possibly there may "be some of this ('scrap') in the s.s. 'Ashton,'" and concludes with the statement that she was writing at the strong and urgent request of the majority of the canal boatmen "who are "very dissatisfied with the present state of affairs."

Immediately certain deaths on board the s.s. "Ashton," which will be referred to later, were reported, her son-in-law Hodgson also wrote to Dr. Simpson, the Medical Officer of Health for Grimsby, suggesting that, as in the case of the Bamfields, the deaths of steerage passengers on the s.s. "Ashton" might have been due to the fumes of ferro-silicon, of which, as stated at the inquest, and reported in the press, a quantity was found to have been stored in the hold beneath the steerage quarters. It was apparently in consequence of this letter that attention came to be directed to the possibility of the deaths on the s.s. "Ashton" having been due to the presence of the ferro-silicon on board, suspicion having arisen, in the first instance, that the fatal illness of the passengers was due to cholera.

The outcome of certain legal proceedings which are pending in connection with the fatalities on the "Harry" is likely to be of special interest, a writ having been issued at the instance of the widow of Captain Bamfield against the Goole and Sheffield Transport Company, Limited, from whom she is seeking to claim damages in respect of her husband's death.

It may be mentioned that the ferro-silicon on board the keel "Harry" was of 50 per cent. grade (actual percentage as determined by chemical analysis 53·87), and that it was manufactured by one of the best known firms in France.

In the course of interviews with the "skippers" of certain barges which happened to be laid up at Sheffield after a journey thither from Hull, I learnt from "Captain" Bisby, of the canal boat "George and Rebecca," No. 163, registered at Wombwell, that about six months previously two boys aged 16 and 14 respectively had been taken ill on the canal boat "Eclipse" as the result of poisoning by the fumes of ferro-silicon. The boys were the sons of "Captain" Fowler, of the "Eclipse," who was navigating the boat from Doncaster to Sheffield. A start had been made from Doncaster about 3 a.m., the boys being at the time asleep in the cabin. An hour or so afterwards the boys were called by their father, but, contrary to custom, did not put in an appearance. Captain Fowler was unable to get down to the cabin to see what was the matter as he could not leave his horse until Sprodborough Lock was reached, about 3½ miles from Doncaster. Here the lock-keeper "lent him a hand" while he went to rouse the boys. On going below, however, he found them both in a state of unconsciousness, lying in their bunks, in the fore-cabin. With the assistance of the lock-keeper they were carried on deck where bucketsful of cold water were dashed over their heads. Under this treatment, together with exposure to fresh air, they eventually regained consciousness. A portion of the cargo was found to consist of casks containing ferro-silicon.

From Captain Bisby I also learnt that on the canal boat "Kate," owned by Messrs. Thomas Wilson and Sons, Hull, during a voyage from Hull to Sheffield, the exact date of which he was unable to give me, two children of the boat's captain, William Graville, had been attacked by illness as the result of breathing the fumes given off by a cargo of ferro-silicon.

The children, who had been put to sleep in the fore-cabin of the boat, were found to be unconscious, but, the fact having fortunately been discovered in time, they recovered on being taken into the open air. But a dog belonging to the captain, which made its way into the cabin at the time the children were removed, was, later on in the day, found lying dead on the floor.

Captain Bisby further informed me that he not infrequently had heard men making complaint of having suffered from diarrhœa and feelings of dizziness as the result of exposure to the fumes of ferro-silicon which they were carrying on their boats.

In this statement he was corroborated by the independent evidence of the captains of other canal boats, and also, of several labourers on the canal wharf at Sheffield, of whom enquiries were separately made as to whether they had knowledge of the occurrence of illness (of any sort) on any of the barges plying on the canal.

The danger to human life incidental, under certain circumstances, to the transport of ferro-silicon, was brought forcibly before the public notice in December of last year (1908) by press reports of a number of fatalities which occurred on the s.s. "Ashton," a vessel belonging to the Wilson line, in the course of a voyage of twenty-four hours' duration only, between Antwerp and Grimsby. The story is an exceedingly sad one, as all the occupants of the emigrant quarters, fortunately only five in number (although the certified accommodation made allowance for a considerably larger number of steerage passengers) died between six o'clock on the evening of December 12th and 12.30 p.m. on the following day.

The customs officer who visited the vessel immediately on her arrival in the Roads, off Grimsby, at once informed Dr. Simpson, the Medical Officer of Health for the port, who promptly went on board and commenced an investigation of the circumstances attending the deaths, as to the cause of which suspicion arose, in the first instance, that they might have been due to cholera.

The bodies were landed, *post-mortem* examinations were carried out, and an inquest held. A full report of all the ascertained facts was subsequently made to this Board by Dr. Simpson, which in view of the importance of the issues, is here transcribed in full:—

On Sunday evening, December 13th, 1908, about 5.10 p.m., a message was received from the Customs that the s.s. "Ashton" had arrived in the Roads, and that there were five emigrants dead on board. The message further stated that the captain was also ill.

I at once proceeded down to the docks, and arrived on board the s.s. "Ashton" about 6 p.m. It appeared that the vessel left Antwerp about 7.30 p.m. the previous evening, having on board, besides her ordinary crew, the following passengers:—

One saloon,
One Belgian transmigrant (transferred in Antwerp to saloon),
Five Russian transmigrants, and
Ten homeward-bound sailors.

The five deceased persons were the Russian transmigrants, who alone occupied the emigrant quarters, the 'tween decks forward. They came on board at Antwerp about 6 p.m. on the previous evening, and were then, as far as was known, in good health. Between 6 and 7 p.m. they partook of a meal consisting of bread and butter, corned beef and tea. They were seen about on deck during the evening, but of their subsequent history very little could be ascertained until they were visited by the steward about 8.30 a.m., when they were suffering from what appeared to be sea-sickness. One of the sailors who occupied the fore-cabin, says they were suffering from thirst during the night, and he gave them some water, which was immediately vomited. On visiting them again about 11.30 a.m. four were found to be dead or dying, and the fifth, who was not quite so far gone, was got up on deck, and stimulants administered, but he died shortly after, about 12.30 p.m.

At the time of my visit the bodies had been removed on deck; the hatches had also been removed from the upper hatch-way, there was free circulation of air, and no special odour was perceptible in the apartment occupied by the deceased. About the floor were signs of vomiting and of fæcal evacuations.

Practically nothing was known of the deceased prior to their coming on board the vessel. It was not known whether they were one party travelling together (three of them bore the same name on one pass). All were bound for Boston, U.S.A.

It seemed impossible, from the available data, to arrive at a definite conclusion as to the cause of death. Broadly, the symptoms pointed to some form of irritant poisoning, but, as a precautionary measure, and until something more definite could be ascertained, it was deemed advisable to detain the vessel, and to remove the bodies ashore for further investigation.

Under my direction, they were removed to the mortuary at the Scarthe Cemetery, and the Coroner communicated with.

Acting under his instructions a *post-mortem* examination of the remains was made during the night and portions of viscera removed and forwarded to the pathologists for the Borough of Grimsby, the Royal Institute of Public Health; together with some portions of food found amongst the belongings of the deceased persons, for bacteriological and chemical analysis.

A preliminary enquiry was held by the Coroner on Monday, December 14th, 1908, which was adjourned to the following Wednesday. On this day, the investigations not being concluded, a further adjournment was made to Monday, December 21st.

Post-mortem Examination.

All the bodies presented very much the same external appearances. The eyelids were closed and the pupils semi-dilated. *Rigor mortis* was noticeably well marked (about 12 hours after death) and the colour of the skin and mucous membranes was dark in colour. There was, however, an absence of the shrunken, shrivelled appearance seen in cases of death from cholera.

The right heart in all cases was distended with blood of a dark red colour, and unusally fluid in character, the left ventricle being empty. Lungs were dark in colour in all cases save one where the lung was adherent to the parietal pleura, and this lung was less dark in colour. Some slight ecchymoses were present on the surface.

For the purpose of further investigation the stomachs were ligatured "in situ" and removed. The peritoneal surface was deeply congested, as was also that of the small intestine, portions of which were removed, after ligature, for bacteriological investigation. The mucous membrane of the intestine was highly congested and covered with a thick tenacious mucus.

The portions of small intestine and the stomachs were placed in suitable receptacles and forwarded to the Royal Institute of Public Health, who do the periodical examination of the water supply and other bacteriological work for this authority.

As regards the exact nature of the cargo on board the s.s. "Ashton," it appeared from the ship's manifest that there was stored in the lower forehold, immediately beneath the compartment occupied by the deceased, a quantity (about nine tons) of a substance known as ferro-silicon.

As some suspicion attached to this substance, I, in company with the Port Sanitary Inspector, again visited the vessel and had one of the hatches removed from the lower hold where the ferro-silicon was stored, and on bending down over the aperture a slight but peculiar garlic-like odour was perceived; hence it was thought that possibly, some poisonous fumes might have been given off which had set up the symptoms of irritant poisoning observed in the case of the deceased persons.

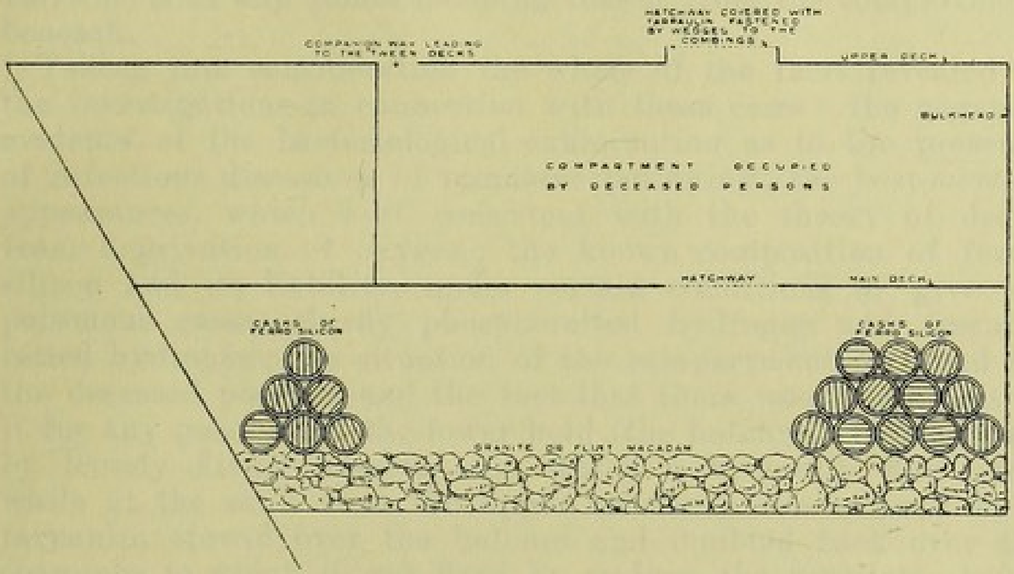
On Tuesday, December 15, the preliminary examination of the viscera proving negative so far as infectious disease was concerned, and there being no further illness on board, it was decided to allow the vessel to enter the dock.

Portions of the ferro-silicon were obtained and forwarded to the Borough Analyst and to the Royal Institute of Public Health for examination and report, as to its chemical composition and liability under varying conditions to give off poisonous gases.

As stated in the opening paragraph, the first message received by me was to the effect that in addition to the five victims the captain was also ill. When I first saw him he complained of a feeling of tightness across the chest and dryness of the throat and thirst. He was generally in a highly excited and agitated state, and his condition was attributed to shock and nervous prostration consequent on the startling events which had happened a few hours previously. In the light of subsequent discoveries it would appear that his condition was the result of attending to the dead and dying emigrants, he having remained down in the compartment longer than others. He was practically all right when seen the following morning.

The compartment occupied by the deceased persons was the "forward 'tween decks." In the floor of this compartment is

Fig. 1.



Diagrammatic sketch of the forward part of S.S. Ashton
(reduced from Dr. Simpson's report).

(*To face page* 24.)

a hatchway leading to the lower forehold, in which the ferro-silicon was stored. (A rough diagrammatic sketch is attached). The hatches are loose-fitting and were covered by a tarpaulin placed thereon, but not fixed to the hatchway coamings as is the case with that which covered the hatches in the upper deck, which latter were made impervious to water by overlapping tarpaulin fixed by wedges to the outer sides of the hatchway coamings.

The evidence was to the effect that the ventilators leading from both the upper and lower compartments of the forehold to the deck were closed, when at sea, on account of the weather, while, as regards the door leading up to the companion way, the accounts were conflicting. It appeared to be left to the caprice of the passengers whether the door was open or closed.

If the latter condition prevailed the apartment would be practically air-tight and the occupants would be subjected to the full effects of any fumes escaping into it from the compartment beneath.

Taking into consideration the whole of the facts revealed in the investigations in connection with these cases: the negative evidence of the bacteriological examination as to the presence of infectious disease or of ptomaine poisoning; the *post-mortem* appearances, which were consistent with the theory of death from deprivation of oxygen; the known composition of ferro-silicon and its liability, under certain conditions to give off poisonous gases, chiefly phosphoretted hydrogen and arseniuretted hydrogen; the situation of the compartment occupied by the deceased persons, and the fact that there was free access to it for any gases from the lower hold (the hatchway being closed by loosely fitting hatches over which a tarpaulin was laid), while at the same time the upper hatchway was covered by a tarpaulin spread over the hatches and doubled back over the coamings to which it was fixed by wedges, the ventilator being closed while at sea to prevent entrance of water and the possibility that the door leading to the companion way was also closed, I had no hesitation in stating as my opinion that the deceased persons were poisoned by the inhalation of poisonous gases evolved from the ferro-silicon stored in the lower hold beneath the compartment which they occupied, the atmosphere in the lower hold having been kept saturated with moisture by the granite (macadam) also present there.

Bacteriological and Chemical Examinations.

On December 14th, certain material was received at the Royal Institute of Public Health, from Dr. Simpson, of Grimsby, with the request that examination should be undertaken with the view of determining the question as to whether the deaths were due to cholera or ptomaine-poisoning.

Pending result of the search for the cholera vibrio by appropriate bacteriological methods, samples of food of which the victims were believed to have partaken, and of material from the stomachs and intestines were subjected to examination with the object of detecting, if present, any food poison or bacteria capable of producing food poisoning. As the deaths had been of such a sudden nature, portions of the viscera, as well as of preserved fruit, and sausage, &c., were chemically examined for alkaloids, arsenic, antimony, and the metallic poisons, but with negative results.

Suspicion was subsequently directed to a portion of the cargo consisting of ferro-silicon, as being a possible cause of death, owing to the poisonous gases which it has been known to evolve. Accordingly portions of the lungs, blood, and urine were examined for arsenic, but without result. The blood was also spectroscopically examined for carbon monoxide, with like negative results. Experiments on animals were therefore undertaken in order to test the action of any gases given off by the ferro-silicon, the results of which afforded abundant proof that ferro-silicon when moistened especially, may give off emanations which are in high degree dangerous to life.

As regards the nature of the gases evolved the suggestion is put forward that these might consist of phosphoretted hydrogen, arseniuretted hydrogen, acetylene, and silicon hydride (siliciuretted hydrogen). In order to determine which of these gases was evolved in greatest quantity when ferro-silicon is moistened, a considerable amount of chemical work was undertaken to which detailed reference is unnecessary here,* the main outcome of which, however, was to the effect that while arseniuretted hydrogen is produced, in small quantities, the chief gas evolved is phosphoretted hydrogen. To emanations from the cargo of ferro-silicon, therefore, consisting mainly of this gas, the deaths of the five Russian immigrants on board the s.s. "Ashton" must be attributed.

CONFERENCES WITH SHEFFIELD FIRMS USING OR DEALING IN FERRO-SILICON.

Visits for the purpose of obtaining information on the different points referred to in the introduction to this Report were paid to all the Sheffield works where, so far as is known, ferro-silicon is used in various processes of manufacture, and to a number of agents for British or foreign firms, by whom this material is supplied.

Certain of these visits were made either by myself alone or accompanied by Mr. Bennett, one of His Majesty's Inspectors of Factories, who is stationed at Sheffield. The greater number, however, were entrusted to Mr. Bennett, whose local knowledge and acquaintance with the representatives of the steel and iron industry in Sheffield proved most valuable in such portions of the investigation as was necessarily conducted in that city.

In the majority of instances all the information sought was readily afforded, although coupled occasionally with the request that certain details should be regarded as confidential. Where such a request has been expressed, it has, needless to say, been respected.

* Some account and criticism, by Dr. Hake, of the results obtained will be found at p. 73 of this report.

The information thus obtained, of which some account is set out in the following pages, has been of the greatest assistance to me in the course of my investigation, and has on several occasions afforded a very valuable clue as to further directions in which enquiry might usefully be extended. To the representatives of all the firms concerned, I desire, therefore, to tender my sincere thanks for the help they so courteously afforded me—often at considerable trouble and inconvenience to themselves.

From several firms making use of ferro-silicon, as well as from the local agents for certain manufacturers of this alloy, I received a number of samples of ferro-silicon of different grades—the product, in some instances, of the blast furnace, in others of the electric furnace. Wherever possible these were accompanied, in accordance with my request, with details as to source and date of manufacture, and of receipt; in addition to a statement, in each case, as to the percentage silicon-content. Occasionally a complete or partial works analysis accompanied the samples, which, immediately on coming into my possession, were handed over to Dr. Wilson Hake for chemical examination.

List of Firms Visited where Ferro-Silicon is Used.

Sheffield District.

1. Allen, Edgar and Co., Ltd., Imperial Steel Works, Sheffield.
2. Andrew, J. H. and Co., Ltd., Toledo Steel Works, Sheffield.
3. Atkins, Wm. and Co., Bessemer Road, Sheffield.
4. Bessemer, H. and Co., Ltd., Carlisle Street East, Sheffield.
5. Brown, John and Co., Ltd., Atlas Steel Works, Sheffield.
6. Brown Bayley's Steel Works, Ltd., Milner Road, Sheffield.
7. Cammell, Laird and Co., Ltd., Cyclops Works, Sheffield.
8. Firth, Thomas and Sons, Ltd., Norfolk Works, Sheffield.
9. Fox, Samuel and Co., Ltd., Stocksbridge, near Sheffield.
10. Hadfield's Steel Foundry Co., Ltd., East Hecla Works, Sheffield.
11. Hadfield's Steel Foundry Co., Ltd., Hecla Works, Sheffield.
12. Jessop, William & Sons, Ltd., Sheffield.
13. Jonas and Colver, Ltd., Bessemer Road, Sheffield.
14. do. do. Stevenson Road, Sheffield.
15. Kayser, Ellison and Co., Ltd., Carlisle Works, Sheffield.
16. Osborn, Samuel and Co., Ltd., Clyde Steel Works, Sheffield.
17. Osborn, Samuel and Co., Ltd., Rutland Road, Sheffield.
18. Parkgate Steel and Iron Works, Ltd., Parkgate, Rotherham.
19. Spear and Jackson, Ltd., Etna Works, Sheffield.
20. Steel, Peech and Tozer, Ltd., Phœnix Steel Works, Sheffield.
21. Vickers, Sons and Maxim, Ltd., River Don Works, Sheffield.

List of Principal Agents for Ferro-Silicon.

Amalgams, Ltd., Attercliffe Road, Sheffield.
Beck, Matthew and Co., Liverpool.
Birch and Co., Ltd., 3, London Wall Buildings, London.
Birch, John and Co., Manchester.
Blackwell, G. G., Sons and Co., Ltd., Liverpool.
British Griffin Chilled Iron and Steel Co., Ltd., 139, Cannon Street, E.C.
British Mining and Metal Co., Ltd., Lloyd's Avenue, E.C.
Burridge, S., Change Alley, Sheffield.
Camplin, A. and Co., Paris.
Chalas and Sons, Ltd., Finsbury Pavement, London, E.C.
Darby, Brown and Co., Navigation Street, Birmingham.
Dobb, J. T. and Son, Westbar, Sheffield.
Everitt and Co., Ltd., 40, Chapel Street, Liverpool.
Giffre Electrochemical Co., Ltd., London.
Grundly, G. G. S., Leeds.
Hirsch and Co., 16, Leadenhall Street, London, E.C.
Iron Ore Co., Ltd., London.
Jacks, W. and Co., Middlesboro'.
Jaeger Bros., Middlesboro'.
Keiffenheim, A. and Sons, Milburn House, Newcastle-on-Tyne.
King, Andrew, Park Station, Sheffield.
Müller, C. E. and Co., Ltd., Middlesboro' and Sheffield.
Needham, J. and Sons., Old Millgate, Manchester.
Owen, D. and Son, Bixteth Street, Liverpool.
Ridge, Beedle and Co., 116, Hope Street, Glasgow.
Stevenson, T., Ltd., Middlesboro'.
Tennant, C., Sons and Co., Ltd., 9, Mincing Lane, London, E.C.
Watson, T. H., Norfolk Row, Sheffield.
Willis and Co., Ltd., 90, Mitchell Street, Glasgow.

Principal British Manufacturers of Blast Furnace Ferro-Silicon.

Darwin and Mostyn Iron Co., Ltd., Mostyn, N. Wales.
Gjers Mills and Co., Ayresonee, Middlesboro'.
North Lonsdale Iron and Steel Co., Ulverston.
Pyle and Blaina Co., Blaina, S. Wales.
Wigan Coal and Iron Co., Wigan.
Workington Iron Co., Workington.

Firm A.

Up to the middle of 1908 about 75 to 100 tons per annum were used by this firm in the manufacture of open-hearth steels. The 50 per cent. grade was mostly used, though some 75 per cent. was also employed, but it has been rather difficult to obtain.

The alloy came in small wooden casks by rail from the most convenient seaports—Hull, Garston, Liverpool, Goole, etc.—being conveyed in open railway trucks. The average quantities stored at the works for some years was 60 to 70 tons, but at present there is but a small amount in stock. When the alloy was first used some ten years ago, it was put in the alloy stores, but owing to the obnoxious smell and the headaches, of which the workers complained, it was removed to the open air, where it is now kept. At that time it was observed that those samples which smelled most contained large percentages of calcium, 5 to 7 per cent. There has been no indication that the material supplied by any particular manufacturer or agent was worse than others. The price has ranged, decreasing in successive years, from £22 to £12 per ton, the firm naturally buying in the cheapest market.

If the importation of high-grade or electrically manufactured ferro-silicon were prohibited, acid steel manufacturers could manage without it, but basic-steel makers would be greatly hampered if only the low-grade alloy were available. The steel expert of the works suggested that if ferro-silicon of the following specification only, with the percentage of impurities regarded as maxima, were imported, no danger whatever need be feared:—

Si as required.
S, P, As, etc. } less than 0·05 per cent.
Ca less than 1·0 per cent.
Al less than 1·0 per cent.
Fe by difference.

Reference was made to the leading article in the February number of the "Foundry Trade Journal and Patternmaker," Vol. II., No. 86, in which the dangers of ferro-silicon are dealt with.

The low-grade blast furnace ferro-silicon, in the form of siliceous "pigs," is largely used.

When working full time, about 60 to 80 tons per week of this material are used. The silicon content is generally not more than 10 or 12 per cent. No emanations of any kind have been detected from low-grade or blast-furnace ferro-silicon. As a rule, ferro-manganese or spiegeleisen are made in the blast furnace until the lining is nearly worn out, when the manufacture of ferro-silicon is carried on, thus quickly scouring the furnace out.

Firm B.

The great majority of ferro-silicon used by this firm is of the blast-furnace kind, in the form of siliceous pig-iron containing 10 to 12 per cent. of silicon, all for open-hearth furnaces. About 40 tons per annum are used, the price ranging from £5 to £6 per ton. It is stacked in "pigs" in the works yard. All came by rail in open trucks. In no instance has the evolution of gaseous exanations been detected.

Silico-spiegel to the extent of 40 tons per month is also used. It is made in the blast-furnace, and comes in pigs. No case of gas-evolution is known, or of smell from the alloy. The usual composition specified is 20 per cent. Mn.. 12 to 14 per cent. Si., with but traces of impurities.

The following small lots of electrically manufactured ferro-silicon were shown by the firm's order books to have been received on the dates specified : —

May, 1906.—26 cwt. ; 30 per cent. ferro-silicon.
August, 1906.—7 cwt. ; 48 per cent. ferro-silicon.
August, 1906.—8 casks ; 24 per cent. ferro-silicon.
September, 1906.—8 casks ; 30 per cent. ferro-silicon.
December, 1906.—8 cwt. ; 97 per cent. ferro-silicon.

None has been used since the last-mentioned date. All came to various ports by sea, and thence per rail in open trucks. The ferro-silicon of low and high percentages (electrically manufactured) are said to be firm and hard, but the 50 per cent. alloy is friable in comparison. The 97 per cent. variety resembled carbon flakes with coke lustre, and came in closed boxes. No smell was noticed from the samples tested until the percentage of silicon was over 20 per cent. However, the amount used being so small the firm's experience was limited.

Firm C.

By far the greater quantity of the ferro-silicon purchased by this firm is of the 10 per cent. grade, which is manufactured by the blast-furnace process in England, about 100 tons of this material having been used during the past year. Smaller amounts of high-grade ferro-silicon are required for use in the Bessemer furnaces.

The Works Manager whom I met by appointment at the works, stated that no special precautions are adopted as regards storage of ferro-silicon, adding that about 4 tons would probably be the largest quantity on the premises at any one time, and that this amount would be divided among three different sections of the works.

No instance of illness or injury due to the action of ferro-silicon has come to the knowledge of the firm, but the chemist informed me that certain of the earlier lots of electrically-produced ferro-silicon supplied gave out a most objectionable smell when the material was being broken up, and, further, that it flamed when put into the muffles. These conditions were found to be associated with the presence of considerable quantities of calcium carbide, and doubtless, therefore, were due to the evolution of acetylene gas. The first occasion on which the presence of calcium carbide was discovered was in June, 1901; the sample in question gave off acetylene gas freely, and as the result of chemical analysis was found to contain 10 per cent. of calcium and 67 per cent. of silicon. In all probability this particular batch of ferro-silicon and others of similar character had been manufactured in a furnace which had previously been employed for the production of calcium carbide, about the time when there had been a severe " slump " in the price of the latter commodity owing to over-production.

Owing doubtless in large measure to the present scare due to reports of various fatalities traced to the action of ferro-silicon, the price of this alloy has also fallen considerably of late, and I learnt that this firm had recently been offered a large consignment of ferro-silicon of 27·5 per cent. silicon content, packed in sacks, at the extremely low price of £7 15s. per ton.

The firm kindly supplied the following particulars as to the nature and source (as to the name of the actual manufacturer, in most instances, no information is available) of the ferro-silicon purchased by them during the past five years:—

Year.	10 per cent.	25 to 30 per cent.	50 per cent.
	Tons.	Tons.	Tons.
1904 ...	50	10	—
1905 ...	80	5	—
1906 ...	155	11	1
1907 ...	140	18	1
1908 ...	100	5	—
Prices ...	£3 15*s.* to £5 2*s.* 6d. per ton.	£9 10*s.* to £12 6*s.* per ton.	£20 10*s.* to £20 17*s.* per ton.

Firm D.

This firm usually holds a stock of about 150 tons of ferro-silicon of various grades, the greater quantity of which consists of the 10 per cent. (blast furnace) grade, known as "silicon pig," for the reason that it is received in a form similar to that of pig-iron. Of electrically-produced ferro-silicon the 26 per cent. variety is preferred, but is not always obtainable. Indeed, of late agents have pressed the 50 per cent. rather than the 28 per cent. grade, probably for the reason that the former is relatively cheaper per unit of silicon to manufacture. All high-grade ferro-silicon in stock is stored in the open air. When 50 per cent. ferro-silicon was first purchased the consignments arrived in iron drums. Explosions were of frequent occurrence when, as was necessary, these drums were opened with a crow-bar; nearly every other drum indeed exploding. Fortunately, however, no injury to workmen resulted. But for at least five years past the use of iron drums has been discontinued, probably in consequence of the serious explosions that occurred in Liverpool in 1904. All consignments of ferro-alloys are delivered by the Midland Railway. Details as to grades and amounts of ferro-silicon purchased for the firm are given below.

The chemist to the firm said that no investigation had been made as to the origin, nature, or amount of gases given off by the various grades of ferro-silicon employed by them, but he undertook to initiate some work in this direction.

Some of the men in the employ of this firm engaged in handling ferro-silicon have from time to time complained of pains in the head and body, and of a feeling of nausea, but no serious case of illness, traceable to exposure to the fumes of ferro-silicon, while breaking up or otherwise working with the alloy, is known to have occurred.

Amounts of Ferro-Silicon used.

Year.	10 per cent. Si.	25 to 30 per cent. Si.	50 per cent.	In stock January 31st, 1901.
	Tons.	Tons.	Tons.	
1904 ...	575	45	—	370 tons 10 per cent.
1905 ...	830	40	5	10 tons 25 to 30 per cent.
1906 ...	887	39	12	12 tons 50 per cent.
1907 ...	784	50	5	
1908 ...	711	18	11	
	3,787	192	33	

Purchases during the above Periods.

Year.	10 per cent.	25 to 30 per cent.	50 per cent.
1904	154 tons 500 ,,	30 tons 5 ,,	
1905	1,000 ,,	33 ,,	1905. 10 tons. 5 ,,
1906	800 ,,	40 ,,	1907. 10¼ tons.
1907	657½ ,,	3 ,,	1908. 20 tons.
1908	942½ ,,	58 ,, 5 ,,	

Firm E.

This firm has employed a total amount of about 60 tons of electrically-produced ferro-silicon per annum, almost wholly of 25 per cent. silicon content, during the last five years.

The consumption has been fairly uniformly at the rate of 5 tons per month during that time. One consignment of 50 per cent. ferro-silicon was obtained for experiment at a price of £19 per ton. The price of the 25 per cent. grade has varied from £10 5s. to £9 15s. All has come by canal from Goole (the last order having been executed in 1906) on barges, packed in wooden casks. Until required for use it is stored at an iron wharf, in Sheffield. The casks are stored in an open shed, being covered with a roof only. No ferro-silicon has been ever received either packed in drums or with the lumps covered with paraffin wax. No complaints as to smell have been received, nor are any cases of even slight indisposition known to have occurred. When lumps of the 50 per cent. grade were broken a slight smell was noticed. No analyses were available.

The steel expert suggested that the actual manufacturers of ferro-silicon should store it in the open for sufficient time to allow the fumes to evaporate.

Firm F.

The firm formerly used low-grade or blast-furnace alloy, but have discontinued doing so for some time. The 30 per cent. and 50 per cent. grades of electrically-produced ferro-silicon were subsequently used.

The use of 50 per cent grade has, however, been discontinued for some time past, because of its liability to disintegrate, and of the consequent waste resulting from its use in the granular state.

About 10 tons of 30 per cent. ferro-silicon are used per annum. The casks containing it come by rail, and are stored in a large open shed. The 30 per cent. grade does not disintegrate, whereas under similar conditions the 50 per cent. material almost invariably did so. Quite recently the firm has received two bags of 30 per cent. ferro-silicon, each bag weighing 2 cwt., from Glasgow. No case of illness of any kind among workmen is known to have occurred.

The following are actual analyses, with dates, of two lots of ferro-silicon :—

Ferro-silicon.	50 per cent.	30 per cent.	Ferro-silicon.	50 per cent.	30 per cent.
Si	53·78	30·40	Al	3·41	×
Fe	42·00	67·10	S	×	0·022
Mn	Nil.	1·08	Ca	0·60	0·54
P	0·056	0·033	C	0·054	0·190
Date of purchase ...	28/11/04	10/10/07			

" × " Constituent not estimated.

Firm G.

About 5 cwts. per annum of 50 per cent. ferro-silicon are used. The alloy comes in small wooden boxes. It is stored in an open shed, and no deleterious effects are known to have been incurred in connection with its use.

Firm H.

No high-grade ferro-silicon is used at these works, only blast-furnace silicon "pig" in three grades—4 per cent., 6 per cent., and 15 per cent. About 2,500 tons per annum are used, the average amount in stock being 250 tons.

Also some ferro-manganese is used, and this is said to smell as badly as any sample of ferro-silicon.

It was strongly represented that most serious injury to the industry would result if the importation of ferro-silicon were arrested for any cause.

Firm I.

Large quantities of 4 to 15 per cent. blast-furnace ferro-silicon "pig" are used.

Of the high-grade electrically-produced ferro-silicon 25 per cent., 50 per cent., 75 per cent., and 90 per cent. grades are, or have been, used.

The amount used during 1908, which may be taken as an annual average, was about 34 tons of 75 per cent. grade and small quantities of 25 per cent., 50 per cent., and 90 per cent. grades.

The alloys are stored in the casks or boxes of transit in a large, well-ventilated shed. Some seven or eight years ago, some alloys were received in plain iron drums, soldered up air-tight, each drum containing $2\frac{1}{2}$ cwt. No trouble was experienced with the drums or danger from the contents.

The alloys come by rail to the nearest railway depot, whence they are carted on drays to the storage sheds. It was confidently asserted that if 50 per cent. ferro-silicon be kept exposed to the air for some time, not more than a year, it will crumble to a granular condition, whereas neither the 40 per cent. nor the 60 per cent. grade will disintegrate.* In fact, when the glass case in which the steel expert to the firm keeps specimens of all alloys purchased, was examined, the space for the 50 per cent. alloy was found to be empty, because the ferro-silicon had disintegrated and been removed.

The following are the actual analyses of ferro-silicon used, with the dates of analysis :—

Ferro-silicon.	90 per cent.	78 per cent.	75 per cent.	50 per cent.
Si	92·85	75·	78·8	49·48
Mn	2·19	0·09	2	0·04
Al	0·087	×	×	×
Fe	3·17	×	×	×
C	×	0·20	0·50	0·33
S	×	×	×	0·05
		traces of Ca	traces of Ca	
P	×	×	×	0·028
Dates of Analyses ...	31/1/08	10/3/03	30/5/01	5/4/06

" × " denotes no analysis made for these constituents.

One case of illness presumably resulting from the use of high-grade ferro-silicon was discovered. George Henry E——, aged 38 years, a charge-wheeler and charge-man of a cupola, made the following statement :—Early in October, 1907, when using a lot of ferro-silicon, about 12 cwts. a day, of 50 per cent. and 75 per cent. grades, he began to feel ill after a few days, and eventually had to give up working. The ferro-silicon had been coated with paraffin wax to prevent exposure to air or moisture, and he was melting off the wax by placing pans of the alloy on hot ingot-moulds, and towards evening was overcome. He went home and

* Apparently also disintegration may occur with samples of alloy containing from 30 to 35 per cent. of silicon, but it does not necessarily follow that any considerable quantity of poisonous gas will be freed in consequence.

was attended by a medical man. He was ill for three weeks, during which time he had an attack of severe vomiting. Before stopping work he had suffered much from headache, his eyesight would occasionally grow dim, and he felt very weak. He thought at the time that it was the illuminating gas in his home which was affecting his eyesight. He was absent from work six weeks and two days in all. Most of the other men dealing with the alloys felt slight indisposition at the time, but none were compelled to give up work. He admitted that his illness *might* have been due to the smell and fumes from the burning wax, but he thought if so it would not have been so serious.

The firm's representative, however, was disposed to scout the idea that E——'s illness was due to ferro-silicon fumes.*

On looking into the issue sheets of the firm to determine what particular alloys were used by E—— about the time his illness had commenced, it was found that only 73 per cent. and 75 per cent. alloys had been used during the fortnight before and after the 4th October, 1907, the date on which he left work. They were: Two lots of 73 per cent., 8 tons 5 cwts., at £31 18s. 6d., and one lot of 75 per cent., 3 tons 12 cwts., at £32 17s. 6d. The latter was first used on 4th October. Both firms who supplied the material were communicated with, and complaints made against "coating" the alloy. Since that time no paraffined material has been used.

Firm J.

Blast-furnace ferro-silicon "pig" of 10 per cent. content is mostly used to the extent of about 400 tons per annum.

About 25 to 30 tons of 50 per cent. electrically-produced ferro-silicon are used annually, together with, occasionally, small quantities of the 25 per cent. grade. The alloy comes in casks from Hull or Grimsby (never any from west coast ports) by rail. It is stored in the open under cover of a high roof, a large sheet of tarpaulin being thrown over the casks in order to keep off wet and moisture. Up to about five years ago the alloy came in galvanised iron drums with the lids soldered on. No deformation of drums due to gases given off was observed, but the storekeeper, who weighs out the alloys, stated that occasionally, when the end of a cask was broken and the contents were being transferred to a sound cask, "bad smells" were given off, which caused an acid taste in his mouth. He noticed that when the 50 per cent. material had been standing for some time the top layer fell into powder on opening the drum.

About ten tons of ferro-silicon are in stock at present, but the average amount is 5 to 6 tons. The last consignment came in square boxes holding about 2 cwt. each. The casks previously received varied in size from 2 cwts. to 10 cwts. capacity.

No paraffined alloy has been used. The firm suggest that thick steel drums hermetically sealed would obviate all danger in

* The heating process necessary in order to get rid of the paraffin would be likely to cause considerable evolution of phosphoretted hydrogen gas.

transit. The following analyses of three different samples were stated to be fairly typical:—

Ferro-silicon.	50 per cent.		25 per cent.
Si	53·9	49 3	24·2
Fe	44·8	45·0	72·0
P	0·035	×	0·097
S	0·010	×	0·02
Mn	0·6	×	0·5

"×" No analysis for these constituents.

Firm K.

The only grades and amounts of ferro-silicon used by this firm are:—

13-15 per cent. English blast-furnace pig; 300 tons per annum; and

50 per cent. foreign, electrically produced, in casks; 30 tons per annum.

All high-grade material comes, and always has come, by rail to the railway depôts, whence it is drawn in drays. The casks—each of about 5 or 6 cwt. capacity—are stored in a large alloy store, the wide door of which is generally open. From 6 to 12 casks are usually kept in stock. The first lot the firm used came in hermetically-sealed drums, but none since then. No paraffined material has been received. Both Bessemer and Siemens' foremen manipulate the alloy from cask to furnace. No illness or mishap of any kind connected with the use of 50 per cent. material has ever occurred. The following are actual analyses, with dates, of 50 per cent. ferro-silicon purchased by the firm:—

——	11/8/08.	29/2/08.	20/2/08.	10/3/05.	10/3/05.
Si	49·5	50·6	50·4	49·0	50·3
S	0·02	0·05	0·03	0·01	0·01
P	0·02	0·04	0·035	0·06	0·06
Ca	1·10	×	×	0·30	0·05
Mn	0·72	×	0·360	0·35	0·10

The analysis of 29th February, 1908, refers to 4 casks from which 12 samples were taken—three from each cask.

The analysis of 20th February, 1908, is from 3 barrels—two pieces being taken from each barrel.

Those of 10th March, 1905, are representative of 2 casks and 6 casks, respectively, from an 8-cask consignment.

The steel expert to the firm suggested that the manufacture of 50 per cent. ferro-silicon could well be dispensed with, because the same result could be easily effected in steel-making by taking aliquot parts of 40 per cent. and 60 per cent. alloy, both of which he believes to be innocuous; not that he considers that the 50 per cent. grade is dangerous; he suggests that this is disproved by his experience of its use.

Firm L.

This firm use 50 per cent. electrically-produced ferro-silicon exclusively, although about 4 years ago a sample order of 25 per cent. was tried. About 10 tons per annum are consumed. The material comes by rail, usually from Hull or Manchester, in casks of 8 cwts. each. It is stored in open sheds, not specially covered over, the casks standing on iron plates. Analyses, for silicon only, are regularly made by the dry fusion method. No paraffined material has been received, nor any in drums.

The alloy is added to the acid Bessemer-converter by itself at the end of the " blow " by being dropped in from a shoot over its mouth. In the acid open-hearth, the lumps of alloy are added to the bath with the charge, the powder being put in the ladle, thus none is wasted. In the basic open-hearth, it is invariably added in the ladle.

About 1 ton of ferro-chrome of 60 per cent. content is used annually. The main uses of this alloy are in the manufacture of armour-plates, high-speed nickel-chrome steels, and crucible steels.

Firm M.

The amount of ferro-silicon used by this firm during the five years 1904-1908 has been—

of 10 per cent " pig," 805 tons;

of 25 per cent. to 58 per cent., 45 tons;

from which an annual average may be fairly estimated. Of the 45 tons of high-grade ferro-silicon, only about 2 tons of 50 per cent. have been used, the remainder having all consisted of 25 per cent. to 30 per cent. alloy. The 25 per cent. material has been found to be perfectly stable, and no case of illness has resulted from its use. All came in casks by rail, the ports of landing not being ascertainable. No paraffined material has been dealt with, and none has come in drums.

The firm's representative produced a copy of " Engineering " for December 25th, 1908, containing an article on the dangers of ferro-silicon, and incorporating a report to the Home Office by Mr. D. R. Wilson. He expressed the opinion that the agents for high-grade ferro-silicon are not consistent in calculating the prices of the alloy based on the rate per unit per cent. of silicon per ton in the manner usually adopted, which is as follows:—A ton of 10 per cent. pig at £4 contains approximately 1 ton of best hematite pig, costing (say) £3 10s., so that the real price per unit of silicon is $\frac{£(4-3\frac{1}{2})}{10}$ or 1s. per unit, whereas the agents calculate it as $\frac{£4}{10}$ = 8s. per unit. Similarly, for 50 per cent. alloy at £20 per ton, the price per unit is properly calculated as $\frac{£(30-3\frac{1}{2})}{50}$ = $6\frac{3}{5}$s. per unit, whereas the agents calculate it as $\frac{£20}{50}$ = also 8s. per unit, thus justifying by uniformity the high prices for electrically-made alloys. Hence a given amount of silicon can be added to steel from pig alloy at practically one-eighth of the cost of using electrical high-grade alloy; but in this statement obviously no account is taken of the great impurities of pig ferro-silicon, the chilling produced by it, and consequent extra cost of fuel, &c.

As calcium silicide has been reported to be a strongly smelling alloy, this firm's representative was asked about it. He stated that the usual composition was Ca 25 to 30; Si 65 to 70; Al 2½; Fe 2½; C traces (?); that calcium carbide was formed; that pure silicide can be heated up and will cool down without any chemical or physical change; that it will not desulphurise steel in the furnace.

About 2 or 3 tons of 60 per cent. ferro-chrome have been used by this firm in the course of the last 5 years, but no ill-effects have been noticed. Its cost is about £22 per ton. It is made either in the crucible or in the blast-furnace.

Firm N.

Only about 10 cwts. per annum of 50 per cent. electrically-produced ferro-silicon are used, some in crucible and some in Siemens' steel furnaces. As soon as the reports of the Grimsby fatalities came to the notice of the firm, the casks were put in an airy place and kept uncovered. A large amount of 10 per cent. "pig" ferro-silicon is also used.

Firm O.

A few cwts. per annum of electrical ferro-silicon are used, the grade of which is unknown. It is kept in a wooden receptacle in an ordinary room; no ill-effects from manipulation have occurred.

Of ferro-chrome (60 per cent. chromium content) about 1 ton per annum is used. This is broken up by workmen in the open, and carried in pans to the crucible melting-house. No indisposition has been caused or any smell noticed. It is of the high carbon quality (*i.e.*, 7 to 9 per cent.), and is stored in 2-cwt. wooden boxes.

Firm P.

This firm desired that all the information supplied by them should be considered as confidential.

Firm Q.

About 8 to 10 tons per annum of 50 per cent. ferro-silicon are used. The firm generally buy in 1 or 2-ton lots from or through local agents, by whom the alloy is delivered at their works in casks or boxes. None has come in drums or bags, and no paraffined material has been used. Up to December, 1908, about a ton or so of 50 per cent. alloy was continually kept in a reserve store in a cellar where metal patterns were frequently made. This cellar was lighted by gas, the use of which is necessary even in daytime. The two patternmakers complained of headaches, but no definite indication as to the cause of their indisposition was obtainable. One of the men who was most troubled in this way has not had headaches so often since the change to an airy room in which the pattern-making work is now carried on. The men have not had occasion actually to go on the sick list. The following are works analyses of the so-called 50 per cent. ferro-silicon :—

Si	51·589	50·294	53·00
Mn	0·25	0·13	0·11
P	0·002	trace	0·0292
S	0·338	0·246	0·023

The alloy is analysed by the wet method.

Firm R.

About 5 tons per annum of 50 per cent. ferro-silicon are used. The material formerly (*i.e.*, up to about 5 years ago) came in drums, hermetically sealed, but since then has been received in 8-cwt. casks. Since the Grimsby fatalities supplies have come through the Manchester Docks at increased expense per rail in open trucks. It is stored on the firm's premises, in a fairly open shed. Occasionally a "strongish smell" is said to have been noticed from the 50 per cent. grade, but no case of illness or mishap from its use has come to the knowledge of the firm. No analyses for the discovery of possible impurities have been made, but recently instructions were given to the laboratory to investigate the subject. No points of special importance were elicited from the workmen.

Firm S.

A small amount of 60 per cent. electrically-produced ferro-silicon is used by this firm. It is stored in the boxes in which it comes from local agents in an open shed. No case of illness has been known.

Of ferro-chrome about 1 ton is used annually, the chromium content being 50 per cent. to 60 per cent. This alloy is stored in casks in the same shed as the ferro-silicon. Nothing in the way of indisposition among workmen has occurred. No analyses of the ferro-silicon employed were available.

Firm T.

The following list gives the amounts and grades of ferro-silicon used by this firm during the past 6 years :—

1903. 40 tons of 25 per cent. grade.
1904. 10 tons of 50 per cent. grade.
1905. 40 tons of 50 per cent. grade.
1906. 43 tons of 50 per cent. grade.
1907. 20 tons of 50 per cent. grade.
1908. 15 tons of 50 per cent. grade.

That is, 40 tons of 25 per cent. and 128 tons of 50 per cent. ferro-silicon in 6 years. During this time the price per ton of the higher grade has fallen from £19 in 1904 to £12 10s. at the end of 1908. The greater part of the material comes by canal from Goole. Some of the ferro-silicon on board the boat at Tinsley, on which an old man and child were poisoned in November, 1908, was consigned to this firm. Up to the time of the Liverpool explosion in 1904 the material was stored in a shed, but since then it has lain in the casks uncovered in the open, exposed to all weathers. About the same time the practice of sending the alloy in drums was discontinued. No case of illness or mishap to employees has resulted from the use of ferro-silicon. The average amount in stock is from 3 to 5 tons. It has been noted that the 50 per cent. alloy is the one most liable to disintegrate, and that it gives off an acetylene-like smell when freshly broken. The material has occasionally been tested for Si and C., but no analyses were available.

The opinion of those in authority is that the material could be quite safely carried as upper-deck cargo in casks.

The expert stated that in July, 1908, when at La Praz, near Modane, he met a deputation from the Swedish Government, who had arrived there for the purpose of a conference with Dr. Heroult at the works of the Société Electro-Metallurgique Francaise.

One of the agents, visited by Mr. Bennett in Sheffield, claims to have been the pioneer in introducing ferro-silicon into the Sheffield district for use in steel manufacture. At present only 25 per cent. and 50 per cent. grades of the electrically-produced alloy are dealt in. No mishap or complaints have been known during his long experience in respect of any material supplied by him. About 10 tons of 50 per cent. alloy are usually kept in stock, stored in casks in a cellar underneath his shop and the adjacent footpath. The following is an actual analysis of the present stock, most of which has been lying in the cellar since August, 1908:—

Si.	C.	Fe.	Mn.	Ca.	Mg.	Cu & Ti.	Al.	S.	P.
50·16	0·02	47·7	0·19	0·17	0·12	traces.	0·49	0·004	0·037

The firm's chemist has noticed that 50 per cent. ferro-silicon, when low in calcium and carbon, has seemed less " smelly." However, there was no evidence to show that calcium carbide existed in combination in the alloy. It was stated that presence of calcium carbide might be due to residue of that substance in furnaces previously used for the manufacture of this substance. Formerly large percentages of Ca and C. were found in ferro-silicon, as instanced by reference to Brearley and Ibbotson's "Analysis of Steel Works Materials," 1902 edition, page 125; but modern improvements in manufacture of ferro-silicon have reduced very largely the quantities of these substances (note the analysis above). He said, " Keep the impurities low, and there will be no complaints, in addition the steel-makers will be delighted." Mr. Bennett visited the store and found it to be a large clean cellar, about 24 feet by 20 feet, and 7 feet 6 inches high, extending from under the footpath under and behind the shop. The principal ventilation was from perforated gratings under the shop-windows and abutting on the footpath. All the cases were, and had been, open for some time, for which reason it was, perhaps, no smell was at all noticeable. The material was in large lumps, and none had disintegrated in the least. To Mr. Bennett it appeared quite different from any other 50 per cent. material he had seen, being so much more solid and stable and not at all porous. But the reason for this difference was not apparent. The head of the firm gave it as his opinion that transport of ferro-silicon by sea on upper or open deck, in casks covered with tarpaulin, would be perfectly safe.

INVESTIGATIONS IN FRANCE.

CONFERENCES IN PARIS; AND VISITS TO PLACES OF MANUFACTURE.

In order to obtain as full information as possible as to the methods of manufacture, storage, and transport of high-grade electrically-produced ferro-silicon, permission was obtained from the Treasury for me to visit certain of the manufactories in the south-eastern district of France, from whence is exported the greater quantity of this material made use of in this country. Having learnt that a number of these manufacturing firms were represented, for commercial purposes, by the Comptoir International de Vente du Ferro-Silicium, of 80, Rue St. Lazare, Paris, formal application was made by the Board to this organisation, as well as to certain individual manufacturers who were found not to be represented by it, requesting that I should be afforded all necessary facilities in the prosecution of my investigation, including, of course, permission to visit and inspect the works where ferro-silicon is actually produced. From Mons. A de Riva-Berni, the director, and from the secretary of the Comptoir International de Vente du Ferro-Silicium, I received every assistance, and on informing them of the proposed lines of my investigation they were kind enough to draw up an itinerary covering all the necessary ground, and at the same time to make arrangements with the various firms represented by them for my visits on the dates and at the times suggested.

The director informed me that their organisation was a commercial one merely, and that they had not, therefore, concerned themselves with the scientific aspects of the manufacture of ferro-silicon or of the other alloys produced by the amalgamated firms, so that he was unable to afford me information of this sort as regards the various works that are now, or have been, included in their syndicate, which he stated had originally been formed early in 1903.

The Comptoir International, I learnt, was a development of the Compagnie Générale Electro-Chimie de Bozel, which firm has manufactured ferro-silicon and supplied it in France, and especially to America, since 1898, although, in the first instance, the amount produced was comparatively small. In England the syndicate is represented (as has been the case from the date of its formation) by the British Griffin Chilled Iron and Steel Company, Limited.

At the present time the syndicate comprises the following firms producing ferro-silicon:—

(1.) Carbidwerk Deutsch-Matrei A. G., with works at Matrei, Meran, and Jajce.
(2.) Usines Electrochimiques de Hafslund, at Hafslund, near Sarpsborg (Norway).
(3.) La Société Electro-chimique du Giffre at St. Jeoire (Hauté-Savoie).
(4.) Société La Volta, at St. Marcel (Savoie).
(5.) Compagnie Générale d'Electro-Chimie de Bozel, at Bozel (Savoie).

There are six other works in the syndicate which, however, do not manufacture ferro-silicon at the present time.

Ferro-silicon is also produced by a number of other firms outside the syndicate, of which the more important are as follows:—

Établissements Keller-Leleux, with works at Livet (Isère).
Société Française Electrométallurgique at Froges (Isère).
Société Universelle d'Acétylène, at Lacroix.
Société Anonyme Métallurgique, Procédés Paul Girod, à Ugine (Savoie).
Société Métallurgique, Procédés Paul Girod, works at Montbovon and at Courtepin, Switzerland.
Kanderwerke, at Hageneck (Switzerland).
Società Italiana di Electrochimica, at Rome.
The Kellner-Partington Paper Pulp Co., Ltd., at Bonegaard, near Sarpsborg (Norway).
The Heroult Works, at Kartfors (Sweden).

M. de Riva-Berni informed me that during the last few years considerable difficulty had been experienced, as regards the carriage of ferro-silicon, with the different transport and shipping companies, owing to the various accidents which have occurred from time to time. Thus not only have the rates for transport increased, especially during the last six months, but much delay is involved in the more circuitous routes which in certain instances have had to be adopted. Thus whereas formerly the syndicate's products were conveyed to New York from Antwerp by the Red Star Line—a voyage of 10 or 11 days only—it is now necessary to consign from Trieste, from whence to New York occupies from 15 to 16 days, this alteration having been rendered necessary by the fact that, about three years ago, the Red Star Line terminated their contract with the syndicate, owing to the fact that as their vessels carry passengers they were anxious to avoid unnecessary risk. Consignments for England have been conveyed by Messrs. Harrison Bros. from Tréport to Liverpool and Manchester; from Antwerp to Middlesbrough by a local line, of which Messrs. Harris and Company, of Middlesbrough, are agents; and by Messrs. Wilson, of Hull, by which latter firm the last consignment consisting of 76 cases of ferro-silicon was accepted on April 14th, 1908, to be carried "upon deck at proprietor's risk." Messrs. Wilson have since refused to convey ferro-silicon under any circumstances, but as regards Messrs. Harrison Bros. further difficulty has been avoided by the issue to them on the 27th January last of a certificate of guarantee on the responsibility of the syndicate.

As regards the percentage grades of ferro-silicon produced by the syndicate firms, I was informed by the directors that 50 per cent. and 70 per cent. are those of which the greatest amount are manufactured. A special grade of 90 per cent. which has been found suitable for the working parts of dynamos is manufactured, especially for use in Germany, but the manufacture of grades between 30 and 40 per cent. has now been discontinued.

Mr. de Riva-Berni was unable to give me any information as to the relative value, from the manufacturing point of view, of the 50 per cent. and 70 per cent. grades respectively, and was unaware of any publication dealing with this point. But whether or not because of the greater ease of calculating the necessary quantities with the 50 per cent. material, since the introduction of electrically-produced ferro-silicon it has been this particular percentage which has most frequently been demanded, although during the past two years a 75 per cent. grade has been sold in Russia and America, to the almost entire exclusion of the 50 per cent. previously exported to those countries.

In regard to prices, a serious drop (from 500 francs for 50 per cent. grade, free at English ports, to an average of 275 francs at present) has come about since 1907.

WORKS OF LA COMPAGNIE GÉNÉRALE D'ELECTRO-CHIMIE DE BOZEL.

This company, whose works, situated at a distance of about 16 kilometres from St. Marcel, were established about 8 years ago, was apparently one, at any rate, of the pioneers in the manufacture of ferro-alloys in the electric furnace, and was, moreover, the parent of the commercial syndicate, the Comptoir International du Ferro-Silicium, having headquarters in Paris, to which reference has been made in the previous section.

All the produce of the Bozel works is sold through this syndicate, for the most part to the U.S.A., none, as I was informed by M. Juen, the Director, so far as he was aware, being marketed in England.

M. Juen further informed me that there had never been an explosion due to ferro-silicon at the works, although the material is sometimes stored here for as long a period as a year.

Every lot of ferro-silicon manufactured is stated to be analysed more or less completely, except in the case of the 25 per cent. grade, which is analysed as regards its phosphorus content only; but no analyses of the gaseous products contained in, or given off from, ferro-silicon of various percentages has ever been attempted at these works. In connection with this point, however, the company's chief chemist informed me that, in his experience, " the 25 per cent. grade sometimes smells worse than that containing 50 per cent. of silicon."

Constituents of the Charge.

The materials employed at the Bozel works are as follows: —

Quartz (or rather quartzite) obtained locally, at a distance of about 3 kilometres from the works. An average analysis shows 95 per cent. silicon, 4 per cent. aluminum, with small amounts of calcium and phosphorus, the latter averaging from 0·3 to 0·8 per cent.

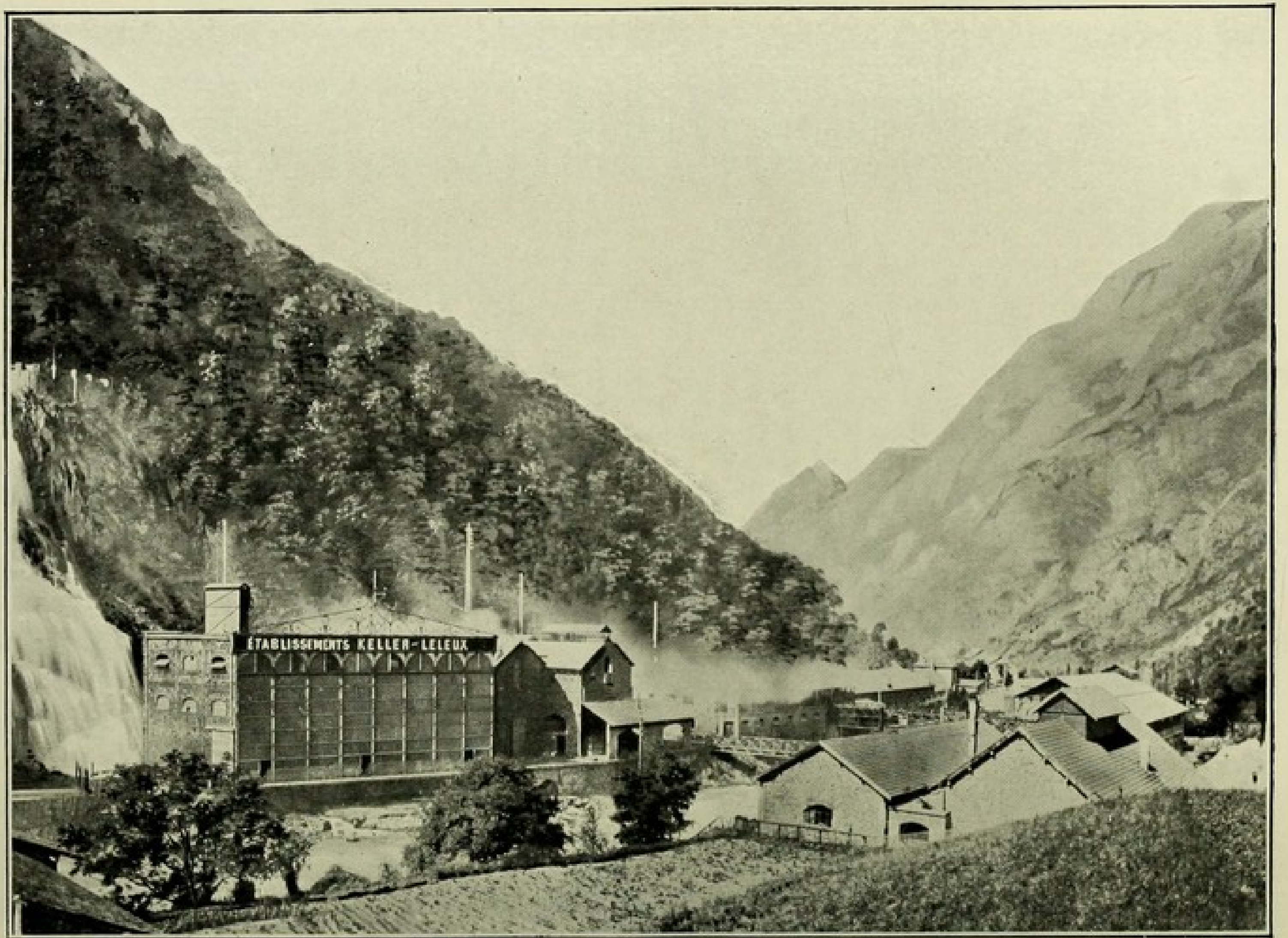
Steel turnings, containing not more than 0·3 per cent. of phosphorus.

Anthracite coal, which is obtained locally and is cheap, but which yields as high a quantity as 20 per cent. of ash.

The grades of ferro-silicon produced at the Bozel works represent percentages of silicon of 25, 50, and 80, respectively. In the manufacture of the 80 per cent. grade, however, charcoal, although much more expensive, is employed instead of anthracite coal, on account of its greater freedom from impurities.

The materials for the charge are not fused together previously to being fed into the furnaces, but are simply mixed in the required proportions on the floor of the shed in which the furnaces are situated. These latter, which are constructed of fire-brick and circular in form, are of the resistance type, with one vertical electrode suspended over the mouth of the furnace, the other, of large size and square in section, forming practically a portion of the floor. By means of a movable crane, which can be operated by a workman, the vertical electrode can be raised or lowered to any required point. The electrodes, which are manufactured on the works, are stated to require renewal about every two days, this statement, however, not applying to the electrodes buried in the bottom of the furnace. The furnaces themselves may run continuously for a year or even more, the charge being replenished as often as room is afforded by the melting of the portions previously added. The molten alloy is removed from the bottom of the furnace by tapping at intervals of ¾ hour.

Nothing apparently is known as to the average temperature attained in the furnaces, no means for estimating or regulating it being available. The total horse-power employed averages about 3,000, being somewhat higher in summer, but the works never cease running altogether, even in the depth of winter. Electrical power is derived from six turbine dynamos (Sneider) which supply current, of which the average voltage is 45 (the governing instrument was I found registering 40 at the time of my visit) with an ampèrage of 10,500 to 15,500. While at the works I witnessed a tapping of ferro-silicon of 50 per cent. grade, the molten alloy being run from a spout in the side of the furnace at its lowermost point into a shallow bed of sand. The mass, as soon as it had cooled sufficiently, was broken up with hammers into small pieces, which were then packed into a large wire tray and lowered into a bath of oil, a method of treatment invariably



General View of the Keller-Leleux Works at Livet (Isère). (*From photograph.*)

(*To face p.* 45.)

adopted at these works in connection with the production of ferro-silicon of this particular percentage. In reply to my request, M. Juen most kindly undertook to send me samples of the various grades of ferro-silicon manufactured at the Bozel works. These were duly received shortly after my return from France, and were at once sent on to Dr. Hake for chemical examination.

KELLER-LELEUX WORKS AT LIVET (ISÈRE).

This company have offices at 3, Rue Vignon, Paris. Calling at this address I met both the partners, of whom M. Leleux is in charge of the commercial and M. Keller of the practical and scientific section of the business. From them I learnt that a Commission had recently been appointed by the Comité des Forges de France, of which M. Leleux was a member, and that in consequence, without consultation with the Chairman of the Commission they did not feel justified in affording me information on the particular points which had been under consideration, prior to the publication of the Commission's report. M. Leleux, however, accompanied me to the offices of the Commission (63, Boulevard Haussmann), where I had an interview with M. Pinet, the Secretary, who informed me that the report of the Commission would be published within the next few days, when a copy would immediately be forwarded to me. Subsequently MM. Leleux and Keller kindly made arrangements for me to visit their works at Livet, where M. Keller promised to meet me at the date agreed upon. A photograph of these works is given opposite.

The works of this company are situated at Livet (Isère), where a total power of 15,000 h.p. is furnished from a fall of water, 60 metres in height, from which turbine dynamos are driven, 25,000 litres of water a minute passing through the turbines. The average voltage and ampèrage at which the furnaces are run average 40 and 15,000, respectively.

The hydro-electric equipment at Livet includes three types of machines:—

(*a.*) Low tension, five groups of monophase generators of 1,200 h.p. (Neyret turbines and Thury alternators).

(*b.*) High tension, three groups of three-phase machines of 2,700 h.p. (Bouvier turbines, Brown-Boveri alternators).

(*c.*) Direct current, four generators of 150 h.p. to supply the motors and accessories of the works.

The low-tension current is led directly to the Keller furnaces, which are of the resistance type. The furnaces, which are of a double form, have each a capacity of 1,200 h.p., and make a melt of ferro-alloy of 500 kilos. every two hours. The high-tension current supplies, by means of transformers, three furnaces, of a total capacity of 1,500 kilowatts, which furnish a daily output of 12 melts each of 1·2 tons.

Actual working results have demonstrated that the energy required for the production of 1 ton 30 per cent. ferro-silicon in the electric furnace is 3,500 kilowatt hours, and at the Livet works it has been found practicable, with an expenditure of 4,000 h.p. to turn out 20 tons 30 per cent. ferro-silicon per day, whilst alloys with as high a silicon content as 70 per cent. to 80 per cent. have been manufactured. The furnaces employed at the Livet works are of a particular form, invented and patented by M. Keller, by whose courtesy I am enabled to append an outline diagram showing their special method of construction.

M. Keller stated that ferro-silicon was first produced by his firm in 1900, at which date a good price was obtainable for the product. At the present time, however, practically no profit is obtainable on its manufacture owing to the fact that prices have fallen, in consequence, as he said, of the action of certain makers. These, in order to undercut their competitors, have been placing on the market a product made from cheap materials, which, although it can be sold at a low price, is likely to be possessed of specially dangerous qualities. Indeed, the market has now for various reasons become so depressed that, as M. Keller informed me, the firm are thinking of discontinuing the manufacture of ferro-silicon altogether.

MM. Keller-Leleux have always preferred making a 48 per cent. grade of ferro-silicon rather than a 50 per cent. one, for the reason that they found the latter liable to disintegration on storage; but commercial pressure demanding the 50 per cent. grade, for what special reason, however, was not at all obvious, compelled them to manufacture and supply it for a time. But since they have had knowledge of accidents that have happened during the transport and storage of this particular grade, they have determined to supply, as formerly, a grade of somewhat lower percentage instead.

Constituents of the Charge.

The materials employed in the Livet works in the manufacture of ferro-silicon are as follows:—

(1.) *Iron and steel shavings.*
(2.) *Quartzite,* containing 94-96 per cent. silica.
(3.) *Anthracite coal.*

I was informed that iron and steel shavings, although more expensive, are exclusively used by this firm rather than "Tournures de fonte," generally employed by other manufacturers, for the reason that they contain much less phosphorus—a maximum of 0·10 as against an average phosphorus content of 0·50 to 0·80 for iron turnings. As evidence of the care taken as to quality of the material used by this firm in the manufacture of ferro-silicon, M. Keller gave me a copy of a guarantee obtained in connection with the purchase by his firm of a consignment of iron and steel turnings, which is to the following effect:—

Ces tournures sont garanties exemptes de toutes matières étrangères au fer et à l'acier (cuivre, fonte, graisse, chiffon) elles ne contiendront pas de buissons ni frisons, c'est-à-dire qu'elles pourront être d'échargées à la pelle ; elles ne seront pas oxydées.

Si les tournures livrées n'ont pas comme provenances des usines travaillant des fers ou aciers de mauvaise qualité, elles ne doivent pas contenir plus de 0·10 de phosphore. Au delà de cette teneur, nos produits sont refusés par nos clients (il en est de même pour tous ceux qui fabriquent les mêmes produits que nous). Nous nous réservons, lorsque nous constaterons que les wagons que vous nous expédiez sont de mauvaise qualité chimique, c'est-à-dire contiennent plus de 0·10 de phosphore, de vous faire suspendre les expéditions non en cours de route.

The *quartzite* employed is obtained from quarries in the Loire district and also from the neighbourhood of Modane.

The *anthracite*, which yields on an average 7 per cent. of ash, is obtained from the Mines des Grandes Rausses, situated in the mountains above the snow level and at a distance of about 15 kilometres from the works. These mines are worked by "La Compagnie des Mines d'Anthracite et de Talc du Dauphine," a recent contract with whom for the supply of 12,000 tons of coal to the Keller-Leleux works was shown to me by M. Keller. Prior to the completion of this contract analysis of a sample of the coal for arsenic, phosphorus, and sulphur, carried out in the laboratory of M. Campredon of St. Nazaire (Loire Inferieur) indicated the entire absence of As., while the amount of P. and S. was given as 0·013 and 0·41 per cent., respectively.

Of the eight *furnaces* formerly used only four were running at the time of my visit. The working is continuous and according to M. Keller can be carried on for 3-4 years without intermission. The electrodes, however, although water-cooled, require replenishing in from 15-20 days. They are manufactured in a special department of the works, but the particular processes employed are regarded as trade secrets.

The mixture of steel turnings, quartzite, and coal, made up in the required proportions, is shovelled into the mouth of the furnace around the electrodes, further amounts being added from time to time as the previous portion of the charge sinks owing to the gradual fusion of the underlying mass. As the result of the reduction of the mixture of steel and silica under the intense heat of the electric furnace, ferro-silicon is formed, which, in the molten condition gradually sinks to the bottom of the furnace, whence it is drawn off every two hours through lateral openings. From these exits, spouts convey it to a bed of sand on which it gradually solidifies to a metallic cake-like mass. Whilst still liquid, however, in order to remove any slag, the surface of the molten ferro-silicon is skimmed with a piece of "green" wood (with the bark still on) fixed like the head of a rake to the end of an iron rod. So soon as the mass has cooled sufficiently it is broken up into small pieces and packed for transport into wooden barrels.

The great care exercised by this firm in the selection of the iron and steel turnings employed by them in the manufacture of ferro-silicon is due to the fact that M. Keller is of opinion that iron is the constituent which is mainly responsible for the introduction of impurities. He further holds that the degree of purity attainable in the case of ferro-silicon manufactured in the electric furnace is governed by the percentage of silicon present; in other words, the larger the silicon content the greater the purity of the alloy; the reason being that, owing to the higher temperatures necessary for the production of alloys with a large silicon content, any impurities present tend either to become volatilized or to be eliminated by secondary reactions.

While at Livet I requested M. Keller to be so good as to send me for examination samples of the various grades of ferro-silicon manufactured by his firm, together with specimens of the raw materials employed. These samples have since been received, together with the appended explanatory letter:—

Usine de Livet,
(Isère),
le 17 mai, 1909.

MONSIEUR,

J'AI l'honneur de vous adresser par colis postal international 7 flacons contenant respectivement :

No. 1—Quartz employé pour la fabrication du ferro silicium aux usines de Livet.

No. 2—Tournures de fer & acier fabrication du ferro silicium aux usines de Livet.

No. 3—Charbon (anthracite) fabrication du ferro silicium aux usines de Livet.

No. 4—Ferro silicium 25–28 par cent. Si. fabriqué aux usines de Livet.

No. 5—Ferro silicium 52–54 „ „ „ „ pour les usines qui exigent 50 par cent. minimum Si comme livraison.

No. 6— „ „ „ „ „ „

No. 7—Ferro silicium 75–80 par cent. Si. fabriqué aux usines de Livet.

No. 8— „ „ 45–47 „ „ „ „

Notres ferro-siliciums 25–28 par cent. Si contiennent actuellement 0·10 par cent. de phosphore environ & 0·05 par cent. de souffre :

Ceux à 52–54 par cent. contiennent environ 0·05 Ph. & 0·3 S.

Ceux à 75–80 par cent. sont encore plus purs.

Les contrats d'achat de matières premières que je vous ai montrés à Livet établissent le soin que nous prenons pour le choix de nos matières premières pour lequel nous sommes absolument intransigeants. Nous employons uniquement des tournures de fer et d'acier à l'exclusion rigoureuse des tournures de fonte qui sont toujours phosphoreuses et qui doivent être proscrites. Nous pensons aussi qu'on doit proscrire énergiquement l'emploi des scories des fours métallurgiques (silicates de fer artificiels), qui contiennent toujours beaucoup de phosphore, ainsi qu'un certain nombre d'autres impuretés, ce qui est d'ailleurs très naturel, puisque ce sont les scories d'épuration de la fabrication des fers aciers et cuivre. L'emploi de ces scories peut, pour certaines usines, apporter une grande économie dans la fabrication, mais elle détermine presque à coup sûr une fabrication de ferro silicium très dangereuse ; c'est là notre avis personnel.

Je vous ferai envoyer par un prochain courrier les photographies des usines de Livet que je vous ai promises.

Veuillez agréer, Monsieur, l'assurance de mes sentiments les plus distingués.

KELLER.

Monsieur le Docteur Copeman,
Local Government Board,
Whitehall, S.W.,
Londres.

The samples referred to in this letter were at once handed to Dr. Wilson Hake for examination and report in due course.

GIFFRE WORKS, ST. JEOIRE, HAUTE-SAVOIE (SOCIÉTÉ ELECTRO-CHIMIQUE DU GIFFRE).

These works are situated at Pont du Giffre at the confluence of two streams, the Giffre and the Risse; the motive power for the works being derived from a waterfall 70 metres high, and at a distance of about a mile.

At these works, which were originally founded for the manufacture of carbide of calcium alone, ferro-alloys of all kinds are now made, except those of iron and aluminium. Of ferro-silicon an average of 1,000 tons per annum are manufactured, the amount varying more or less from year to year, according to the demand. This alloy has been manufactured at the Giffre works for the past seven years, during the first five of which the company sold their output themselves. Since then, however, all their sales have been carried out through the Paris syndicate (Comptoir International).

At the time of my visit two furnaces were in use for the production of ferro-silicon, but I was informed that during the following week, in order to meet a special demand from the syndicate, three furnaces would be running.

Electric power for these and other furnaces is produced by ten groups of turbine dynamos, each being capable of developing an average of about 1,000 h.p.

Water power is supplied to the turbines from an artificial canal through a couple of immense iron tubes, each 1·8 metres in diameter, which run parallel to one another for a distance of 280 meters, as shown in the photograph appended. The water brought to the works in this manner, after passing through the turbines, is returned to the river at a point just below the works.

The electric furnaces used for the production of ferro-silicon are of the resistance type, but differ, however, somewhat in appearance from those in use in other works, mainly for the reason that they are completely encased in iron plates bolted together around the outside of the furnace. Another point of difference from the general type consists in the provision of two tap-holes, one of which is opened every hour. Thanks to the courtesy of Mons. Barut, who supplied the original, a photograph of one of the furnaces in use at the Giffre works is reproduced. The temperature attained in these furnaces is stated to rise to 2,000° C. during the stage of reduction, although it is probably much lower during the preliminary fusing of the charge. The voltage and ampèrage of the electric current employed range from 60 to 65, and from 12,000 to 14,000 respectively, and the furnaces, the capacity of each of which is about 1,500 kilos., may run for the period of a year without intermission.

Of the electrodes, the upper one (kathode) is suspended over the furnace in such a manner that its position can be altered by hand as may be necessary. It is built up of a group of four carbon blocks in one, and usually lasts from eight to ten days. The lower electrode (anode) is formed by ramming into an opening of the floor of the furnace retort graphite which has been powdered, mixed with coal-tar, and heated.

The ferro-silicon produced at the Giffre works up to the time of their joining the syndicate was for the most part of 66 per cent. of silicon content, but the 50 per cent. grade is that which is now generally made, for the reason that this is the particular grade which the syndicate find to be in special demand.

The constituents of the furnace charge consist of (1) quartz-rock, (2) anthracite, and (3) steel turnings, of which the quartz-rock contains about 96 per cent. of silica. The anthracite, of good quality from the point of view of small phosphorous content, is obtained locally.

M. Barut, the administrator of the Giffre works, most kindly afforded me the fullest information as to the chemistry of the manufacture of ferro-silicon and as to the precise manner of making up the charge necessary for its production in the electric furnace, the details concerning which are given in the section of this report dealing with the manufacture of ferro-silicon.

The molten material, after being run from the furnace into a bed of sand, while still fluid is skimmed to get rid of slag. As soon as the material has solidified it is broken up, and if of the 50 per cent. grade is dipped while still hot into a cauldron of melted pure paraffin for several minutes. Notwithstanding this precaution, it is found that the 50 per cent. alloy occasionally disintegrates. M. Barut was unable to suggest any reason as to why certain samples should disintegrate while with others this is not the case.

No accident has occurred so far as is known in connection with the transport and storage of the product of the Giffre works. But M. Barut informed me that the workmen engaged in packing ferro-silicon, especially of the 30 per cent. and 60 per cent. grades, are apt to suffer somewhat severely from headache and general malaise. In view of the difficulties which have recently arisen in connection with the transport of ferro-silicon owing to fatal accidents which have been caused in certain instances by poisonous gases given off by this product, the Société Electro-Chimique du Giffre, in the belief that their product is perfectly innocuous, have adopted the system of supplying with each consignment a certificate to this effect based on the results of an ordinary chemical analysis of the sample. A copy of such a certificate is appended. In no instance, however, has investigation been made as to gases given off from any particular sample of ferro-silicon for the reason, as I was informed, that clients have never asked for information on this point.

Société Electro-Chimique du Giffre,
St. Jeoire, le 27/1/09.

Certificat.

Nous certifions, par la présente, que l'envoi de ferro-silicium de l'ordre No. 2099/G. 44 qui a quitté notre Usine le 26 Janvier courant, à destination du Tréport Maritime, lequel se compose de 89 caisses bois marquées D.B.C. et numérotées de 1 à 89, pesant brut 10·265 kil., est absolument sans danger et inexplosible. Ce produit, fabriqué dans notre Usine, a une tenur de 51·74 par cent. de silicium ; d'après la moyenne des analyses ci-dessous indiquée, une décomposition spontanée du produit avec dégagement de chaleur ou phénomènes explosifs, paraissent être complètement écartés ; il peut donc, sans inconvénient, être logé à bord.

Analyse Moyenne.

Silicium	50·97	par cent.
Fer	46·72	,,
Carbone	0·29	,,
Calcium	0·78	,,
Soufre	0·021	,,
Aluminium	1·02	,,
Phosphore	0·05	,,
Total	99·851	,,

Signé : le Chimiste de la Sté. Electro-Chimique du Giffre.

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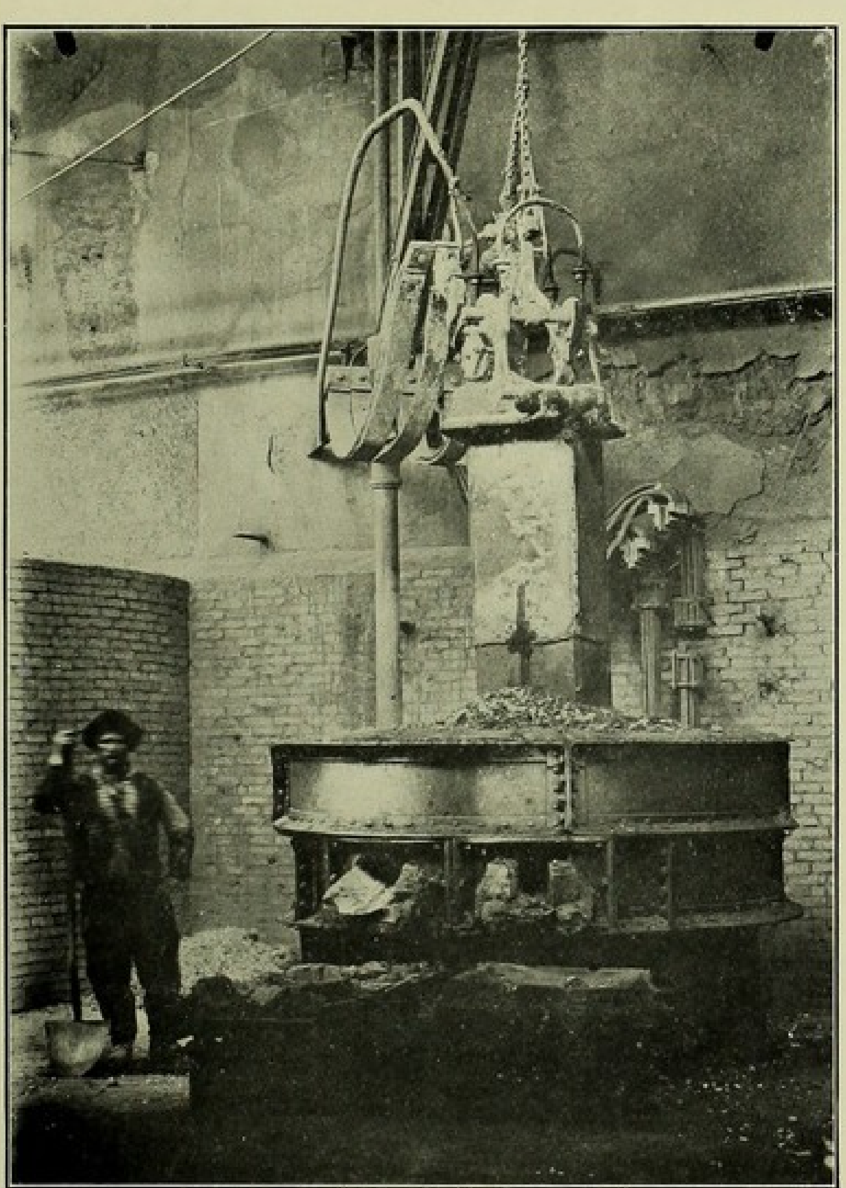
Fig. 2.



Photograph of one of the ferro-silicon furnaces (type of Resistance furnace) installed at the Giffre Works, St. Jeoire.

Showing the methods adopted for suspension and water-cooling of upper electrode; the flexible copper-band conductors for conveyance of the electric current; the manner of feeding the furnace; the "tapping" holes from which the molten ferro-silicon is run off; and the receptacles in which the alloy is cooled. (For full description, *see* text.)

(*To face p.* 50.)

SOCIÉTÉ ANONYME ELECTROMETALLURGIQUE (PROCÉDÉS PAUL GIROD), UGINE, SAVOIE.

This company owns three factories, of which two, the Courtepin Works and the Montbovon Works, are both situated in the Canton of Fribourg, Switzerland. The principal factory, however, and the only one visited by me is at Ugine, Savoie, where water-power is obtainable from the River Arly. The waterfall at present utilized is stated to have a drop of 125 metres, and to generate a force of 8,000 h.p. The water is conveyed from the barrage through a tunnel of three kilometres, and on through two steel conduit pipes each of 1·32 metres diameter, and 550 metres in length. Further sources of electrical energy have recently been obtained, and at the time of my visit to Ugine, I found extensive building operations in progress which will result in provision being made for utilization of the extra power now available, and so for considerable increase in the output of these works.

It has been well said by Dr. R. S. Hutton, in a paper dealing with the subject, that the French Alps offer many surprises to those unfamiliar with the remarkable hydro-electrical installations in this part of the European continent; among which, as regards the beauty of surroundings and evidence afforded of extensive and successful development, the works at Ugine are probably unsurpassed. Situated as they are at the foot of snow-clad mountains, in a peaceful valley, almost luxuriant in its vegetation, the contrast with the more usual surroundings of works connected with the iron and steel industry is very marked.

The power-house, 120 metres long and 10 metres broad, contains nine 600-h.p. and nine 300-h.p. Neyret-Brenier turbines, driving six 600-h.p. and nine 300-h.p. continuous-current machines, and three 600-h.p. alternators. The total horse-power devoted to the production of ferro-silicon varies from about 3,500 h.p. in winter to 4,500 h.p. in the summer months. The furnace-house runs parallel with that in which the turbines and dynamos are installed, and is equipped with a large number of furnaces of "resistance" type, provided with automatic regulation, efficient ventilation, and all necessary equipments for successful and continuous working.

These furnaces are supplied with electric power at a voltage and ampèrage of 50-60 and 8,000-10,000 respectively. The electrodes of graphite are manufactured at the works, but I did not see the process.

Constituents of the Charge.

(1.) *Quartzite* containing about 92 per cent. of pure silica, with traces only of phosphorus and sulphur.

(2.) *Coal* (forging) obtained from St. Etienne—of best quality, and guaranteed not to average more than 8 per cent. of ash, or more than ·005 per cent. of phosphorus or sulphur.

(3.) *Steel and Iron Scraps.*

A mixture of these constituents in the necessary proportions is "fed" to the furnaces almost continuously; while the molten alloy is run off through "tapping holes" at the base of the furnace at frequent intervals. When solidified, the resulting "cakes" of ferro-silicon are broken up into small pieces before being packed for transport.

M. Paul Girod was, I found, absolutely convinced as to the perfectly innocuous character of the ferro-silicon manufactured by his firm, as evidence of which he cited the small percentage of phosphorus as shown in certain analyses and the total absence of accidents in connection with its transport and storage. The greater portion of the output, he said, has always been an alloy of a grade just below 50 per cent. of silicon—usually about 47 or 48 per cent.—although occasionally higher grades, up to 70 or 80 per cent. are manufactured for special purposes.

M. Girod also explained to me, at length, the findings of the Paris Ferro-silicon Commission (*vide* p. 57 *et seq.*), of which he was a member, and which had recently concluded its labours, although at the date of my visit to Ugine its report had not been actually issued. In the work of this Commission M. Girod had evidently been much interested, somewhat naturally perhaps, seeing that his firm is one of the largest manufacturers of ferro-silicon in France, at any rate, and he it was who had supplied samples of his alloy which, at the instance of the Commission, were examined and reported on by Mr. Watson Gray, of Liverpool. For a copy of Mr. Gray's report, and for samples of ferro-silicon subsequently forwarded to me from Ugine, I desire to express my thanks to M. Girod.

The Ugine works, I found, are equipped with excellent laboratories, but chemical examination of the separate batches of ferro-silicon is confined, almost exclusively, to the percentages of silicon present, this being of primary commercial importance, since it is the amount of this constituent which regulates the price. In a few instances the laboratory records showed that the amount of phosphorus and sulphur in the alloy had also been determined, but in no instance as M. Girod himself informed me, has research been there directed to estimation of the gases evolved from samples of ferro-silicon, for the reason, as he added, that customers have not asked for information on this point.

Of the total output of ferro-silicon manufactured at the Ugine and Courtepin works, amounting to about ten tons per day, comparatively little has hitherto reached this country, by far the greater quantity being consigned to Germany, Austria, and America.

I append analysis by Mr. Watson Gray, dated June 8th, 1907, representing the average composition of a series of samples of ferro-silicon received from the Société Anonyme Electrometallurgique; and also a certificate issued at the commencement of the present year (1909) in which Mr. Gray gives expression to his personal opinion as to the safety, in transport, of the ferro-alloys manufactured by this firm.

(COPY.)

Chemical Laboratory,
8, Inner Temple, Dale Street,
Liverpool.
June 8th, 1907.

I hereby certify that I have examined the undermentioned sample of Ferro-silicon, No. 160, and that I find the following results :—

Sample marked : Moyonne de 183016 Kos. des échantillons 31, 32, 40, 46, 47, 51, 54, 56, 57, 58, 60, 61, 62, 66, 68, 71, 72, 74, 75 et 77.

Silicon	47·10	per cent.
Iron	49·05	„
Manganese	0.27	„
Aluminium	2·73	„
Calcium	Nil.	
Magnesium	Nil.	
Carbon	0·04	„
Sulphur	0·010	„
Phosphorus	0·028	„
Copper	Nil.	
Chromium	Nil.	
Oxygen, loss, etc.	0·772	„
	100·000	

G. WATSON GRAY.

Mr. le Directeur de la S. A. E.
procédés Paul Girod.

(COPY.)

Chemical Laboratory,
8 Inner Temple, Dale Street,
Liverpool.
January 18th, 1909.

To whom it may concern.

DEAR SIRS,

Ferro-silicon and other Ferro-alloys.

I HEREBY certify that I have regularly sampled and analysed the Ferro-silicon, Ferro-chrome, Ferro-tungsten, Ferro-molybdenum and Silico-manganese made by the S. A. E. Procédés Paul Girod, since their first introduction as commercial articles and have never known any to explode, take fire or generate Arseniuretted or Phosphuretted Hydrogen or other poisonous gases, although I have repeatedly examined them for such. As a matter of fact I have had samples of this make of Ferro-silicon lying exposed to all the various changes of the atmospheric conditions of my laboratory for a number of years and have not noticed anything take place that would render the carriage of them in ships objectionable.

I am quite of the opinion that the Ferro-alloys made by the S. A. E. Procédés Paul Girod are quite safe to carry in steamships.

I am, Gentleman,
Yours faithfully,
G. WATSON GRAY, F.I.C.,
Member of the Society of
Public Analysts.

SOCIÉTÉ D'INDUSTRIE, ÉLECTRO-CHIMIQUES "LA VOLTA," ST. MARCEL, SAVOIE.

During the summer months, at any rate, these works produce more power (12,000 h.p.) than is required for their own purposes, and consequently the Company leases about half their available electrical energy to the municipality of Lyons, who utilize it for providing motive power for their tramway-system. As this is required all the year round, whereas the source of water on which the Volta Company depends (a waterfall 75 metres in height) is more or less frost-bound in winter, metallurgical operations are then necessarily discontinued, in whole or in part. This condition of affairs, however, the Company will presently be in a position to obviate in large measure, as they now possess another waterfall, at present not "harnessed," from which 3,000 h.p. can be developed.

The President of the Volta Company, M. Coutagne, was unable to meet me, but in his absence, his deputy M. Cousçanza afforded me all possible help and information.

This gentleman informed me that the Company was a constituent member of the Paris Commercial Syndicate, the Comptoir International de Vente du Ferro-silicium, through whom all sales are negotiated. He had, however, no knowledge as to certain samples of ferro-silicon, purporting to be the product of the La Volta Works, which I had received through the Comptoir International. I, therefore, requested that further samples should be sent me for examination, comprising the various percentage grades manufactured by the Company. In response to this request I received, shortly after my return from France, nine samples of grades ranging from 20 per cent. to 72 per cent. in respect of their silicon content. These were at once handed over to Dr. Hake, who has duly recorded, elsewhere in this report, the results of his chemical examination.

From M. Cousçanza I learnt that the La Volta Company rarely produced ferro-silicon of a higher grade than 50 per cent., and this only in the summer season, from May 1st onwards. Samples of every lot manufactured are examined in the works laboratory; and special care is taken in the selection of the materials from which the 50 per cent. grade is produced for the reason that it is recognized that this particular grade is potentially dangerous. In future, however, consequent on the recommendation of a Commission instituted by the Chambre Syndicate des Forces Hydrauliques of Paris (to which further reference will be made later), it is probable that the manufacture of this particular grade will be discontinued

The electric furnaces at the La Volta Works are of the usual resistance type, but differ in shape from those generally employed, in that they are square externally instead of circular. They are cased with iron plates. Internally their capacity is about 1,500 kilogrammes.

The lower electrode (anode) is buried in the hearth of the furnace while the upper (kathode) is suspended above in such manner that its position over the mouth of the furnace can be regulated. The kathodal electrodes have an average "life" of five days.

The necessary electrical energy, supplied to the furnaces at a pressure of 125 volts, is produced by a series of nine turbine-dynamos, actuated by water-power.

Constituents of the Charge.

(1.) *Quartzite* obtained in the neighbourhood of the works. This, as I was informed, contains an average of 98 per cent. of silica, together with traces of magnesia, but no lime.

(2.) *Gas-coke*, if for production of the 50 per cent. grade of ferro-silicon. In the manufacture of 25 per cent. alloy or other comparatively low grades this is replaced by anthracite coal, which is cheaper, but not so free from impurities.

(3.) *Iron-ore* (50 per cent. ferro-silicon) or *Steel Shavings* (lower grades).

The iron-ore is stated to contain 85 per cent. of iron oxide (Fe_2O_3), but no trace of aluminium, manganese, or calcium.

The furnaces are "tapped" and the molten alloy run off at regular intervals of two hours. This does not subsequently undergo treatment with oil or paraffin.

BRITISH COALITE COMPANY, LIMITED.

Experimental Station, Wednesfield, Staffordshire.

Having been informed, at an early stage of my investigation, that the British Coalite Company had laid down plant for the manufacture of ferro-silicon, at their Wednesfield works, I communicated with the Company, who promptly and readily afforded me every possible facility through their Works Manager, Mr. C. H. Parker, for inspecting the operations being conducted under his superintendence.

On arrival at Wednesfield I found as I had been given to understand, that the production there of high-grade ferro-silicon in the electric furnace was only in the experimental stage, none of the output having been sold, up to that time, although I was informed that enquiries as to whether it could be supplied commercially had been received from several different manufacturers.

From Mr. Parker and the Chemist to the Works, I learnt that their experiments had been directed to the production of ferro-silicon of a 50 per cent. silicon content, and that a series of seven recent analyses of samples of the alloy had shown a range of from 44·76 per cent. to 50·5 per cent. of silicon.

Constituents of the Charge.

Great care had evidently been exercised in obtaining the necessary materials in as pure a form as possible, consistent with trade considerations as regards prime cost, and cost of carriage to the works.

(1.) *Natural Sandstone Rock.*

(2.) *Pitch, with addition of* 10 *per cent. Anthracite Coal.*

(3.) *Iron Oxide.*

The *Sandstone Rock* utilized as the source of silica is of a greyish colour, owing to the fact that it is impregnated with about 8·5 per cent. of bitumen; in addition to which it contains small quantities of other volatile constituents, including traces of nitrogenous matter. On being heated, it yields a whitish grey, extremely friable material, small pieces of which can be readily broken down in the fingers to a fine powder, which consists of pure silica to the extent of 99 per cent.

The *Pitch* is obtained as a by-product in the manufacture of coalite. This is used with addition of 10 per cent. of its weight of anthracite coal. Mr. Parker said that he would prefer to employ pitch-coke, but that this from the electrical point of view would form too good a conductor.

The *Iron Oxide* consists of Fe_2O_3 precipitated in the form of a fine powder, which owing to its purplish colour is useless as a paint, and so is obtainable at a much less price than the red oxide. The average of several analyses indicates the presence of 95·4 per cent. of pure iron oxide.

In making up the charge certain proportions of silica and iron oxide, depending on the proportion of silicon required in the ultimate product are mixed with the anthracite coal; and the whole bound together into a mass with pitch.

After mixing, the volatile hydro-carbons in the pitch are driven off by heating, as the result of which the charge is left in a compact mass, which is broken up into small lumps of a suitable size for use in the furnace.

No flux is employed.

I was informed that the object of using pitch is the double one of ensuring that the carbon should be intimately mixed with the iron-oxide and silica, and of making the whole mass a conductor of the high resistance.

The experimental furnace, which is of the resistance type, is built of brick-work lined with moulded composition of similar nature to the charge. The furnace is of cylindrical form, the alloy being tapped from the bottom. Of the electrodes formed of carbon showing about 96 per cent. graphite, one is suspended over the top of the furnace, while the other passes through the side of the furnace, on the floor of which it lies. The upper electrode is water-cooled. The horse-power taken in each of the experimental furnaces varies from 250 to 300 h.p.

The furnaces, while running, are worked continuously.

From the Wednesfield Works of the British Coalite Company I have received, since the date of my visit, a number of samples of the ferro-silicon produced there, which have been handed over to Dr. Wilson Hake for chemical examination. None of these proved to be free from phosphoretted hydrogen, although some were better in this respect than others.

As bearing on the effect exerted by variations in the working of the furnace on the chemical composition of the final product especially as regards the amount of phosphoretted hydrogen obtained, reference may be made to the records kindly supplied to me by the Company of two experiments carried out with separate portions of the *same* lot of charging material. This, in one instance yielded an alloy of an average silicon content of

47 per cent., and in the second instance, 51 per cent.; of which the former sample yielded, as may be seen on reference to Dr. Hake's report (Table I., p. 86), considerably more phosphoretted hydrogen than the latter.

Comparative Data of Experiments.

	47 per cent.	51 per cent.
Charging, same	—	—
Engine, different	—	—
Furnace, same	—	—
Volts, average	higher	—
Amperes, average	—	higher
K.W. hours	—	higher
Metal made	higher	—
K.W. per lb.	—	higher
Phosphoretted hydrogen	higher	—

I have recently learnt that experimental work has been discontinued, for the time being, for the reason that the coalite gas has not proved suitable for use in the gas-engines, from which dynamos, supplying the necessary electrical power, were run.

REPORT OF THE FERRO-SILICON COMMISSION OF THE CHAMBRE SYNDICALE DES FORCES HYDRAULIQUES ET DE L'ELECTROCHIMIE, ETC., OF PARIS.

In the " Iron and Coal Trades Review " for March 3rd, 1909, appeared a statement to the effect that the fatalities on board the s.s. " Ashton " had come under consideration at the last meeting of the Chambre Syndicale des Forces Hydrauliques et de l'Electrochimie, in Paris, and that a Commission had been appointed by that body to report upon the subject of the dangers connected with the transport and storage of ferro-silicon, and the best means of obviating them.

I have already referred to the fact that, while in Paris, I learnt of the existence of this Commission, and of the further facts that their labours had then practically ended, and that their Report would probably be issued within a few days. On interviewing the secretary he promised to supply me with a copy of the Report on my return to Paris from the South of France.

The Commission, consisting of four members only, was constituted as follows:—MM. Coutagne (President), Barut, Girod, and Keller—these gentlemen representing four of the chief firms engaged in the manufacture of ferro-silicon in France.

I was unable to learn whether the Commission had received any formal evidence from chemical or metallurgical experts in the course of their deliberations, or whether the Report, a copy of which was handed to me just previous to my return to England, merely reflected the opinions derived from practical experience of the members of the Commission.

When visiting, however, the works of M. Girod at Ugine, he gave me to understand that Mr. Watson Gray, consulting metallurgical chemist, of Liverpool, who, among the firms visited, is evidently regarded as the chief authority on the scientific study of the various ferro-alloys produced in the electric furnace, had been engaged to carry out a special investigation of the composition and properties of samples of ferro-silicon manufactured in the Ugine and other works under the control of M. Girod, with special reference to the nature and amount of the poisonous gases likely to be evolved under various conditions.

Thanks to the courtesy of M. Girod, and by his instructions, I have received copy of Mr. Watson Gray's report, and have since had the opportunity of conferring with the latter gentleman on the subject, and of obtaining from him details, not originally included in his report, as to the chemical methods employed by him. This report is stated to have been made to M. Girod as a member of the Ferro-Silicon Commission of the Chambre Syndicale des Forces Hydrauliques, etc., but it deals only with examination of the products of the Girod works, and it is not clear as to whether the work was authorised by the Commission as such,* especially as certain suggestions made by Mr. Watson Gray in his report are not even referred to in that of the Commission.

The results of Mr. Watson Gray's work are criticised by Dr. Wilson Hake in the special section of the present report dealing with research work on the chemistry of ferro-silicon (p. 72).

The Report of the Ferro-Silicon Commission (to which a translation into English is subjoined) is as follows:—

Chambre Syndicale des Forces Hydrauliques de l'Électrométallurgie, de l'Électrochimie et des industries qui s'y rattachent.

Paris, 63, Boulevard Haussmann,
le 5 Mai, 1909.

RAPPORT.

La Commission désignée par la Chambre Syndicale des Forces Hydrauliques, de l'Electrométallurgie, de Electrochimie et des Industries qui s'y rattachent, pour l'étude des mesures à prendre en présence des accidents causés par certains ferro-siliciums fabriqués au four électrique, Commission composée de MM. Coutagne, Président, Barut, Girod et Keller a formulé l'avis suivant :

Les ferro-siliciums fabriqués au four électrique présentent des teneurs en silicium variables au gré du fabricant. Pour certaines teneurs le ferro-silicium présente un état physique instable, en ce qu'il se désagrège peu à peu au bout de quelques jours ou de quelques semaines : il "tombe en poussière" suivant l'expression consacrée par l'usage. Cette instabilité est d'autant plus grande que le produit renferme plus d'impuretés. L'humidité accélère cette désagrégation.

En même temps que les morceaux de ferro-silicium perdent leur compacité et se fragmentent, ils laissent dégager de petites quantités de gaz très délétères, par exemple de l'hydrogène phosphoré si le ferro-silicium renferme comme impureté du phosphore. Quelques décigrammes de phosphore en plus ou en moins par kilogramme de ferro-silicium semblent avoir une influence très importante à cet égard. Quelques litres de ces gaz délétères, si le local où ils se dégagent n'est pas aéré, suffisent pour causer la mort des personnes qui y restent trop longtemps exposées.

On a cherché à remédier à ces graves inconvénients soit en employant des matières premières très pures, soit en trempant les morceaux de ferro-silicium dans de la paraffine, du pétrole ou d'autres substances analogues qui empêchent ou retardent la pénétration de l'humidité. Mais le premier de ces moyens est

* It should however be stated that in a letter from M. Paul Girod dated 3rd July, 1909, the following statement occurs :—" The 'Commission du Ferro-Silicium' has submitted a full set of samples to Mr. Watson Gray, and I am asking the President of this Commission to send you the report of this chemist."

mis en défaut par l'introduction accidentelle de quelques impuretés dans les matières premières, et le second ne fait que dissimuler et retarder les risques.

Nous proposons, en conséquence, de renoncer complétement à la fabrication des *teneurs critiques*, lesquelles, actuellement bien connues, sont de 30 à 40 par cent. et de 47 à 65 par cent.

En s'écartant notablement de ces teneurs critiques et en évitant de fabriquer des ferro-siliciums ayant de 30 à 40 par cent. et de 47 à 65 par cent., on n'aurait plus que des ferro-siliciums parfaitement compacts, aussi peu dangereux à transporter et à emmagasiner que des morceaux de fonte ordinaire.

En résumé :

1° Les Compagnies de Chemins de fer et de Navigation et tous les entrepositaires de ferro-silicium ne seront plus exposés à aucun danger, s'ils exigent dorénavant des certificats par lesquels les fabricants déclareraient que leurs ferro-siliciums ne sont pas compris entre 30 et 40 par cent. de silicium, ni entre 47 et 65 par cent. de silicium.

2° Les consommateurs de ferro-siliciums auraient tout intérêt, en vue d'avoir un produit non majoré de frais de transport ou d'entrepôt exagérés, d'adopter exclusivement les types commerciaux suivants :

1° en-dessous de 30 par cent.
2° 40 à 47 par cent.
3° au-dessus de 65 par cent.

et de renoncer complètement à demander les teneurs comprises d'une part entre 30 et 40 par cent. et d'autre part entre 47 et 65 par cent.

Ont adhéré aux déclarations ci-dessus, les fabricants de ferro-siliciums ci-après :

Sté Electrométallurgique (Procédés Paul Girod).
Sté Electrochimique du Giffre.
Sté des Etablissements Keller-Leleux.
Sté d'Industrie Electrochimique "La Volta,"
etc., etc.
(l'ordre alphabétique serait adopté).

Translation.

The Commission appointed by the Chambre Syndicale des Forces Hydrauliques, etc., etc., for the study of measures to be taken in view of accidents caused by certain grades of ferro-silicon made in the electric furnace, composed of MM. Coutagne, President, Barut, Girod and Keller, has formulated the following opinion :—

Ferro-silicon manufactured in the electric furnace presents variations of silicon content according to the will of the manufacturer.

In certain grades ferro-silicon exhibits an unstable physical state, in that it disintegrates little by little at the end of several days or several weeks—it "falls in powder" according to the expression consecrated by use. This instability is greater in proportion as the product contains more impurities. Damp hastens this disintegration. At the same time as pieces of ferro-silicon break down and fall into fragments, they evolve small quantities of very poisonous gas, for instance, phosphoretted hydrogen, if the ferro-silicon contains phosphorus as an impurity. Some decigrammes of phosphorus more or less per kilogramme of ferro-silicon appear to have a very important influence in this respect. Several litres of this poisonous gas, if the place where it is evolved is not ventilated, is sufficient to cause the death of persons remaining too long exposed to it.

Attempts have been made to remedy these grave inconveniencies either by employing very pure ingredients in the first place, or else by soaking the pieces of ferro-silicon in paraffin, in petroleum or other analogous materials which prevent or retard the absorption of moisture. But the first of these methods is rendered useless by the accidental introduction of impurities in the primary materials, and the second does nothing but disguise and retard the risks.

In consequence, we, therefore, propose to give up making dangerous grades completely, which now are known to be those ranging from 30 to 40 per cent., and from 47 to 65 per cent.

By discarding these specially dangerous grades and ceasing the manufacture of 30 to 40 per cent. and 47 to 65 per cent. ferro-silicon, there would remain nothing but perfectly compact alloys as free from danger to transport and to warehouse as ordinary pieces of cast-iron.

SUMMARY.

1st. Railway and Steamship Companies and dealers in ferro-silicon will be exposed to no danger if they demand henceforth certificates in which the makers declare that their ferro-silicon does not comprise the grades between 30 and 40 per cent., nor between 47 to 65 per cent. of silicon.

2nd. It will be to the interest of dealers in ferro-silicon in order to avoid a product overwhelmed by the expense of transport or exaggerated warehouse charges, to adopt exclusively the following commercial grades :

1st, under 30 per cent.
2nd, 40 to 47 „
3rd, upwards of 65 per cent. (above 65 per cent.),

and to completely give up ordering grades comprising on the one hand between 30 and 40 per cent., and on the other between 47 and 65 per cent.

The following manufacturers of ferro-silicon agree to observe the terms of the declaration as set out above.

(The complete list of firms is now as follows :—)

Acétylène (Compagnie Universelle d').
Allevard (Société des Hauts-Fourneaux et Forges d').
Bertolus (Mme. Vve.).
Bozel (Compagnie Générale d'Electro-chimie de).
Carbures Métalliques (Société des).
Electrométallurgique Française (Société).
Giffre (Société Electrochimique du).
P. Girod (Société Electrométallurgique, Procédés)
Keller-Leleux (Société des Etablissements).
La Volta (Société d'Industrie Electro-chimique).
Rochette Frères (MM.).
Saint-Béron (Société Electrométallurgique de).

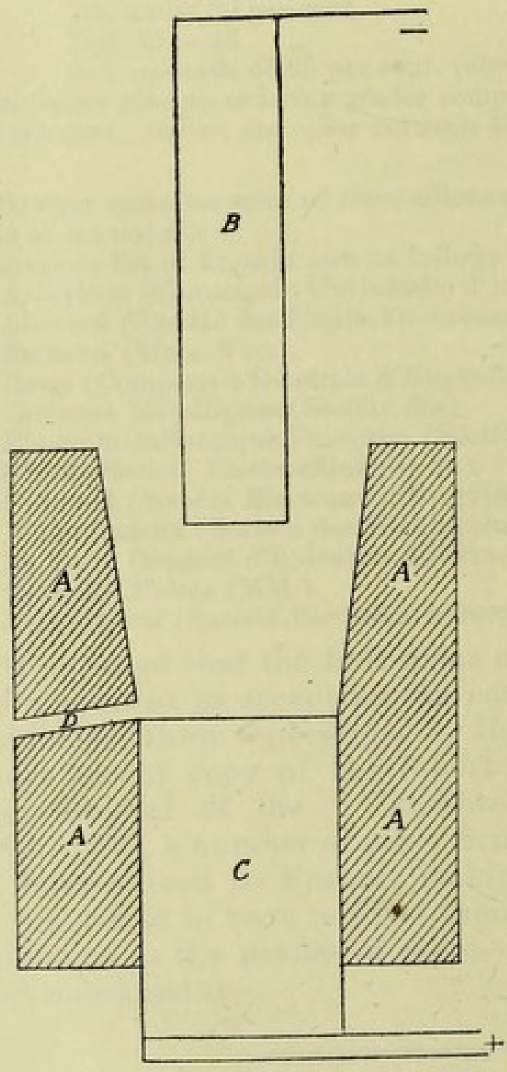
It will be noted that the four firms mentioned at the end of the original document as accepting the conclusions arrived at by the Commission are those represented by the four Commissioners. But in a more recent copy of the report transmitted to me by the Secretary-General of the "Chambre Syndicale," under date, June 18th, 1909, a number of other firms engaged in the manufacture of ferro-silicon in France, making twelve in all (as shown above), are stated to have notified their approval of the suggested restrictions as to the grades of ferro-silicon that, for the future, they will manufacture.

MANUFACTURE OF FERRO-SILICON.

Brief reference has already been made, in the introduction to this report, to the methods and materials employed in the production, on a commercial scale, of high-grade ferro-silicon in the electric furnace.

But, in view of the information obtained as the result of visits to the chief centres for the manufacture of this and other ferro-alloys in the South of France, and, in this country, to the experimental plant being operated at Wednesfield by the British Coalite Company, it is desirable here to present a more detailed account of the actual practice of manufacture.

Fig. 3.



A. Walls of furnace.
B. Upper electrode (kathode).
C. Lower electrode (anode), forming hearth of furnace.
D. Tapping channel.

Outline diagram, drawn to scale, of usual form of Electric Resistance Furnace employed in the manufacture of ferro-silicon.

(Scale 1 inch to 1 metre $= \frac{1}{39.370}$)

(*To face p.* 61.)

This is specially needed in view of the fact that at each of the works visited by me during the course of my official inspections I observed certain variations either in the materials utilized or in the actual manufacturing processes employed, which may be supposed to exert some influence on the nature and characteristics of the final product, the more so as recent research seems to indicate that ferro-silicon (of certain percentage grades, at any rate) cannot be regarded as a definite chemical compound.

The Electric Furnace.

According to M. Keller, to whom I am indebted for much interesting and useful information on the subject, four distinct types of electric furnace may be distinguished :—

1. Electric arc furnaces.
2. Electric resistance furnaces.
3. Electric surface resistance furnaces.
4. Electric induction furnaces.

Of these, the second type is the only one employed for the production of ferro-silicon, and other ferro-alloys such as ferro-chrome; but the general form and method of construction varies somewhat in different installations, as does also the shape, size, method of manufacture, and arrangement of the electrodes.

In an electric furnace of the resistance type the electrodes are immersed in the material in process of fusion, which latter constitutes a resistance conductor between the electrodes and the hearth. The temperature attained in a furnace of this type and of a given capacity is in proportion to the section of the electrodes. As a consequence, the distribution of the calorific action can take place over extensive surfaces, and as regards the regulation of the temperature, this depends solely upon the regulation of the power converted. The electric resistance furnace is therefore specially suited for reduction processes, since the control of temperature during working is a simple matter, and the molten metal or alloy can always be readily run off from the lower part of the furnace.

The working of a resistance furnace in its simplest form may be compared to that of a blast-furnace. The region of contact of the lower part of the electrode with the mass intervening between two poles of the furnace is the hottest zone, and may be compared to the tuyère zone of the blast-furnace. As the metal is reduced it percolates in thin streams through the mass in process of fusion and collects in the lower part of the furnace which forms the crucible, where it remains hot. This portion of the furnace is maintained at a high temperature by the electric current which traverses it and by the calorific conduction, the loss by radiation being inappreciable. The whole of the portion situated between the electrode and the hearth may be regarded as the zone of fusion. The portion of the furnace rising above the lower end of the electrode represents the boshes of a blast-furnace and should be constructed upon the same principles.*

* The Application of the Electrical Furnace in Metallurgy.—Albert Keller, Journ. Iron and Steel Institute, 1903.

In the blast-furnace it has been found that, when working very hot, a ferro-silicon containing 10 to 12 per cent., or even 15 per cent. of silicon can be produced. The electric furnace, however, even when working at comparatively moderate temperatures is capable of producing without difficulty alloys vastly richer in silicon than those yielded by any blast-furnace; and it is only since the use of the electric furnace has become developed on a commercial scale that ferro-silicon containing from 25 per cent. up to even as high an amount as 95 per cent. of silicon has been produced in quantity.

The furnaces which I saw in operation at the different works visited were, for the most part, of very similar character and size, the main differences being in the external shape—usually circular (as are all internally), but in one or two instances square in section—in the size and shape of the upper electrode (kathode), and in the mechanical means adopted for raising and lowering and usually for water-cooling this electrode. The furnaces at the Bozel works are provided with two " tapping " holes, from which the molten ferro-silicon is run alternately, whereas in the case of the furnaces at other works, one vent only is provided.

The furnaces are built up of fire-brick, sometimes lined with a composition of graphite somewhat similar to that employed in the manufacture of the electrodes, and the exterior of the furnace is usually braced with iron " stays " or completely enclosed in a circular or square iron casing made up of sections bolted together.

Except in the case of the furnace specially designed by M. Keller, of which an outline illustration is given (*see* opposite), the second electrode (anode) is placed beneath the floor of the furnace, its upper surface being flush with the level of the furnace hearth. At the Giffre works, for instance, this lower electrode is formed *in situ* by ramming into an open space in the floor of the furnace a mixture formed by heating together powdered retort graphite and coal tar.

The power employed in each furnace ranges from 250 or 300 h.p. to as much, in some cases, as 750 or 800 h.p.

In the type of furnace used in the Keller-Leleux works the mode of electric distribution is such as to obviate the use of the furnace hearth as a conductor. According to the inventor, M. Keller, this result is effected by using, both for the supply and return of the current, vertical electrodes which are independently adjustable. Further to ensure the continuity of working, several electrodes are placed in parallel in the system, any one of which is renewable without the necessity of stopping or varying the working of the furnace as a whole. M. Keller's furnace, constructed on these principles, contains at least two groups of two electrodes each, the two latter being arranged in parallel, and the two groups themselves in series. These four electrodes of equal capacity project through refractory walls, and each electrode is provided with independent mechanism by which it can be raised or lowered at will. The intensity is equalised in each focus of the same group by means of readings

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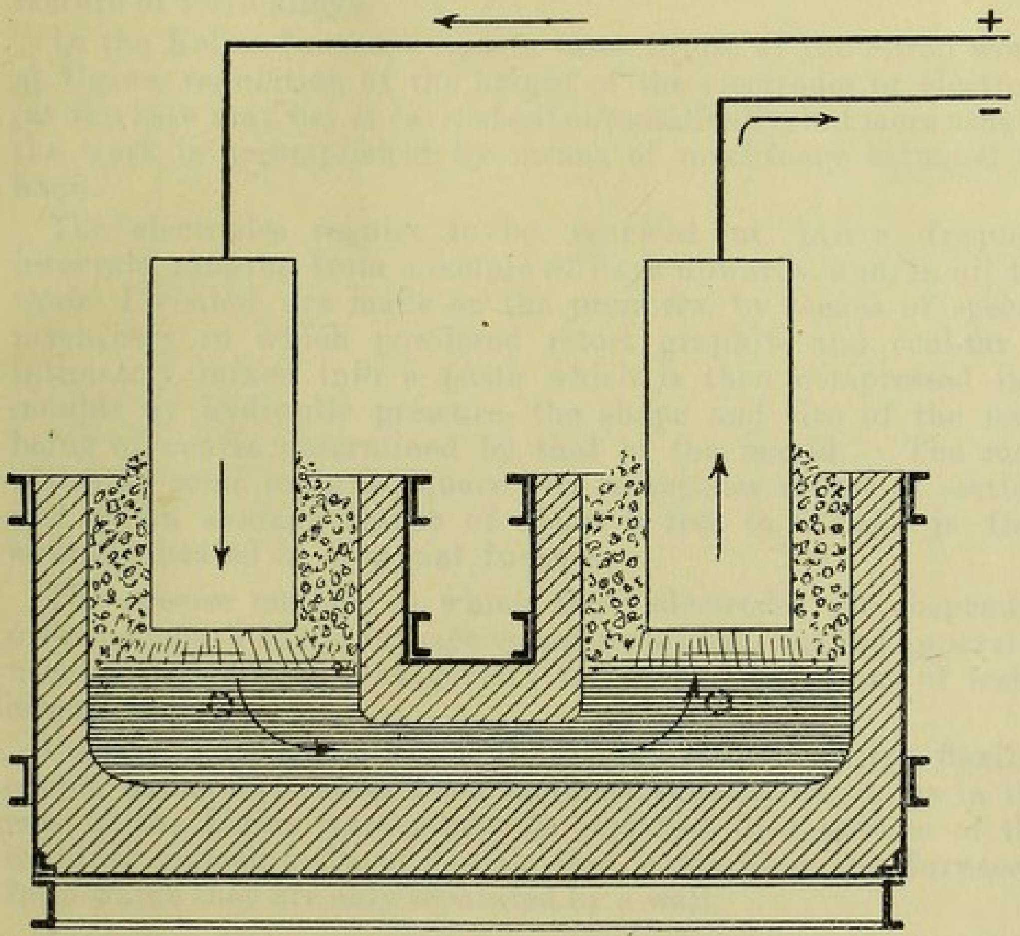
FIG. 4.



Special type of electric furnace in use at the Livet Works (Isere, France).
Invented and patented by Ch. A. Keller.

(*To face p.* 62.)

taken with an ammeter, and the pressure of the groups is controlled by means of two voltmeters inserted respectively between the furnace hearth and each group.

Dr. Heroult, of the Société Electro-Metallurgique Française, La Praz, also has invented a furnace of somewhat similar kind, having, in 1899, modified his original type, first introduced in 1887, by constructing the hearth of some neutral material in place of carbon, and employing two vertical carbon electrodes; but, as at the time of my visit to France this firm had temporarily ceased manufacturing ferro-silicon, owing to the " slump " that had occurred in the price of this material, I am unable to say whether this special form of furnace is employed for the manufacture of ferro-alloys.

In the Keller furnaces, and in those in use at the Girod works at Ugine, regulation of the height of the electrodes or electrode (as the case may be) is carried out automatically, but more usually the work is accomplished by means of machinery actuated by hand.

The electrodes require to be renewed at fairly frequent intervals, ranging from a couple of days upwards, and, in all the works I visited, are made on the premises, by means of special machinery in which powdered retort graphite and coal-tar is intimately mixed into a paste which is then compressed into moulds by hydraulic pressure, the shape and size of the mass being of course determined by that of the mould. The mass which in some cases is square and sometimes round in section, and of an average length of about 5 feet to 6 feet, is then strongly heated in a special furnace.

The precise method in which these electrodes are suspended over the mouth of the furnace varies somewhat, but the apparatus usually includes an arrangement for cooling by means of water circulation.

Current is led to the electrodes by means of thick but flexible copper bands and cables from turbine-dynamos, which, as in the case of the Ugine works, may be installed in a portion of the building immediately adjoining that containing the furnaces, from which they are only separated by a wall.

Ammeters and voltmeters are of course interposed at appropriate points, the readings of which are recorded at regular intervals. But, as having a possible bearing on the special series of reactions occurring in the furnaces, and so, in turn, on the precise chemical and physical composition of the alloy produced, it is of interest to note that, as I myself observed, the voltage and ampèrage employed (the former especially) varied somewhat widely at the different establishments inspected, ranging from 40 to 75, and from 10,500 to 15,000, respectively.

When once charged and started, the furnaces are run continuously for an average period of a couple of years, although, as I was informed at the Keller-Leleux works, the period may be extended to as much as 4 years. While running, the furnaces are tapped at intervals of 1 or 2 hours, the men working in shifts so that the furnaces can be attended to by night as well as by day, fresh amounts of charge being shovelled on the top of the furnace around the upper electrode as often as is rendered necessary by the melting and consequent shrinkage of the underlying mass.

Composition of the Charge.

From the earlier writings on the subject it appears that originally the furnace charge was composed of a mixture of (1) iron-pyrites or other form of iron-ore; (2) siliceous material in the form of quartzite or sand; and (3) of carbon in the form of charcoal, coal, or coke, together with a certain amount of (4) lime as a flux. Owing, however, to the obvious impurity, due especially to a high phosphorus and sulphur content, of the earlier samples of ferro-silicon as produced in the electric furnace, scrap-iron and steel shavings have now come to be preferred to iron-ore; and quartzite to sand, as being less productive of obstructions in the furnace. Moreover, the use of both iron and silica in as pure a form as practicable ensures that the working shall proceed with the formation of a minimal quantity of slag. The addition of lime appears to have been entirely abandoned as unnecessary, since in each instance in which I made special enquiry on the point I was informed that, under existing conditions, reduction readily takes place without the addition of a flux. Special importance may attach to this change of procedure owing to the fact that certain investigators, among whom Mr. Watson Gray may be mentioned, have advanced the suggestion that the tendency to the formation and evolution from ferro-silicon of explosive gases is, to some extent, at any rate, dependent on the calcium content of any particular sample of the alloy.

As the cost of transport, especially in the more mountainous districts, constitutes an important factor, the particular form in which the necessary carbon is supplied is, as might be expected, found to depend on the facility with which one or another kind of fuel is obtainable within reasonable distance from the works.

In most instances I found that anthracite coal is employed, of which large deposits are worked in the mountainous regions of the south-east of France, in some instances at as great a height as that of the snow level. Unfortunately, however, this anthracite is apt to be somewhat impure, yielding, as it does, as much as 10 per cent. or more of ash.

Since, as will subsequently appear, the necessary amount of carbon increases *pari passu* with that of the percentage of silicon required in the final product, it has been found desirable, where, as in the case of the Bozel works, the anthracite usually employed is of decidedly poor quality, to substitute charcoal, a purer but more expensive form of carbon, in making up a charge intended for the production of an alloy of high silicon percentage.

As a general rule little difficulty appears to be encountered in obtaining, at a reasonable cost, quartzite or other comparatively pure form of silica, but, as Dr. Hake has pointed out (Note at foot of p. 74) in the chemical section of this report, rock, consisting of silica to the extent of 96 per cent., or even more, contains calcium phosphate in appreciable amount. As the result of reduction at the high temperature of the electric furnace this becomes converted, in all probability, into calcium phosphide, which under the influence of moisture, evolves phosphoretted hydrogen gas.

Calculation of Charge in reference to required Percentage of Silicon.

In the making up of a " charge " for the production of ferro-silicon in the electric furnace, the relative amounts of the various constituents will of course depend on the percentage of silicon required in the final product. As, however, silicon is derived from the silica contained in the quartzite or other similar material employed, as the result of a reduction process, involving the interaction of the silica and carbon at a high temperature in accordance with the following equation :—

$$\underset{(28 + 32 = 60)}{SiO_2} + \underset{2 \times 12}{2C} = \underset{28}{Si} + \underset{[2\,(12 + 16)]^*}{2CO}$$

it is obvious that, as previously stated, the amount of quartz and coal must be always proportioned so that the weights of pure silica and carbon retain the relationship indicated by the equation —in other words, that for every 60 parts by weight of pure silica, 24 parts by weight of pure carbon must be also present in the constituents of the charge.

In order therefore to obtain an alloy of any required silicon percentage, it is the amount of the iron only that has to be varied, this being less for a high silicon content and *vice versâ*, the relative proportion of silicon and carbon remaining unchanged.

But the calculation of the actual amount of the several ingredients of the charge is complicated by the fact that each of the three constituents, iron, quartzite, and anthracite—notably the anthracite—will certainly contain impurities, the amount of which in each case has therefore to be determined and allowed for in the calculation. This may be illustrated by a concrete example, for which I have to thank M. Barut, Administrator of the Giffre Works at St. Jeoire, Haute-Savoie.

The composition of the anthracite coal in use at the time of my visit was, he informed me, roughly as follows :—

Carbon	82 per cent.
Ashes	10 ,,
Moisture and gases	8 ,,

while analysis of the quartzite showed that it contained about 96 per cent. silica (SiO_2).

Taking then the combining weights represented by the equation already referred to, viz. :—

$$\underset{60}{SiO_2} + \underset{24}{2C} = \underset{28}{Si} + \underset{56}{2CO}$$

and noting that 24 kilogrammes of carbon will be represented by 30 kilogrammes of 80 per cent. anthracite, the required proportion of silica to coal will be the simple one of 2 : 1, on which,

* The numbers given below the symbols in the equation represent the combining weights of the elements, thus :—Si = 28, O = 16, C = 24. Reference to these will render clearer the calculations in the text.

however, allowance has to be made for the fact that 100 parts by weight of quartzite contain 96 parts only of silica, or about 144 kilogrammes of silica in 150 kilogrammes of quartz.

As regards the source of the iron also, some allowance is, of course, necessary, seeing that the steel turnings employed will contain a certain amount of iron oxide in addition to small amounts of impurities.

Taking these different factors into consideration, the respective weights of the several ingredients required to make up a charge for the production of, say, a 50 per cent. ferro-silicon, will be as follows:—

Quartz	150 kgms.	(= about 144 kgms. SiO_2).
Anthracite	72 ,,	(= about 66 kgms. Si).
Steel turnings ...	55 ,,	
	277 ,,	

Dealing with these quantities—

66 kilos silicon + 55 kilos steel turnings should theoretically yield 121 kilogrammes, all the carbon of the anthracite being given off as CO (carbon monoxide gas). But, as matter of fact, in addition to the total disappearance of the carbon a certain proportion of the silicon and iron (about 11 kilogrammes on the quantities here dealt with) is also not accounted for in the final product, being presumably lost through incorporation with the slag. Consequently the amount of alloy actually obtained from the above charge of 277 kilogrammes will be 110 kilogrammes only of 50 per cent. ferro-silicon.

In the event of a lesser or greater silicon percentage being required, the weight of steel turnings in the charge must be increased or diminished accordingly.

In practice the requisite amounts of the three ingredients of the charge are weighed out separately, the quartz and anthracite coal having previously been reduced to small fragments of a size varying roughly from that of a filbert to that of a walnut. After weighing, the different materials are thrown together into a heap on the floor of the furnace-house where they are mixed as thoroughly as possible with a shovel. The resulting rough mixture is then thrown on to the top of the furnace a shovelful at a time, care being taken to heap it up around the vertical electrode or electrodes, as the case may be.

To receive the molten material when the furnace is "tapped," a shallow bed of sand is prepared, either on the floor or, as was the case at one of the manufactories visited, in an iron box on wheels, which accordingly can be removed, so soon as the "tapping" shall have come to an end. Usually, however, immediately the flow of white-hot liquid has ceased, the surface of the resulting pool of molten alloy is skimmed to remove the layer of slag on the surface; a short thick log of "green" wood fixed crosswise on the end of a long iron bar being employed for this purpose at the Keller-Leleux works.

As soon as the cake or slab of ferro-silicon has solidified, it is broken up with heavy iron hammers into comparatively small pieces which, in the case of the 50 per cent. grade, at any rate, it has recently become the custom, at several of the works I visited, to treat, while still hot, by immersing them in a bath of kerosene oil or melted crude paraffin.

This method of treatment has been adopted on the assumption that by thus preventing contact with the air by means of a coating of oil or paraffin, it would prove possible to obviate the well-known tendency of certain samples of 50 per cent. ferro-silicon to disintegrate spontaneously, and thus, incidentally, to prevent evolution of noxious gases, mainly phosphoretted and arseniuretted hydrogen, which under certain circumstances appear to be associated in specially large quantity with this particular grade of electrically produced ferro-silicon. Dr. Hake has shown (p. 84) that considerable quantities of these gases may, on occasion, be present as such, being merely occluded in minute spaces in the substance of the alloy.

But as regards the prevention of the process of disintegration, the precise causation of which by the way is still to seek, the kerosene or paraffin bath treatment has not proved successful; while the fumes given off when ferro-silicon, which has been "coated" after this fashion, is subsequently heated, as appears to be considered desirable before being utilized for its specific action on addition to a bath of molten steel or iron, are most objectionable, owing to the crude material usually employed. In addition, the heating of the alloy thus rendered necessary before use at ironworks must obviously promote in special degree the evolution of poisonous gases, and thus prove a special source of danger—as indeed in certain instances to which reference has been made in an earlier section of this report—to workmen engaged in handling the material, and to whom this preliminary treating of the alloy is entrusted.

In view, therefore, of the complete futility of the process of "pickling," which I have described above, for the intended purpose, coupled with the fact that it may actually involve, later on, an added source of danger to workers in the iron foundries, it is certainly desirable that the method should be abandoned.

Another point deserving of attention as bearing on possible danger in connection with transport and storage of ferro-silicon has reference to the fact that, owing to the somewhat unremunerative prices for this substance at present prevailing, manufacturers are naturally indisposed to produce and hold any considerable stock, merely therefore turning out the required amount to order, and at once forwarding it to their customers. Under these circumstances the ferro-silicon will reach the consignee without such degree of safeguard as, in view of Dr. Wilson Hake's researches, will be likely to be afforded by free exposure to the atmosphere, with consequent removal, especially in the event of the alloy undergoing more or less disintegration, of some proportion, at any rate, of those poisonous gases to which reference has so frequently been made.

I found indeed that, in most instances, the ordinary practice is to pack the ferro-silicon, as soon as its condition permits, into barrels or other receptacles, and to despatch the consignment with the least possible delay.

In view of these considerations, it would appear desirable that each batch of ferro-silicon should in all cases be stored at the works where it is produced for at least a month subsequent to the date of manufacture, the method of storage being such as to ensure complete exposure to the air.

So far as I am aware ferro-silicon is no longer packed in closed iron drums, so that, to this extent, likelihood of explosion is avoided, but as in transport, even when packed in wooden barrels, a considerable amount of friction must inevitably occur between the rough lumps, in which form the ferro-silicon is ordinarily sent out from the works, I would offer the suggestion that, in the course of packing the alloy into barrels, all interstices might usefully be filled in with shavings, wisps of hay, or other similarly cheap material.

It is also important that each barrel or other package of ferro-silicon should have the name of the material boldly marked on it, together with the percentage grade of the particular sample contained in it, the maker's name, and the date of manufacture.

REPORT ON THE CHEMICAL EXAMINATION OF VARIOUS SAMPLES OF FERRO-SILICON, WITH SPECIAL REFERENCE TO THE POISONOUS GASES EVOLVED FROM THEM. BY H. WILSON HAKE, PH.D., F.I.C., F.C.S.

At various dates between March 4th and May 27th, 1909, I received from Dr. S. Monckton Copeman, F.R.S., sixty-one samples of ferro-silicon, on June 4th four more samples, on June 24th one sample, on July 1st two samples, and finally on July 6th three samples—making seventy-one in all.*

The samples were obtained by Dr. Copeman (1) from English agents or manufacturers; (2) from foreign manufacturers.

The percentage of silicon in these samples has varied from 10 to 96 per cent. Each sample on arrival was labelled by me with an identification number (Table I., col. 1).

As, however, the *percentage of silicon* is the determining factor both as regards the physical and what may be termed the "dangerous" chemical properties of these alloys, I have set out the summary of my results in the increasing order of the percentages of silicon (Table I., Col. 3), and have noted, in addition, the *sources of the samples* in a separate special list arranged in the numerical order of the identification numbers (viz., I. to LXXI., Table II.).

I have also added in the summary of results the *date of manufacture* against all samples when known (see Table I., col. 2). This will be seen later to have a special bearing in connection with certain grades of ferro-silicon.

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* A few samples had to be rejected for reasons which are referred to in Table II. (Sources of Samples) so that only 64 appear in Table I. (Summary of Results).

Appearance of Samples.

The general appearance of the samples may be briefly described as follows:—They all have a metallic lustre, and, speaking broadly, vary in colour from iron-grey in the lowest grades, through silver or leaden-grey to blue or steel-blue-grey in the highest grades. The following is a more detailed description applied to special groups:—

10 *to* 14 *per cent. Silicon* (4 samples).—Bright iron-grey colour, crystalline appearance, close texture, no bubble cavities, patches of iron rust on exterior.

20 *to* 35 *per cent. Silicon* (12 samples).—Bright to dull silver-grey, crystalline appearance, close texture, no bubble cavities (with two exceptions, viz., XL. 25 per cent., and LVII. 26·5 per cent.).

42 *to* 52 *per cent. Silicon* (33 samples).—Dull to bright leaden-grey (sometimes silvery-grey), crystalline fracture, mostly more or less permeated with numerous small or large bubble cavities.

60 *to* 75 *per cent. Silicon* (9 samples).—Mostly dull to bright blue-grey, crystalline fracture, close texture, few or no bubble cavities.

80 *to* 96 *per cent. Silicon* (6 samples).—Mostly bright steel-blue-grey, crystalline fracture, very close texture, few or no bubble cavities.

By thus dividing the samples into groups, according to the percentage of silicon, special differences are obvious on simple inspection. I would note, apart from the variations in colour observable, the close texture and absence of bubble cavities in the 10 to 35 per cent. samples, and the equally close texture and comparative freedom from bubble cavities in the 60 to 96 per cent. samples, while in the 42 to 52 per cent. samples the presence of bubble cavities is characteristic, and the texture as a rule much coarser.

As pointed out in Dr. Copeman's Report (p. 11) the history of ferro-silicon shows that some of these alloys containing certain percentages of silicon are liable, under the influence of moist air, especially when accompanied by friction, to evolve gases, having very dangerous properties, and during the past five years a number of fatalities have occurred which have been traced to its carriage on board ship, or to its storage and use in factories.

The nature of these regrettable accidents has been twofold. In some instances passengers on ships or canal boats carrying ferro-silicon have, somewhat suddenly, died; in others workmen have suffered more or less from the effects of breathing the fumes evolved from the material; and, in a few instances, explosions have occurred spontaneously, or on handling drums in which it was contained.

In my investigation I have paid special attention to the nature of the dangerous gases evolved by this material with a view both to their ready identification and especially to their quantitative estimation by chemical methods.

Literature relating to previous Chemical Investigations.

Before describing my own methods and results in detail it will be desirable briefly to refer to the chemical work on the subject by previous investigators.

Dupré and Lloyd ("Explosions Produced by Ferro-Silicon," *Journal of the Iron and Steel Institute,* No. 1, 1904) investigated the cause of three separate explosions which occurred within a few days of one another, of two iron drums and a barrel containing ferro-silicon, which were stored in a warehouse in Liverpool.

The ferro-silicon on examination was shown to yield phosphoretted hydrogen (PH_3) in contact with water at ordinary temperatures. No acetylene and no siliciuretted hydrogen were found. It was suggested, in explanation of the explosions, that water had got into the drums, and that the heat due to the friction of the lumps of ferro-silicon in moving them had ignited the mixture of phosphoretted hydrogen and air present in the drums. Phosphoretted hydrogen was stated to have a low ignition temperature, viz., 200° C.

No estimation was made of the amount of phosphoretted hydrogen evolved by the action of water on the ferro-silicon. It was further shown that a sample of ferro-silicon subjected to the action of ordinary water evolved gas continuously for one week, but that if salt was added to the water the evolution of gas continued for six weeks. No mention is made of the nature of the gas evolved by the action of water containing salt in solution, nor was it suggested, as seems probable, that this action was largely electrolytic.

Lehnkering ("Phosphorwasserstoff Vergiftung durch im elektrischen Ofen hergestelltes Ferro-silicium," Zeitschr. f. Unters. der Nahrungs und Genussmittel, 1906, Bd. XII., p. 132) investigated the cause of death of several individuals, including two young children, on board the Rhine boat "Caroline," carrying 700 centners of ferro-silicon in barrels. The ferro-silicon contained 57·69 per cent. of silicon. An odour of phosphoretted hydrogen was noticeable on opening a barrel. When a dish containing a solution of silver nitrate was lowered into the atmosphere of the barrel a black precipitate was formed. Air passed over some of the ferro-silicon in a flask and then into a solution of nitrate of silver also caused a black precipitate. No acetylene was found.

From a quantitative experiment with silver nitrate solution, all details of which are omitted, the author calculated that 0·0227 gramme of phosphoretted hydrogen was evolved from 1 kilogramme of the ferro-silicon by the action of water. The author also found that the water used had become alkaline by the formation of lime (CaO), and he estimated (method again not given) that 0·0476 gramme lime was produced for every kilogramme of ferro-silicon acted upon. He calculates that this lime is in excess of that which would be produced from the phosphide of calcium corresponding to the phosphoretted hydrogen found, and infers that some of the phosphide of calcium had already been decomposed by exposure to moist air.

I think the author is under a misapprehension here, as 0·0476 gramme lime would correspond to 12·6 c.c. PH_3 evolved from Ca_3P_2 and the weight of phosphoretted hydrogen found, viz., 0·0227 gramme, corresponds to 14·8111 c.c. PH_3, per kilogramme. I note this point, because many of my own results show a similar *deficiency* in the lime estimated (*see* p. 83).

A. Werner Cronquist, Royal Swedish Inspector of Explosives (*Report to the Swedish Foreign Office, May*, 1907), investigated the cause of death of four passengers on board the "Olaf Wyjk," which arrived at Antwerp from Gottemborg on February 12th, 1907, having 15 tons of ferro-silicon stored in the hold immediately below the cabins occupied by the victims. Professor Cronquist showed that phosphoretted hydrogen and arseniuretted hydrogen were evolved from the ferro-silicon. He collected the gases mixed with air which were evolved by the action of water on the ferro-silicon, and calculated the amount of the former gas by oxidation of the phosphorus present in the gases collected and subsequent determination as phosphate. This method would, I think, tend to under-estimate the amount of phosphoretted hydrogen present. He calculated from his results that 1 kilogramme of ferro-silicon gave 12·25 c.c. of phosphoretted hydrogen (PH_3).

Professor Cronquist also read a paper at the International Congress of Applied Chemistry in London in May last (1909). In this paper Cronquist and Petrén describe a special method for the estimation of the gases evolved from ferro-silicon; a spherical mortar consisting of two hemispheres screwed together and fitted with an air-tight pestle was used for crushing the ferro-silicon. An inlet-tube admitted dry or moist air, while an exit-tube fitted to an aspirator drew off the evolved gases, which were passed into a 10 per cent. solution of silver nitrate, and the phosphorus estimated by weighing the precipitate produced, on the assumption that Ag_3P, 3 $AgNO_3$ represented its composition. The authors admit a difficulty as regards accuracy of the method owing to the rapid oxidation of the silver phosphide. Professor Cronquist's experiments are only tentative, so far, and further investigations are promised.

Bruylants and Druyts ("Le Ferro-Silicium en Toxicologie," *Bulletin de l'Academie Royale de Médecine de Belgique*, IVe Série, Tome XXIII., Séance du Janvier, 1909, p. 26) also investigated the fatality which occurred on the "Olaf Wyjk" (see above), and also found phosphoretted hydrogen and arseniuretted hydrogen among the gases evolved by the ferro-silicon, and estimated their amount. They noted the blackening of paper moistened with a solution of nitrate of silver and the odour of the gas evolved by the action of moist air on the ferro-silicon. They made an approximate estimation of the phosphoretted hydrogen as follows:—(1) The total phosphorus was estimated by powdering 100 grammes of the ferro-silicon *under* aqua regia with the object of oxidising the calcium phosphide, as well as the phosphorus, in combination with the iron; (2) the residual phosphorus was estimated by first treating 50 grammes of the sample with water, evaporating to dryness on a water bath, and then oxidising with aqua regia. The phosphate obtained in both cases was precipitated as phospho-molybdate, and eventually weighed as magnesium phosphate. From the difference between the two estimations the amount of phosphorus present as phosphoretted hydrogen (PH_3) in the gas evolved by the action of water was calculated.

The arsenic, estimated on almost identical lines, taking 20 and 10 grammes respectively, was ultimately weighed as a mirror obtained in a heated glass tube connected with a Marsh-Bezelius apparatus.

Notwithstanding the tendency which these very elaborate methods would have to under-estimate the amount of gas actually evolved, the authors calculated, as a mean of six experiments, that the 15 tons of ferro-silicon on board were capable of evolving 2,400 litres (5·6 cub. ft. per ton) of phosphoretted hydrogen containing about 5 per cent. by volume of arseniuretted hydrogen.

The authors further made a most ingenious experiment to show that on shaking a drum containing ferro-silicon through which moist air was being passed an increased evolution of gas occurred.

Professor W. R. Smith ("The Poisonous Gaseous Emanations of Ferro-Silicon," *Journal of the Royal Institute of Public Health*, January, 1909, p. 1) investigated the cause of death of some emigrants on board the s.s. "Ashton," which arrived at Grimsby from Antwerp on December 12th, 1908.

Samples of the ferro-silicon on board were examined. 200 grammes were taken in a horizontal glass tube and air passed over it for three hours, the air passing on to a 10 per cent. solution of silver nitrate. The black precipitate so obtained was placed in an apparatus in which pure hydrogen was being evolved, and caused a green colour to be imparted to the flame of the hydrogen when burnt. The filtrate from the black precipitate was shown to contain arsenic and a mirror was obtained with a Marsh-Berzelius apparatus. Siliciuretted hydrogen and acetylene were searched for but not found.

Professor Smith concludes that phosphoretted hydrogen (PH_3) was the chief gas evolved when air was passed over the ferro-silicon, but no quantitative estimations were made. He quotes Eulenberg ("Die Lehre von den giftigen Gasen," 1865) as stating that 0·25 per cent. of phosphoretted hydrogen in air is poisonous to man, and Schulz, who stated that 0·46 per cent. in air was fatal to rabbits, but more recent researches have shown that one-tenth of the proportion given by Eulenberg, viz., 0·025 per cent., may be fatal.

The following two unpublished documents were also placed in my hands by Dr. Copeman:—

Report by Mr. G. Watson Gray, of Liverpool (*June*, 1909), *on six samples of ferro-silicon* sent to him by M. Paul Girod, Membre de la Commission de Ferro-Silicium de la Chambre Syndicale de l'Electro-Metallurgie. Mr. Watson Gray reports that the silicon content of the samples varied from 36·2 to 49·05 per cent., and that 1 kilogramme acted on by water at ordinary temperature for thirty consecutive days evolved from 30 c.c. to 120 c.c. of gas consisting, for the main part, of hydrogen containing a small proportion of phosphoretted hydrogen, and a still smaller amount of arseniuretted hydrogen, while with water at 100° the same weight of the various samples evolved still greater quantities of these gases amounting, in some samples, to more than ten times the previous volume. The state of division of the ferro-silicon in these experiments is not mentioned. On heating the samples a similar mixture of gases was evolved, but the heating did not prevent the fresh evolution of gas when in contact with water later. No siliciuretted hydrogen, acetylene, carbonic oxide, or nitrogen was evolved, and Mr. Watson Gray expresses the opinion that these six samples " are quite harmless as regards poisonous or explosive properties." Mr. Watson Gray does not, however, enter into details of his methods. I am not, therefore, in a position to comment upon his results beyond stating that the amount of phosphoretted hydrogen which he finds is far less than I have found in ferro-silicon of these grades. Moreover it is difficult to account for the large volume of hydrogen which he obtains. This cannot be due to the presence of calcium silicide, as the quantity of calcium he found does not exceed 0·5 per cent. in any of the six samples. On the evidence afforded, the presumed safety of all these samples must also, I think, be open to question.

Report by Mr. J. A. Foster, F.I.C., Public Analyst for Grimsby, May, 1909. Mr. Foster examined some of the ferro-silicon from the s.s. " Ashton." He proved by qualitative tests the presence of phosphoretted hydrogen, but his estimations of the volume of gases evolved are only approximate, owing to admixture with air. Mr. Foster, in testing for arsenic, acted on the ferro-silicon with sulphuric acid, and not with water alone, for which reason his results are comparatively valueless. He also found acetylene and sulphuretted hydrogen evolved by the action of moist air on ferro-silicon. The latter gas has not been found by other investigators.

Object and Scope of the present Chemical Investigation.

It will be seen from the foregoing abstracts that among the various gases alleged to be evolved from ferro-silicon by the action of water or moist air, phosphoretted hydrogen (PH_3), arseniuretted hydrogen (AsH_3), siliciuretted hydrogen (SiH_4), acetylene (C_2H_2), and hydrogen are specially mentioned.

The two first-named gases are deadly poisons, and the symptoms caused by their inhalation, even when present in only minute quantities in air, are severe abdominal pains, nausea, vomiting, great weakness and prostration, gradual loss of consciousness deepening into coma, and death, frequently within twenty-four hours.

Although hydrogen appears to be present in ferro-silicon I have not taken this gas into account in my estimations, owing to its entirely non-toxic character. I presume its presence is due to occlusion, almost entirely; and far less probably to the decomposition by water of calcium silicide.

I have not found acetylene or siliciuretted hydrogen in the samples I have examined, and I have reason to believe, as will presently be shown, that neither the gases themselves nor compounds which would produce them in contact with water, are likely to be formed in the process of manufacture of ferro-silicon.

Dr. Copeman has described this process of manufacture after personal inspection of many factories. To briefly recapitulate his statement, a mixture of steel turnings obtained from gun foundries, together with quartz and coal from neighbouring mines, is put into an electric furnace of a capacity of about 1,500 kilogrammes and heated to a temperature roughly computed at from 1,800° to 2,000° C. The quantities of quartz (which contains about 96 per cent. of silica or silicon dioxide, SiO_2) and anthracite coal (containing about 90 per cent. of carbon and 10 per cent. of ash) are always used in the proportion of one molecule of silica to two atoms of carbon so that complete reduction of the former to silicon (Si) shall occur, according to the chemical equation :— $SiO_2 + 2C = Si + 2CO$.

The proportion of iron taken, varies and depends on the grade of ferro-silicon required, that is, on the desired percentage of silicon in the alloy ultimately produced.

Certain impurities originally present in the coal, iron and quartz used, or formed from them during the process of manufacture, are always present, and some of these, although amounting to a very small percentage of the finished product, are the ultimate cause of the serious mishaps which have arisen from the extended use of ferro-silicon.

Calcium phosphate [$Ca_3(PO_4)_2$], one of the impurities present in coal and in quartz,* which in itself is a perfectly harmless salt, insoluble in water and widely diffused in nature, is responsible for the production of a dangerous compound by reduction in the electric furnace, in the presence of carbon, to *calcium phosphide* (Ca_3P_2). This calcium phosphide remains in the ferro-silicon, and in contact with water or moist air is decomposed with evolution of *phosphoretted hydrogen* (PH_3), the intensely poisonous character of which has been referred to above.

Arsenic again, an element closely allied to phosphorus in its properties, is another impurity liable to be present in various combinations in coal and in iron, and this element also finds its way into the ferro-silicon apparently as *calcium arsenide*. Calcium arsenide is also decomposed by water or moist air, evolving *arseniuretted hydrogen* (AsH_3), a gas scarcely, if at all, less poisonous than phosphoretted hydrogen.

Acetylene (C_2H_2), which is not commonly regarded as poisonous unless present in large proportion in air, would be evolved by the action of moisture on ferro-silicon if calcium carbide (CaC_2) were present as an impurity, since this substance also is decomposed by water with formation of lime (CaO) and evolution of acetylene. But the presence of calcium carbide is improbable seeing that lime, as a flux, is not now used in the manufacture of ferro-silicon.

It has been stated by certain writers that lime was formerly used as a flux in making ferro-silicon, but if so its use has now

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* I examined three samples of quartz and three samples of coal or coke used by various manufacturers of ferro-silicon and found calcium phosphate in considerable quantities in all of them.

been abandoned. It has also been stated that furnaces previously used for the manufacture of calcium carbide had been employed for ferro-silicon, but this also is certainly not now the case. Hence these sources of calcium carbide and acetylene are no longer possible.

With reference to *siliciuretted hydrogen* (SiH_4) a gas which is spontaneously inflammable in contact with air, it has been somewhat loosely suggested by some writers that owing to the possible formation of calcium silicide, as an impurity in the manufacture of ferro-silicon, this substance would evolve siliciuretted hydrogen in contact with water. Such a statement is based on an imperfect appreciation of the properties of calcium silicide which, in contact with water, evolves hydrogen gas, not the hydride of the element as is the case with calcium carbide. Further, its decomposition in contact with air removes it from the category of poisonous gases likely to be evolved from ferro-silicon.

On the other hand siliciuretted hydrogen if present, for some unexplained reason, and certainly liquid phosphoretted hydrogen ($P_2 H_4$), a gas evolved by the action of water on impure calcium phosphide which is also spontaneously inflammable, might, as has been suggested by Dupré (p. 70), be the cause of explosions which have occurred in connection with the storage of ferro-silicon. Moreover, in this connection, ordinary phosphoretted hydrogen (PH_3) has a very low temperature of ignition, and like any other inflammable gas, forms an explosive mixture with air.

From my own experiments as well as from a consideration of the chemical facts above referred to, and of the mode of manufacture, it became finally evident that the poisonous emanations evolved from ferro-silicon by the action of water consist mainly of phosphoretted hydrogen; sometimes alone, but for the most part accompanied by varying proportions of arseniuretted hydrogen.

In pursuing my own investigations I found it unnecessary, except in two instances, to make an ordinary analysis of the samples of ferro-silicon, as in all cases the samples were accompanied either by a certified statement on the part of the manufacturers or by a copy of the works' analysis, in which the percentage of silicon was always given. In some cases a complete analysis including the iron as well as the small proportions of phosphorus, sulphur, calcium, &c., present as impurities was also furnished. Much time was thus saved and I was able to restrict my investigation more especially to the detection and estimation of the poisonous gases evolved from the large number of samples submitted to me.

In addition to my chemical experiments, I made two series of observations connected with the physical properties of these alloys, for purposes of general comparison, and for which the large number available offered a special opportunity. I refer to the *hardness and specific gravity* of the samples (Table I., cols. 4 and 5).

I also made a series of experiments showing the *result of prolonged exposure to dry and moist air* in some of the samples of ferro-silicon (*see* p. 87).

Before describing my chemical experiments I will, for the sake of clearness, deal first with these two physical properties of ferro-silicon alloys.

Hardness of the Samples (Table I., col. 4).

The varying hardness of the samples seemed an important point to record, as considerable differences in this respect were noticeable.

By the term "hardness" I would imply the resistance offered to mechanical disintegration, or in other words the varying difficulty experienced in breaking up and powdering the samples. To give two extreme instances No. LVII. (26·5 per cent. Si) required a steel ore-crusher to break it up before it could be powdered, while No. VIII. (50 per cent. Si) could be crushed between the fingers. It is a little difficult to express these differences of hardness in suitable terms, and I have only used two, viz., refractory and brittle; the latter does not satisfactorily express the shades of difference coming under this description and it is necessary to qualify both terms to some extent.

It will be seen, however, from an inspection of the table that, up to 30 per cent. silicon content, the samples are described as more or less refractory without exception. Here evidently the high percentage of iron exerts its influence and an important consequence is the absence of any tendency on the part of these grades of ferro-silicon to disintegrate *spontaneously*.

Similarly from 70 to 96 per cent. where the silicon is in excess, although the samples are more or less brittle, they are not so easy to break up and to reduce to powder as those containing between 42 and 60 per cent. silicon, and they also do not show a tendency to disintegrate spontaneously.

On the other hand the samples containing from 42 to 60 per cent. show a distinct tendency to spontaneous disintegration. They crumble on keeping, and some of them actually fall to powder after the lapse of a few weeks or months. This spontaneous disintegration is usually accompanied by a very noticeable evolution of the evil-smelling and poisonous gases already referred to (p. 73).

The same phenomenon is apt to occur, I am informed, with 33-35 per cent. grades, but I have no personal experience of the fact. I received two samples of 35 per cent. (Nos. LXX. and LXXI., Table I.), one in powder which I am told was entirely the result of spontaneous disintegration, the other solid which showed no obvious tendency to disintegrate. Both samples were practically free from poisonous impurities.

This tendency to disintegration on the part of certain grades, has an important bearing on the practical aspect of this enquiry, but has not as yet received any completely satisfactory explanation. It has been suggested that the varying stability of these alloys which are generally regarded as so-called "eutectic mixtures" depends on the presence of various definite compounds

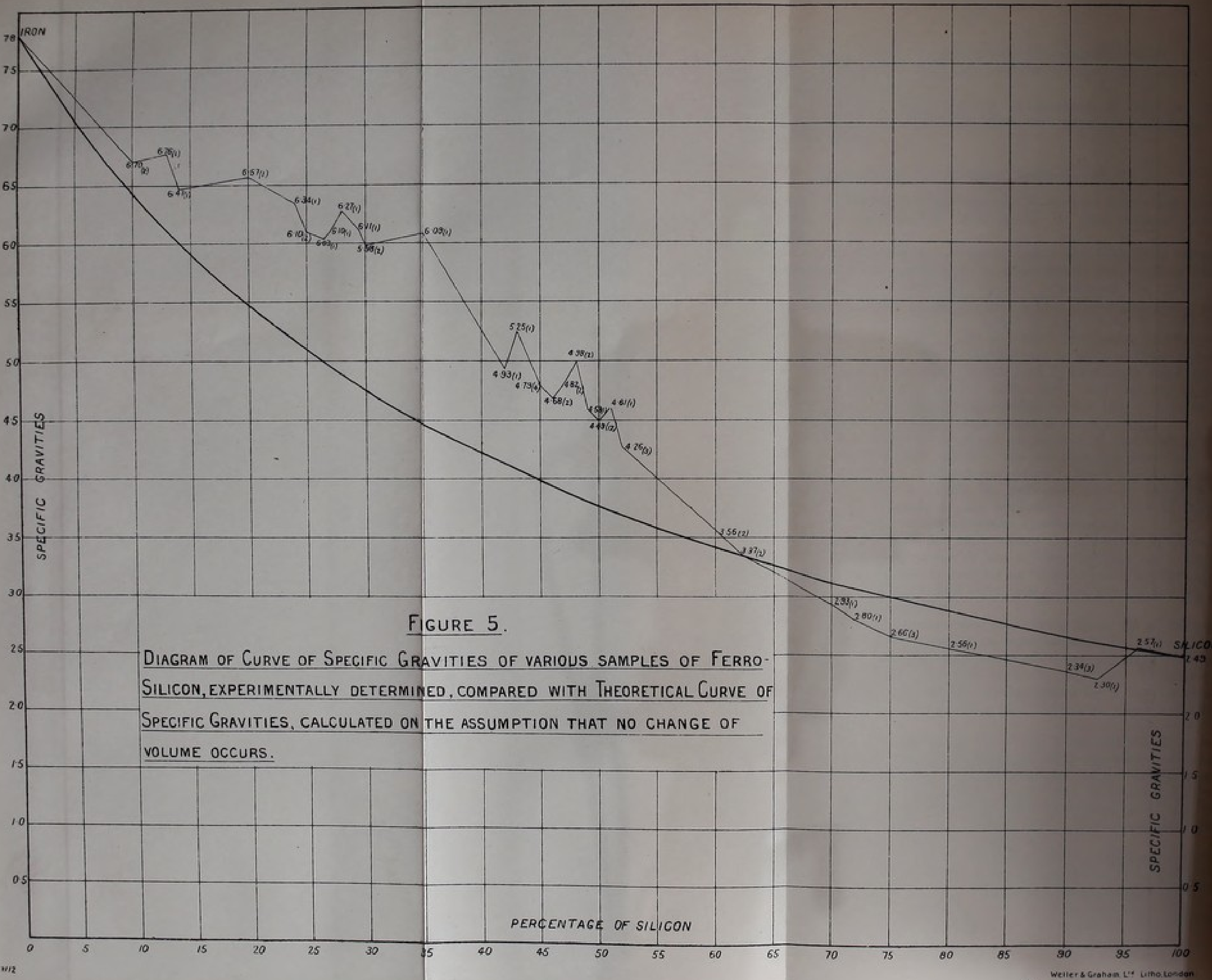

FIGURE 5.

DIAGRAM OF CURVE OF SPECIFIC GRAVITIES OF VARIOUS SAMPLES OF FERRO-SILICON, EXPERIMENTALLY DETERMINED, COMPARED WITH THEORETICAL CURVE OF SPECIFIC GRAVITIES, CALCULATED ON THE ASSUMPTION THAT NO CHANGE OF VOLUME OCCURS.

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(To Face p. 77.)

of iron and silicon in them. Moissan (*Traité de Chimie minerale*, Ed. 1904, Vol. III., p. 404) states that the silicides of iron at present known are:—

Fe_2Si	containing	20	per cent.	of silicon.
Fe_3Si_2	,,	25	,,	,,
$FeSi$	,,	33·3	,,	,,
$FeSi_2$	,,	50	,,	,,

As all these silicides are crystalline it has been suggested that the tendency to disintegrate, shown by certain grades of ferro-silicon, is intimately connected with this fact, but no such tendency is shown up to 30 per cent. silicon. An alloy containing 60 per cent. silicon would correspond to a silicide of iron of the formula $FeSi_3$, but such a compound has apparently not yet been isolated.

As nearly 8 months had elapsed during the progress of Dr. Copeman's investigation, I have been able to observe the condition of all the samples which had been in our possession for periods varying between 4½ and 7¾ months. The results of this examination, as regards the presence or absence of disintegration, are shown in the accompanying table. (*See* also classification of samples, p. 87.)

Specific Gravity of the Samples. (Table I., Col. 5.)

The specific gravity of the samples of ferro-silicon was determined. This determination is not usually made in connection with commercial samples, but some interesting points arose in connection with the figures so obtained.

The specific gravity, for example, as will be shown later, apparently bears a more or less definite relation to the percentage of silicon in the alloy, and might, on occasions, serve as a useful check, or even, for rough purposes, be substituted for that estimation if a rapid examination of a sample were required.

In this connection it is not without interest to note that in one instance in determining the specific gravity of two samples which had arrived in one package and were labelled 30 per cent. and 50 per cent. silicon, respectively, I found that the figures obtained corresponded to the reverse order of the percentages stated. The hardness of the samples, as well as the relative quantities of gas evolved from them by the action of water, indicated a similar discrepancy. I therefore myself determined the percentage of silicon in each, and the results confirmed the conclusion I had already arrived at, namely, that by some inadvertence the samples had been interchanged. This conclusion was subsequently further confirmed by the sender of the samples, who was not aware that I had already detected the error.

I determined the specific gravities of all the samples, with one or two exceptions, where owing to their being of too porous a nature or in powder, the determination would have been unreliable. The figures obtained are stated against each sample in Table I., col. 5, and will be seen, on inspection of this table, to *decrease* as the percentage of silicon *increases*, which obviously follows from the fact that the specific gravity of iron is 7·8 while that of silicon is 2·49.

My main object in making the determinations was a practical one, but it seemed also a matter of interest to plot out a curve (Fig. 5) indicating the relation of the specific gravities found to the percentages of silicon given, and to compare it with a theoretical curve (*see* thick line in Fig. 5) representing the calculated specific gravities for all percentages on the assumption that mixtures of iron and silicon are formed *without change of volume*.

A comparison of the two curves demonstrates, what is indeed already well-known, that such is not the case and the specific gravities found are partly above and partly below the theoretical curve, showing that contraction of volume has occurred in the alloys formed up to 60 per cent. silicon and expansion of volume from this to 96 per cent. silicon, presumably owing to the presence of definite silicides of iron in the alloys (*cf*. Hardness, p. 77). This presentation of the facts observed may prove useful and will doubtless be more advantageously commented on by expert physicists better able to interpret the indications afforded by the curve.

The specific gravities as determined by me represent averages of not greatly differing determinations of several samples containing the same stated percentage of silicon. Some of them, however, are necessarily based on the examination of one sample only. In doubtful cases two or three determinations were usually made and, in calculating the averages, some of the figures were rejected as obviously incorrect. The figures in brackets against the specific gravity figures in Fig. 5 indicate the number of samples on which the average specific gravity is based, *e.g.*, 50 per cent. (17).

Special Preliminary Test for Phosphoretted Hydrogen in Samples of Ferro-Silicon.

Bruylants and Druyts (p. 71) and certain other investigators have used paper moistened with a solution of silver nitrate as a test for the presence of phosphoretted hydrogen, in the gases evolved from ferro-silicon by the action of moisture. Such a test-paper shows a more or less intense darkening in the presence of this gas owing to the rapid reduction of the silver salt and formation of black silver phosphide.

These experimenters however omitted an important precaution in using the test, viz., the simultaneous testing for sulphuretted hydrogen which also blackens silver nitrate paper owing to the formation of black silver sulphide. Hence in the presence of sulphuretted hydrogen this test for phosphoretted hydrogen is valueless.

Paper moistened with a solution of lead acetate however is not affected by phosphoretted hydrogen but is darkened by sulphuretted hydrogen owing to the formation of black lead sulphide.

Strictly speaking, it is therefore necessary to use both test-papers simultaneously in order to prove the presence of phosphoretted hydrogen and the absence of sulphuretted hydrogen.

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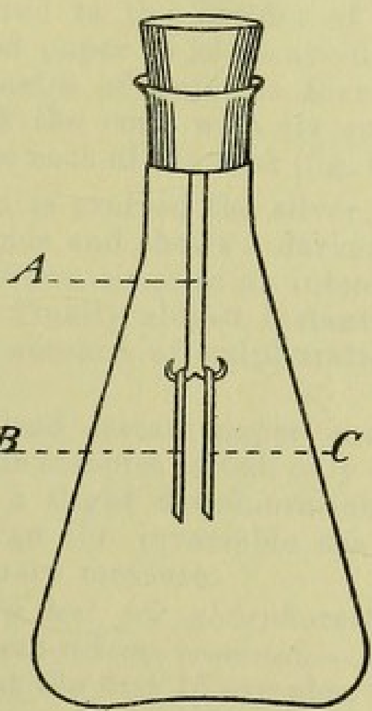
FIG. 6.

APPARATUS FOR QUALITATIVE PROOF OF PHOSPHORETTED HYDROGEN.



A. Glass rod with terminal hooks.
B. Silver nitrate paper.
C. Lead acetate paper.

(*To face page* 78.)

Scherer originally pointed this out in suggesting a similar test for detecting phosphorus in cases of poisoning by that element.

As a preliminary test I therefore devised the following experiment with a view to suggesting a simple and rapid method which would enable the operator to say at once whether phosphoretted hydrogen was or was not evolved from a given sample of ferro-silicon.

A conical (Erlenmeyer) flask of about 70 c.c. capacity and $9\frac{1}{2}$ c.m. in height is fitted with a cork into which is inserted a short piece of glass rod about 3 c.m. long, the free end of which is drawn out to form a double hook. On these hooks are hung two strips of filter-paper (0·5 × 2·5 c.m.) the free ends of which are moistened with (α) a decinormal solution of nitrate of silver, (β) a 1 per cent. solution of lead acetate.

About 1 gramme of the ferro-silicon to be examined is powdered and quickly transferred to the bottom of the flask, by means of a cylinder of rolled paper so as to avoid touching the sides. Half a cubic centimetre of water is then added so as to moisten the powder, and the cork with its suspended test-papers quickly replaced in the neck of the flask (fig. 6).

If phosphoretted hydrogen is evolved the silver nitrate paper is affected within a few seconds and shows a darkening, varying in colour from the faintest brown tinge to an intense black. In the latter case the action is usually almost instantaneous. The lead acetate paper, in the absence of sulphuretted hydrogen, remains entirely unaffected.

As a matter of fact the lead acetate paper is almost superfluous since, in the seventy-one samples tested, only one (No. VI., 50 per cent. silicon) caused a slight discolouration of the lead salt. I would however urge the invariable use of the lead acetate paper as a precautionary measure.

Results of the preliminary test for phosphoretted hydrogen applied to the samples of ferro-silicon received.—An inspection of Col. 6, Table I., shows that the first 16 samples, including all the samples containing between 10 and 35 per cent. of silicon showed *little or no action* on the silver nitrate paper and quantitative estimations subsequently made on some of these samples indicated either the entire absence or the presence of negligible amounts only of phosphoretted hydrogen in the samples.

In those instances where the silver nitrate paper showed a *dark brown colouration* (XXVII., 47 per cent. silicon) or a *deep orange brown* (XXXIX, 48 per cent. silicon) or where there was a *gradual blackening* of the silver nitrate paper, *i.e.*, arriving at completion after 5 to 15 minutes (XXVI., 49 per cent. silicon, and LV., 60 per cent. silicon) subsequent quantitative estimations of gases evolved showed an amount of phosphoretted hydrogen which was small in comparison with the quantities obtained in a third class of samples which caused an *immediate intense black* discolouration of the silver nitrate paper.

This last class of samples, causing an immediate intense black discolouration include by far the greater number of the samples containing from 42 to 96 per cent. silicon.

The following table summarises the results of this preliminary test, and I have added a fourth column showing the results of the subsequent quantitative estimation of gases evolved:—

Percentage of Silicon in Samples.	Effect produced on test-paper, moistened with silver nitrate solution, by gases evolved from 1 gramme of powdered ferro-silicon samples by the action of water at ordinary temperatures. Number of samples producing:—			Result of subsequent quantitative estimation of total Poisonous Gases evolved by the action of water and expressed in cubic feet per ton.
	(a.) Faint or no colouration.	(b.) Brown, orange, or gradual black.	(c.) Immediate intense black.	
10 to 35 per cent.	16	none	none	*Nil.* to 0·26
42 „ 52 „	1	4	28	2·1 „ 16·4
60 „ 75 „	none	2	7	1·0 „ 5·2
80 „ 96 „	none	2	4	2·1 „ 5·7

In most instances where an immediate intense blackening of the silver nitrate paper occurred, a similar reaction was given when the paper was held over the unmoistened powder, and usually a perceptible and sometimes very marked odour of phosphoretted hydrogen was noticeable.

I venture to suggest that this preliminary test might be of especial value, where a rapid examination of a sample of ferro-silicon was necessary, as indicating not only the presence or absence of phosphoretted hydrogen but also as affording a rough estimate of the proportion of this gas liable to be evolved in contact with moist air when the percentage of silicon in the sample is known or approximately known.

Quantitative Determination of Poisonous Gases Evolved from the Samples.

It will be obvious from a consideration of the chemical work already published (p. 70) that the object of the various investigators has been in each case to show that under the particular circumstances of a given fatality sufficient amounts of phosphoretted (and arseniuretted) hydrogen were yielded by the action of moist air on the ferro-silicon cargoes to produce an atmosphere containing a toxic proportion of these gases.

To prove this point, they took samples of the ferro-silicon, and having broken them up into small fragments, they placed them in a tube, flask, or other convenient vessel, so that moist air could be passed over the lumps and be subsequently examined by qualitative or quantitative tests. Great ingenuity and skill has been displayed in such experiments, but the processes employed were for the most part capable of affording approximative results only, and tended rather to under-estimate than otherwise the phosphorus and arsenic present in gaseous combination.

The problem I had before me in examining a large number of samples of ferro-silicon from very various sources was, however, of an entirely different character, for it was obvious, in the first place, that it was essential not only to prove the presence or absence of phosphoretted and arseniuretted hydrogen, but to make the experiments in such a manner as to compare all the samples without prejudice to any particular manufacturer.

In order to cope with this problem successfully it was clearly necessary to determine the *total poisonous impurities* in each of the typical samples examined. On this basis only was it possible to make a complete and entirely fair comparison. It further became necessary to devise some of the methods by which both the phosphoretted hydrogen and arseniuretted hydrogen could be accurately and separately determined, as especially in the case of the first-named gas no generally recognised methods have been suggested. I think, however, I have successfully overcome this difficulty.

Before describing my methods, reference must be made to the fact that while the estimation of the total poisonous impurities tends to emphasise the safety of some grades of ferro-silicon, it may perhaps somewhat exaggerate the potential danger pertaining to other grades, though not invariably. To make this point clearer, it is important to consider the total poisonous impurities in connection with the tendency already referred to (*see* Hardness, p. 76) of certain grades to disintegrate *spontaneously*, and so to offer a larger surface to the action of moist air, while it must not be forgotten that other grades, though brittle and not entirely free from poisonous impurities, are yet less dangerous since they do not show this tendency. Further reference to this point will be made later in discussing the results of the quantitative estimations.

Estimation of Phosphoretted Hydrogen.—After several attempts to oxidise the phosphoretted hydrogen by passage of the gas evolved from the samples into (1) nitric acid, (2) permanganic acid, (3) bromine water, &c., none of which methods proved satisfactory for various reasons, I finally made the following three series of experiments on a number of typical samples, approaching the estimation from three entirely different standpoints, with what, I think, may be considered a practically perfect agreement of results.

The following is a description of the methods employed :—

In all cases immediately before making the estimations the sample was powdered and three quantities of 10 or 20 grammes weighed at once and placed in three flasks of 100 c.c. capacity, with 20 c.c. of water, and the flasks corked.

Identical samples were thus secured, and the following three estimations carried out without delay.

(a.) *Estimation of Silver Precipitated from a Decinormal Solution of Silver Nitrate by the Gas Evolved from a Known Weight of the Powdered Sample by the Action of Water.* [$3Ag = PH_3$].—One of the flasks containing the sample mixed with water, as above described, was next fitted with a cork through which a piece of thermometer tubing, bent twice at right angles, was passed, a pipette being attached to the free end of this delivery tube. The flask with cork and fitted tubes attached was then fixed over a sandbath, and the end of the pipette arranged to dip to the bottom of a conical vessel containing 10 c.c. of decinormal silver nitrate solution (Fig. 7). The sandbath was then heated and the temperature gradually raised till the water in the flask boiled. As the gas evolved bubbled through the silver nitrate solution, a black precipitate of silver phosphide was immediately produced. The heating was continued usually for about ten to fifteen minutes until no more gas was evolved, which was proved by disconnecting the pipette from the delivery tube and testing the issuing steam with a moist silver nitrate paper, when usually no discoloration occurred or the faintest brown tinge was produced. The pipette was then rinsed into the conical vessel, and the silver solution filtered from the black precipitate which was washed until the washings were free from silver. To the filtrate was then added 10 c.c. of strong nitric acid and 5 c.c. of saturated iron alum solution, and it was then titrated with decinormal ammonium thiocyanate according to the well-known method of Volhard. The residual unreduced silver was thus estimated. By this process, which has the special advantage not only of extreme accuracy, but also of great rapidity, the weight of silver reduced by the gas evolved from a known weight of the sample is found.

From the relation $3Ag = PH_3$ the number of cubic centimetres of phosphoretted hydrogen corresponding to the weight of silver precipitated can be calculated. Absolutely identical results are obtained on repeating the estimations, provided that the material for experiment is taken from the same powdered sample.

(b.) *Estimation of Gold Precipitated from a Solution of Gold Chloride by the Gas Evolved from a Known Weight of the Powdered Sample by the Action of Water.* [$Au = PH_3$.]—In this estimation the same apparatus as described under (a.) was used, and the experiment carried out in exactly the same manner, except that the gas evolved was led into 25 c.c. of a solution of gold chloride containing about 0·5 per cent. of this salt. As the gas evolved bubbled into the gold chloride solution, an immediate precipitate of metallic gold occurred. At the conclusion of the experiment the pipette was rinsed out as described under (a.), and the partially reduced gold chloride solution was transferred to a porcelain dish, and evaporated to dryness on a water bath. On taking up with water, the reduced gold, which could now be easily collected on a filter without passing through, was washed, dried, ignited, and weighed. From the relation $Au = PH_3$ the number of cubic centimetres of phosphoretted hydrogen corresponding to the weight of gold precipitated can be calculated.

(c.) *Oxidation, and Estimation as Magnesium Pyrophosphate, of Phosphorus Precipitated as Silver Phosphide in a Solution of Silver Nitrate by the Gas Evolved from a Known Weight of the Powdered Sample by the Action of Water.* [$Mg_2P_2O_7 = 2PH_3$] —The experiment was carried out, in the first instance, in all respects exactly as described under (a.), but instead of filtering the reduced silver solution, this solution, together with the suspended silver phosphide, was transferred to a porcelain dish and warmed with nitric acid; the precipitated silver phosphide was thus oxidised to silver phosphate, which dissolved in the excess of nitric acid. The oxidised solution was evaporated to near dryness on a water bath, taken up with water, and sulphuretted hydrogen then pased through it until all the silver was precipitated as sulphide. On filtering and washing the precipitated

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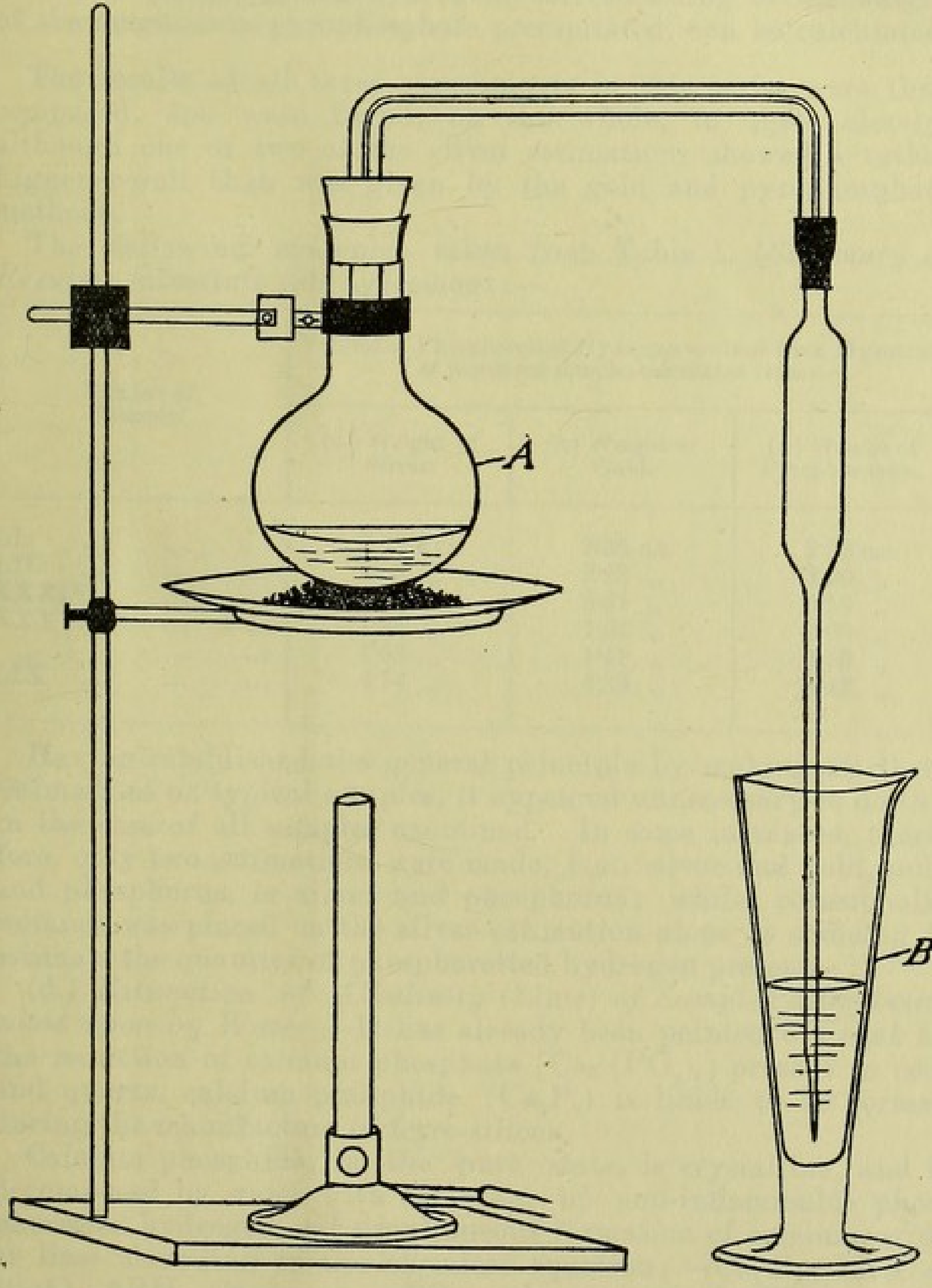
FIG. 7.

APPARATUS FOR ESTIMATION OF PHOSPHORETTED HYDROGEN.

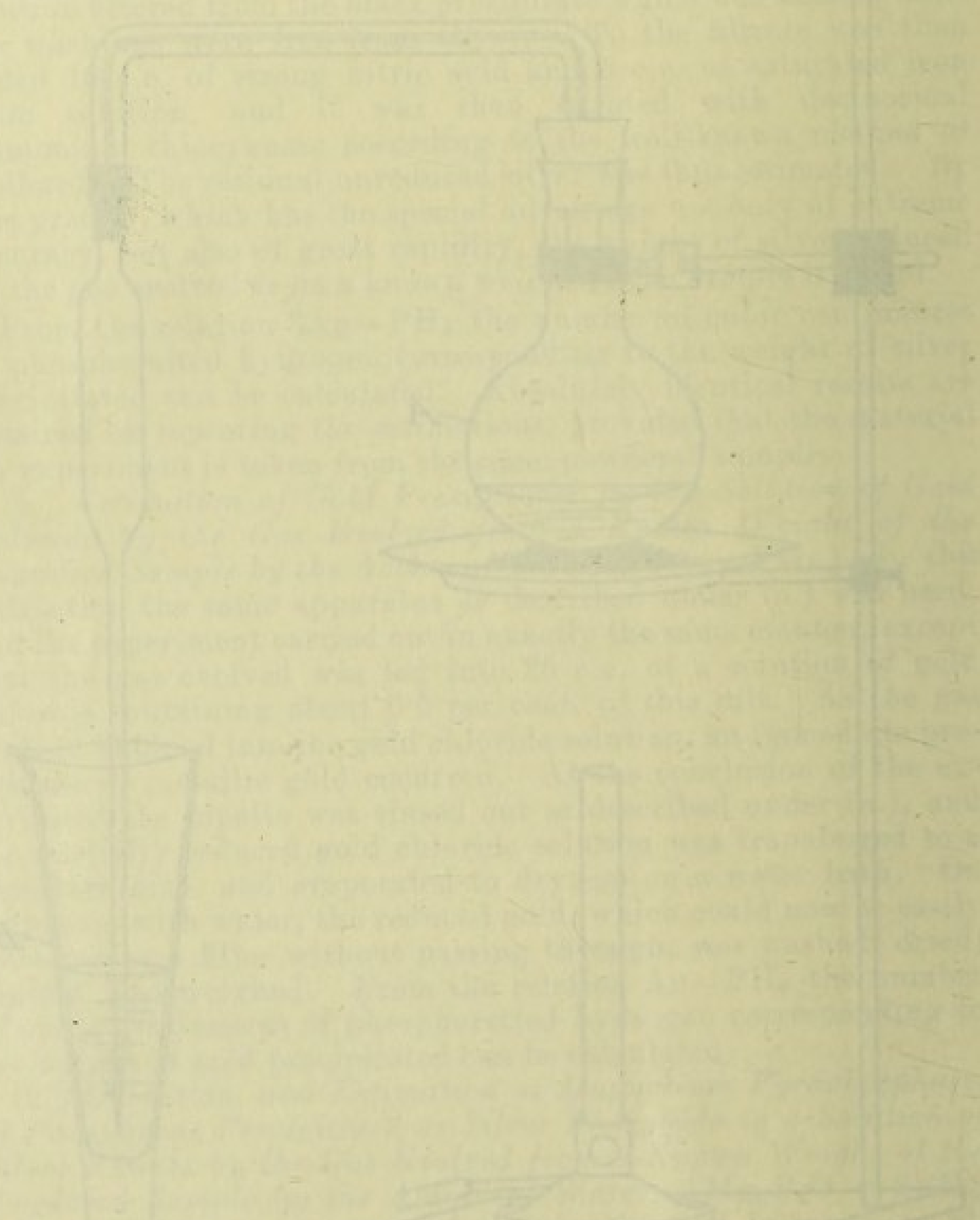


A. Flask containing 10 grammes of powdered ferro-silicon with 20 cc. water.

B. Conical vessel containing 10 cc. decinormal silver nitrate.

(*To face p.* 82.)

APPARATUS FOR ESTIMATION OF PHOSPHORETTED HYDROGEN.



silver sulphide, all the phosphorus was now present in the filtrate as phosphoric acid. Ammonia and ammonium chloride were next added, and the ammonium phosphate so formed precipitated with magnesium sulphate in the usual way; the precipitate, after duly washing and drying, being finally ignited and weighed as magnesium pyrophosphate.

From the relation [$Mg_2P_2O_7=2PH_3$] the number of cubic centimetres of phosphoretted hydrogen, corresponding to the weight of the magnesium pyrophosphate precipitated, can be calculated.

The results of all three experiments in this series were then compared, and were found, on the whole, to agree closely, although one or two of the silver estimations showed a rather higher result than was given by the gold and pyrophosphate methods.

The following examples, taken from Table I. (*Summary of Results*), illustrate this agreement:—

Number of Sample.	Volume of Phosphoretted Hydrogen evolved from 10 grammes of powdered sample, calculated from:—		
	(*a.*) Weight of Silver.	(*b.*) Weight of Gold.	(*c.*) Weight of Pyrophosphate.
LI.	2·52 c.c.	2·36 c.c.	2·50 c.c.
LII.	3·03 „	2·93 „	3·00 „
XXXIV.	3·60 „	3·61 „	3·50 „
XXXV.	1·26 „	1·01 „	1·08 „
„	1·63 „	1·41 „	1·50 „
LIX.	4·74 „	4·39 „	4·42 „

Having established the general principle by making all three estimations on typical samples, it appeared unnecessary to do this in the case of all samples examined. In some instances, therefore, only two estimations were made, *e.g.*, silver and gold, gold and phosphorus, or silver and phosphorus; while occasionally reliance was placed on the silver estimation alone as sufficing to estimate the quantity of phosphoretted hydrogen present.

(d.) *Estimation of Alkalinity* (Lime) *of Samples after being acted upon by Water.*—It has already been pointed out that by the reduction of calcium phosphate [$Ca_3(PO_4)_2$] present in coal and quartz, calcium phosphide (Ca_3P_2) is liable to be formed during the manufacture of ferro-silicon.

Calcium phosphide, in the pure state, is crystalline, and is decomposed by water with evolution of non-inflammable phosphoretted hydrogen and simultaneous formation of calcium oxide or lime according to the chemical equation:—$Ca_3P_2+3H_2O=3CaO+2PH_3$ (Moissan). When the vapour of phosphorus is passed over lime at a red heat a so-called impure phosphide of calcium is formed which yields with water the volatile liquid phosphoretted hydrogen (P_2H_4), which is spontaneously inflammable in contact with air (Thénard). The older chemists assumed the presence, in this compound, of a phosphide of calcium, of the formula CaP_2, but this compound has not been isolated.

I tested the samples of ferro-silicon after they had been acted upon by water and found that when any gas had been evolved the contents of the flask were invariably alkaline to litmus and that the water used contained free lime. I therefore made the following determinations of the alkalinity after the action of water in a large number of samples:—

The flask, with its contents, after the conclusion of the gold, silver, or phosphorus determinations, was corked and allowed to cool. 10 cubic centimetres of decinormal acetic acid was added to the contents, which were then shaken. After filtering and washing the insoluble residue in the filter till it was no longer acid, the filtrate was titrated with decinormal soda solution. From the residual free acetic acid so determined, the amount of lime present which had neutralised the remainder was calculated.

I had hoped that these lime estimations would add a fourth method to those already described for the estimation of phosphoretted hydrogen. But assuming the lime to have been originally present in the sample as calcium phosphide (Ca_3P_2), the quantities found corresponded, in the majority of instances, to only one-third or one-half of the volume of phosphoretted hydrogen found by the previous three methods, except in the case of samples containing from 60 to 96 per cent. silicon, where, for the most part, the agreement was fairly close, while in two instances an excess of lime was found.

I was at first somewhat puzzled to account for these discrepancies. Theoretically the amount of calcium phosphide formed in the manufacture of ferro-silicon should increase with the higher grades, inasmuch as more coal and more quartz are employed for the production of these grades, but, on reviewing the lime determinations, it would appear that as regards the production of this impurity there is no very great difference observable in the case of samples ranging between 42 per cent. and 96 per cent. silicon content.

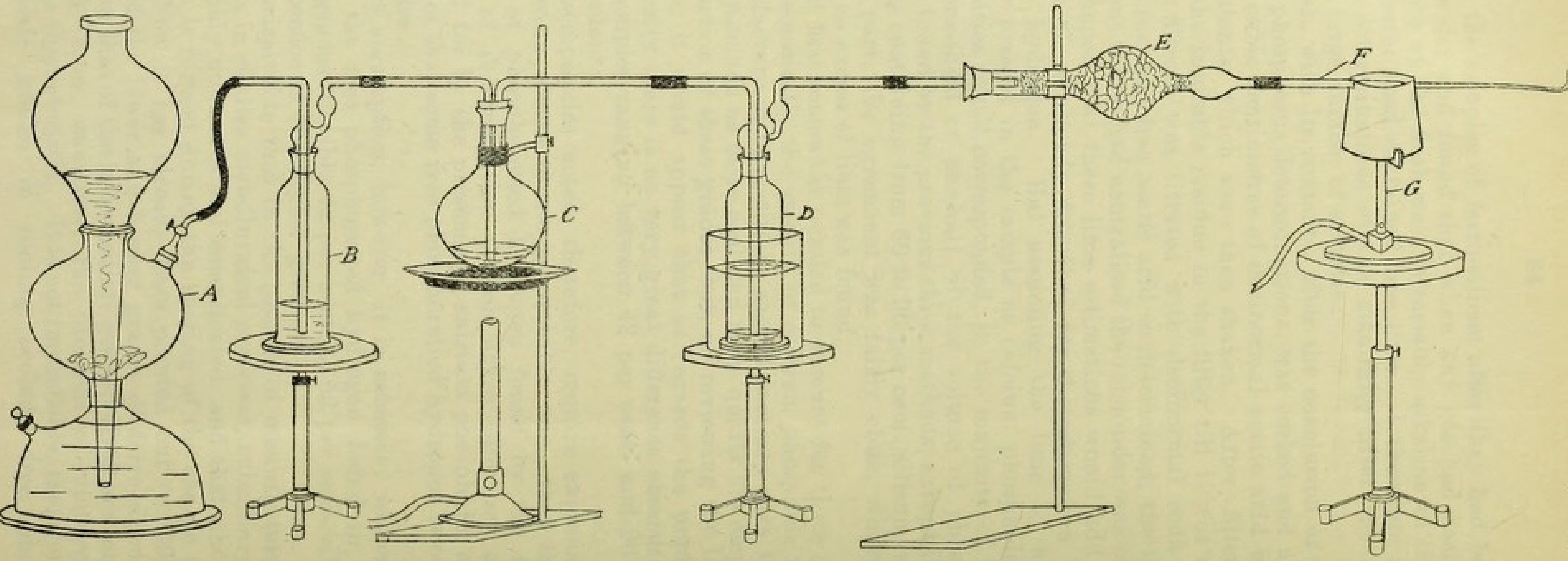
The discrepancies noted, therefore, require explanation, and the following occurs to me as probable, viz., that the greater amounts of phosphoretted hydrogen found by the first three methods of determination (which agree *inter se*) are partly accounted for by the presence of calcium phosphide, and partly by the fact that some free phosphoretted hydrogen is occluded in the samples.

On this assumption, however, it is necessary to account, not only for the free phosphoretted hydrogen found in the intermediate grades (notably 42 per cent. to 52 per cent. silicon), but for its absence in the higher grades.

It is conceivable that in the process of manufacture of ferro-silicon, as in similar metallurgical processes, subsidiary reactions are probably numerous and complicated, and that phosphoretted hydrogen is formed during the heating of the charge in the furnaces. Now it has already been pointed out (p. 69) that the *texture* of the lower and higher grades of ferro-silicon is much closer than that of the intermediate grades (42-52 per cent. silicon), in which latter, moreover, the presence of numerous bubble cavities is characteristic. It is not improbable, therefore, that the intermediate grades in cooling occlude free phosphoretted

Fig 8.

Apparatus for Demonstrating the Presence of Phosphoretted and Arseniuretted Hydrogen in Gases Evolved by the Action of Water on Ferro-silicon.



A. Kipp's apparatus for generating carbon dioxide.
B. Drechsel wash-bottle containing sodium bi-carbonate solution.
C. Flask containing 10 grammes of powdered ferro-silicon with 20 cubic centimetres of water.
D. Drechsel wash-bottle containing a little water.
E. Calcium chloride drying tube.
F. Jena glass tube heated with small Bunsen burner G.

(*To face p* 85.)

hydrogen during their production, while in the higher grades this gas is expelled at the higher temperature necessary for their formation.

The assumption of occlusion in certain grades is also strengthened by the sudden evolution of gas which occurs on breaking lumps of ferro-silicon containing about 50 per cent. of silicon. This sudden evolution of offensive gas which is so characteristic can scarcely be accounted for by the decomposition of calcium phosphide only, which, although it occurs rapidly in a moist atmosphere, is not instantaneous.

The suggested explanation is further to some extent confirmed by experiments I have made with reference to the effect of prolonged exposure of the samples to dry and moist air (*see* p. 89), but these experiments are not sufficiently extended to entirely justify the inference.

On the other hand, the excess of lime found in Samples LV. (60 per cent.) and XXXVI. (70 per cent.) might very well be due to previous decomposition by moisture of some of the calcium phosphide originally present.

Arsenic.—That arseniuretted hydrogen is present in some samples has already been demonstrated by previous investigators. Apparently, however, no attempt has been made to test directly for arsenic in the gas evolved by the action of water on ferro-silicon, to effect which I devised the following experiment:—

Carbon dioxide evolved from pure marble and pure hydrochloric acid in a Kipp's apparatus was passed first through a Drechsel wash-bottle, containing a solution of sodium bicarbonate, to arrest any traces of hydrochloric acid, and next into a flask containing the powdered ferro-silicon and water. This flask was fitted with an indiarubber stopper perforated by two tubes, one for the inlet of the carbon dioxide, the other for the outlet of the same gas, together with any other gases evolved. The mixed gases were then passed through another Drechsel wash-bottle containing a little water, and finally through a calcium chloride tube before passing through a narrow tube of Jena glass with its end drawn out, such as is used for the deposition of arsenic from a Marsh-Berzelius apparatus. The Jena glass tube was heated by a small Bunsen flame (*see* Fig. 8).

The carbon dioxide gas was first tested for arsenic by passing it for a considerable time through the apparatus before putting the flask containing the sample into connection. The flask containing 10 or 20 grammes of the powdered ferro-silicon together with 20 c.c. of water was then connected up and heated and the carbon dioxide slowly passed through.

In the majority of cases, with the exceptions noted in Table I. (*Summary of Results*), a black deposit was obtained, which in all instances was proved to be arsenic by the production of well-defined microscopic crystals (tetrahedra and octohedra) of arsenious oxide in the usual way.

I had hoped to estimate the arsenic by this method, by weighing the Jena tube before and after the experiment, and did in fact make a few such weighings. Obviously, however, some phosphorus was also deposited, the amount of which, though exceedingly small, proved sufficient to entirely vitiate the quantitative estimation of the arsenic. Sometimes the phosphorus was just visible as an orange deposit near the flame, while sometimes, though present, was not to be seen. I therefore resorted to another method of estimating the arsenic after the removal of the phosphoretted hydrogen which is described later.

These preliminary experiments however served a useful purpose, and it is for this reason that they are mentioned, viz., *they proved the simultaneous presence of phosphoretted and arseniuretted hydrogen in the gases obtained direct by the action of water on ferro-silicon samples.*

The phosphorus deposited with the arsenic in these experiments, was proved to be such by conversion into phosphoric acid with nitric acid and application of the molybdate test. Some experiments were made with calcium phosphide and water alone, under the same experimental conditions, the results of which showed that about 20 per cent. of the phosphorus present in the phosphoretted hydrogen evolved was thus deposited, the remaining 80 per cent. being volatilised.

Estimation of arsenic in the samples.—The gases evolved from 10 or 20 grammes of a powdered sample of ferro-silicon by the action of water, in the apparatus illustrated in Fig. 2 were passed into decinormal silver nitrate solution and the reduced silver solution filtered. Any traces of arsenic present would be contained in the filtrate in the form of arsenious acid (Hoffmann's reaction). The filtrate was then poured into a Marsh-Berzelius apparatus in which hydrogen was being evolved.

In nearly all cases, with some exceptions specially noted in Table I., arsenic was deposited as a mirror in the Jena glass tube and its weight obtained.

All the usual extreme precautions were taken in these estimations. The Marsh-Berzelius apparatus was entirely constructed of glass, the zinc and hydrochloric acid used for the evolution of hydrogen were specially tested for purity, &c., in the manner well known to toxicologists.

From the amount of arsenic obtained from a known weight of the sample the corresponding volume of arseniuretted hydrogen was calculated from the relation $As = AsH_3$.

The greatest amount of arsenic obtained from 10 grammes of any sample was 1·6 milligrammes. In some cases, however, the reaction was negative and in others varied from an unweighable trace to 1·2 milligrammes. The volumes corresponding to these weights are 0·0 cc. to 0·47 cc., or expressed as percentage volume of total poisonous gas evolved, from 0·0 per cent. to 13·0 per cent., the average being about 7·5 per cent. (*see* Table I., col. 10).

Approximate Expression of Volume of Total Poisonous Gases evolved from Samples by the Action of Water in Cubic Feet per Ton.

In column 9 of Table I. is given the approximate volume of poisonous gases evolved by the action of water on the various samples of ferro-silicon, expressed in cubic feet per ton.* These

* *Note.*—This calculation is made on the average volume of gas (in cc.) evolved from 10 grammes of the samples ; which figure, multiplied by 3·5, gives approximately cubic feet per ton.

TABLE I.

SUMMARY OF RESULTS OF EXAMINATION OF VARIOUS SAMPLES OF FERRO-SILICON RECEIVED THROUGH DR. COPEMAN.

[Not liable to Spontaneous Disintegration.]

(1.) Identification Number of Sample.	(2.) Date of Manufacture.	(3.) Percentage of Silicon.	(4.) Hardness.	(5.) Specific Gravity.	(6.) Qualitative Test for presence of Phosphoretted Hydrogen. Effect of gas evolved by action of Water only. (α) On Silver Nitrate paper.	(6.) (β) On Lead Acetate paper.	(7.) Estimation of Total Phosphoretted Hydrogen (mostly containing arseniuretted hydrogen) in gas evolved by Action of Water on 10 grammes of Sample. (a.) Weight of Silver precipitated from solution of N/10 Silver Nitrate.	(7.) (b.) Weight of Gold precipitated from solution of Auric Chloride.	(7.) (c.) Weight of Magnesium Pyrophosphate obtained by oxidation of Phosphorus in reduced Silver solution (a).	(7.) (d.) Weight of Lime produced by decomposition of Calcium phosphide in Sample.	(7.) Volume of Phosphoretted Hydrogen corresponding to (a.)	(b.)	(c.)	(d.)	(8.) Estimation of Arseniuretted Hydrogen in gas evolved by Action of Water only on 10 grammes of Sample. Weight of Arsenic obtained.	(8.) Corresponding Volume of Arseniuretted Hydrogen.	(9.) Approximate Volume of Poisonous Gases (evolved by action of moist air), expressed in Cubic Feet per Ton.	(10.) Percentage Volume of Arseniuretted Hydrogen in Total Poisonous Gases.
I	—	20	Very refractory	6·74	Very faint	Nil	—	—	—	—	—	—	—	—	—	—	—	—
XVII	—	20	Very refractory	6·66	Faint	Nil	—	—	—	—	—	—	—	—	—	—	—	—
II	—	23	Rather refractory	6·76	Very faint	Nil	—	—	—	—	—	—	—	—	—	—	—	—
III	—	24	Very refractory	6·47	Faint	Nil	—	—	—	—	—	—	—	—	—	—	—	—
XLVIII	1909	20	Refractory	6·37	Nil	Nil	—	—	—	—	—	—	—	—	—	—	Nil	—
XLIX	1909	24	Very refractory	6·34	Nil	Nil	Negative	—	—	—	Negative	—	—	—	—	—	Nil	—
IV	—	25	Rather refractory	5·96	Very faint	Nil	0·00108 grms.	—	—	—	0·074 c.c.	—	—	—	—	—	0·25	—
XXX	1909	25	Very refractory	6·38	Faint	Nil	—	—	—	—	—	—	—	—	—	—	—	—
XL	1909	25	Very refractory	—	Faint	Nil	—	—	—	—	—	—	—	—	—	—	—	—
LVII	1909	26·5	Extremely refractory	6·03	Faint	Nil	—	—	—	—	—	—	—	—	—	—	—	—
V	—	27	Refractory	6·30	Faint	Nil	—	—	—	—	—	—	—	—	—	—	—	—
L	1909	28	Refractory	6·27	Very faint	Nil	—	—	—	—	—	—	—	—	—	—	—	—
XXIV	—	29	Refractory	6·21	Very faint	Nil	Negative	—	—	—	Negative	—	—	—	—	—	Nil	—
XX	1908	30	Refractory	6·24	Very faint	Nil	0·00054 grms.	—	—	—	0·037 c.c.	—	—	—	Negative	Negative	0·13	0·00 %
LXX	—	35	Rather brittle	6·09	Very faint	Nil	—	—	—	—	—	—	—	—	—	—	—	—
LXXI	—	35	[In powder]	—	Very faint	Nil	—	—	—	—	—	—	—	—	—	—	—	—
XIX	1907	42	Rather brittle	4·93	Immediate intense black	Nil	0·06558 grms. (2) 0·07128 grms.	—	—	—	4·52 c.c. 4·88 c.c.	—	—	—	0·0031 grms.	0·33 c.c.	16·4	6·8 %
LI	1909	43	Very brittle	5·25	Immediate intense black	Nil	0·03672 grms.	0·0209 grms.	0·0125 grms.	0·00308 grms. 0·00336 grms. 0·00336 grms.	2·52 c.c.	2·36 c.c.	2·50 c.c.	0·81 c.c. 0·89 c.c. 0·89 c.c.	0·0005 grms.	0·15 c.c.	8·6	6·1 %
XXXIII	1909	45	Brittle	4·52	Immediate intense black	Nil	0·02382 grms.	0·0198 grms.	—	—	1·76 c.c.	2·22 c.c.	—	—	0·0004 grms.	0·12 c.c.	7·0	6·0 %
LXVII	1909	45	Brittle	4·95	Immediate intense black	Nil	0·0396 grms.	—	—	0·00672 grms.	2·74 c.c.	—	—	1·76 c.c.	0·0006 grms.	0·18 c.c.	9·7	6·6 %
LXVIII	1909	45	Brittle	4·91	Immediate intense black	Nil	0·03564 grms.	—	—	0·00588 grms.	2·46 c.c.	—	—	1·55 c.c.	—	—	8·7	—
LXIX	1909	45	Brittle	4·87	Immediate intense black	Nil	0·0486 grms.	—	—	0·00644 grms.	3·33 c.c.	—	—	1·70 c.c.	—	—	11·7	—
LII	1909	45	Brittle	4·65	Immediate intense black	Nil	0·04428 grms.	0·02582 grms.	0·0150 grms.	0·0070 grms. 0·0064 grms. 0·0042 grms.	3·03 c.c.	2·93 c.c.	3·00 c.c.	1·85 c.c. 1·70 c.c. 1·77 c.c.	0·0008 grms.	0·24 c.c.	10·4	8·0 %
LVIII	1909	46	Brittle	4·72	Immediate intense black	Nil	—	—	—	—	—	—	—	—	—	—	—	—
XXVII	1909	47	[In powder]	4·91	Dark brown	Nil	0·00216 grms.	—	—	—	0·15 c.c.	—	—	—	—	—	0·5	—
LXII	1909	47	Brittle	4·74	Immediate intense black	Nil	—	—	—	—	—	—	—	—	—	—	—	—
XXXIX	1909	48	Very brittle	5·19	Deep orange brown	Nil	0·00864 grms.	—	—	—	0·59 c.c.	—	—	—	—	—	2·1	—
LIII	1909	48	Very brittle	4·77	Immediate intense black	Nil	—	—	—	—	—	—	—	—	—	—	—	—
XXVI	1909	49	Brittle	4·59	Gradual intense black	Nil	0·01188 grms.	—	—	—	0·81 c.c.	—	—	—	0·0002 grms.	0·06 c.c.	2·8	7·3 %
VI	—	50	Very brittle	4·55	Immediate intense black	Slight brown	—	—	—	—	—	—	—	—	—	—	—	—
VII	1908	50	Extremely brittle	4·41	Immediate intense black	Nil	—	—	—	—	—	—	—	—	—	—	—	—
VIII	1905	50	Extremely brittle	4·22	Immediate intense black	Nil	0·05148 grms. 0·05048 grms. 0·04320 grms. (2) 0·04968 grms.	0·0248 grms.	—	—	2·29 c.c. 4·25 c.c. 2·96 c.c. 3·41 c.c. mean 3·23 c.c.	2·80 c.c.	—	—	0·0012 grms.	0·35 c.c.	11·0	11·1 %
IX	—	50	Very brittle	4·37	Immediate intense black	Nil	—	—	—	—	—	—	—	—	—	—	—	—
X	—	50	Very brittle	4·35	Immediate intense black	Nil	—	—	—	—	—	—	—	—	—	—	—	—
XI	1908	50	Very brittle	4·47	Immediate intense black	Nil	0·05616 grms. (2)	—	—	—	3·85 c.c.	—	—	—	—	—	13·5	—
XII	—	50	Very brittle	4·50	Immediate intense black	Nil	—	—	—	—	—	—	—	—	—	—	—	—
XXIII	1908	50	Brittle	4·83	Immediate intense black	Nil	0·00972 grms.	—	—	0·00252 grms.	0·67 c.c.	—	—	0·67 c.c.	—	—	2·4	—
XXXI	1909	50	Brittle	4·49	Immediate intense black	Nil	—	—	—	—	—	—	—	—	—	—	—	—
XXXII	1909	50	Brittle	4·87	Immediate intense black	Nil	—	—	—	—	—	—	—	—	—	—	—	—
XXXIV	1909	50	Brittle	4·83	Immediate intense black	Nil	0·05832 grms. 0·06048 grms. 0·05292 grms.	0·0283 grms. 0·0313 grms.	0·0160 grms. 0·0175 grms.	0·00784 grms. (2) 0·00840 grms. 0·01088 grms. 0·00896 grms. (2) 0·00952 grms.	4·00 c.c. 4·14 c.c. 3·60 c.c.	3·20 c.c. 3·61 c.c.	3·20 c.c. 3·50 c.c.	2·32 c.c. (2) 2·22 c.c. 2·06 c.c. 2·37 c.c. (2) 2·52 c.c.	0·0016 grms.	0·47 c.c.	12·6	13·0 %
XXXV	1909	50	Rather refractory	4·32	Immediate intense black	Nil	0·02376 grms. 0·01836 grms.	0·0125 grms. 0·0090 grms.	0·0075 grms. 0·0054 grms.	0·00336 grms. 0·00364 grms. 0·00392 grms. 0·00322 grms. 0·00336 grms. (2)	1·63 c.c. 1·26 c.c.	1·41 c.c. 1·01 c.c.	1·50 c.c. 1·08 c.c.	0·80 c.c. 0·96 c.c. 1·08 c.c. 0·85 c.c. 0·80 c.c. (2)	—	—	4·6	—
XLI	1909	50	Very brittle	—	Immediate intense black	Nil	—	—	—	—	—	—	—	—	—	—	—	—
LIV	1909	50	Brittle	4·44	Immediate intense black	Nil	—	—	—	—	—	—	—	—	—	—	—	—
LXIII	1909	50	Brittle	4·60	Immediate intense black	Nil	—	—	—	—	—	—	—	—	—	—	—	—
LXVI	1909	50	Brittle	4·37	Immediate intense black	Nil	0·01188 grms.	—	—	—	0·81 c.c.	—	—	—	0·0003 grms.	0·09 c.c.	2·3	11·1 %
XXVIII	1909	51	[In powder]	4·61	Very faint	Nil	—	—	—	—	—	—	—	—	—	—	Negligible	—
XXIX	1909	52	Very brittle	[illegible]	Gradual intense black	Nil	—	—	—	—	—	—	—	—	—	—	—	—
LIX	1909	52	Very brittle	4·[illegible]	Immediate intense black	Nil	0·06912 grms.	0·0389 grms.	0·0225 grms.	0·00644 grms. 0·00672 grms. 0·00672 grms.	4·74 c.c.	4·39 c.c.	4·62 c.c.	1·70 c.c. 1·78 c.c. 1·78 c.c.	0·0008 grms.	0·24 c.c.	15·8	3·3 %
LX	1909	52	Very brittle	[illegible]	Immediate intense black	Nil	0·06804 grms. 0·0540 grms.	—	0·0224 grms.	0·00896 grms. (2) 0·00840 grms.	3·70 c.c. 4·67 c.c.	—	4·48 c.c.	2·37 c.c. (2) 2·22 c.c.	—	—	15·0	—
XXV	1909	60	Very brittle.	3·[illegible]	Gradual intense black	Nil	—	—	—	—	—	—	—	—	—	—	—	—
LV	1909	60	Brittle	3·[illegible]	Gradual intense black	Nil	0·00432 grms.	—	—	0·00196 grms.	0·30 c.c.	—	—	0·51 c.c.	Not weighable.	Trace	1·0	Traces.
LXIV	1909	62	Brittle	3·[illegible]	Immediate intense black	Nil	—	—	—	—	—	—	—	—	—	—	—	—
XXXVI	1909	70	Rather brittle	2·[illegible]	Immediate intense black	Nil	0·0108 grms.	—	—	0·00588 grms.	0·74 c.c.	—	—	1·53 c.c.	—	—	2·6	—
LVI	1909	72	Brittle	[illegible]	Immediate intense black	Nil	—	—	—	—	—	—	—	—	—	—	—	—
XIII	—	75	Rather refractory	2·46	Immediate intense black	Nil	0·0216 grms. (2)	—	—	—	1·48 c.c. (2)	—	—	—	0·0004 grms.	0·12 c.c.	5·2	8·1 %
XXXVII	1909	75	Brittle	2·80	Immediate intense black	Nil	—	—	—	—	—	—	—	—	—	—	—	—
XLII	1909	75	Brittle	2·71	Immediate intense black	Nil	0·01512 grms.	0·0098 grms.	—	0·0042 grms. 0·00476 grms.	1·04 c.c.	1·10 c.c.	—	1·15 c.c. 1·26 c.c.	0·0002 grms.	0·06 c.c.	3·7	1·6 %
LXV	1909	75	Brittle	—	Immediate intense black	Nil	—	—	—	—	—	—	—	—	—	—	—	—
LXI	1909	80	Very brittle	2·56	Immediate intense black	Nil	0·02376 grms.	—	—	0·0049 grms.	1·63 c.c.	—	—	1·30 c.c.	—	—	4·6	—
XXXVIII	1909	90	Brittle	2·32	Immediate intense black	Nil	—	—	—	—	—	—	—	—	—	—	—	—
XLIII	1909	90	Brittle	2·35	Immediate intense black	Nil	0·00864 grms. (2)	—	—	0·00196 grms. (2)	0·59 c.c. (2)	—	—	0·52 c.c. (2)	—	—	5·7	—
XIV	—	87·5	Brittle	2·33	Gradual intense black	Nil	—	—	—	—	—	—	—	—	—	—	—	—
XV	1908	93	Rather refractory	2·44	Gradual intense black	Nil	—	—	—	—	—	—	—	—	—	—	—	—
XVI	1907	96	Brittle	2·32	Immediate intense black	Nil	0·00864 grms. (2)	—	—	—	0·59 c.c. (2)	—	—	—	0·0001 grms.	0·03 c.c.	2·1	5·1 %

[Not liable to Spontaneous Disintegration.]

A line thus — in any space means "not estimated"; (2) in any space means two estimations giving identical results.

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H. W. H.

EXAMINATION OF SAMPLES OF FERRO-SILICON AS TO PRESENCE OR ABSENCE OF DISINTEGRATION, AFTER THE LAPSE OF SOME MONTHS.

Class I.—10-30% (Page 87).

Identifying Number.	°/o Si.	Time elapsed since receipt of sample.	Present condition.
I	10	7¾ months	No signs of disintegration.
XVII	10	7¼ "	" " "
II	13	7¾ "	" " "
III	14	7¾ "	" " "
XLVIII	20	5 "	" " "
XLIX	24	5 "	" " "
IV	25	7¾ "	" " "
XXX	25	6¼ "	" " "
XL	25	5½ "	" " "
LVII	26·5	5 "	" " "
V	27	7¾ "	" " "
L	28	5 "	" " "
XXIV	29	7¼ "	" " "
XX	30	7½ "	" " "

Class II.—70-96% (Page 87).

XXXVI	70	6 months	No signs of disintegration.
LVI	72	5 "	" " "
XIII	75	7¾ "	" " "
XXXVII	75	6 "	" " "
XLII	75	5½ "	" " "
LXV	75	4½ "	" " "
LXI	80	5 "	" " "
XXXVIII	90	6 "	" " "
XLIII	90	5½ "	" " "
XIV	92·5	7¾ "	" " "
XV	93	7¾ "	" " "
XVI	96	7¾ "	" " "

Summary of Classes I. and II.—26 samples have shown no tendency to disintegrate during periods of 4½ to 7¾ months.

Class III.—35-60% (Page 87).

Identifying Number.	°/o Si.	Time elapsed since receipt of sample.	Present condition.
LXX	35†	3 months	No signs of disintegration.
XIX	42	7¼ "	" " "
LI	43	5 "	" " "
XXXIII	45	6 "	" " "
LXVII	45	3¾ "	" " "
LXVIII	45	3¾ "	" " "
LXIX	45	3¾ "	" " "
LII	46	5 "	Rather friable at edges.*
LVIII	46	5 "	Easily broken by the hand.*
LXII	47	4¾ "	No signs of disintegration.
XXXIX	48	5½ "	" " "
LIII	48	5 "	Easily broken by the hand.*
XXVI	49	7 "	No signs of disintegration.
VI	50	7¾ "	" " "
IX	50	7¾ "	" " "
XII	50	7¾ "	Easily broken by the hand.*
XXIII	50	7¼ "	Rather friable at edges.*
XXXI	50	6¼ "	No signs of disintegration.
XXXII	50	6¼ "	" " "
XXXIV	50	6¼ "	" " "
XXXV	50	6¼ "	Showing signs of disintegration.*
XLI	50	5½ "	" " " *
LIV	50	5 "	Marked signs of disintegration.*
LXIII	50	4¾ "	No signs of disintegration.
LXVI	50	4 "	" " "
XXIX	52	7 "	" " "
XXV	60	7¼ "	Easily broken by the hand.*
LV	60	5 "	" " " *
LXIV	62	4¾ "	Tending to become friable.*

Summary of Class III.—38 samples in all, of which 9 were either in powder or small fragments (when received) and are not placed in the above Table. Of the 29 samples in this Table, 11* have shown a tendency to disintegrate during periods of 4 to 7¾ months.

† Sample LXXI, which accompanied LXX, was in powder when received, said to be the result of disintegration, *see* Report, p. 76.

figures are given with a view to emphasising the potential danger of some grades of ferro-silicon in connection with its transport, storage, and use in large bulk; and when it is remembered that phosphoretted hydrogen acts fatally when present in so small a quantity as 2½ volumes of the gas in 10,000 volumes of air, and that arseniuretted hydrogen is scarcely less dangerous, it will be seen that the atmosphere of a cabin on board ship might under certain conditions, very rapidly assume a toxic character if ferro-silicon forms a part of the cargo, as has indeed been sadly demonstrated by the fatalities already recorded.

It is however only fair to those interested in the manufacture of ferro-silicon to recur to the observations made on p. 83 as to the relation of the total poisonous impurity to the possible danger arising from transport, storage, and use. In addition to the observations referred to I would therefore add that, as a general conclusion based on the examination of 64 samples (Table I.) these might be classified in three groups, viz.:—

Class I., 10 to 30 per cent. silicon, containing practically no poisonous impurities and not liable to spontaneous disintegration.

Class II., 70 to 96 per cent. silicon, not entirely free from poisonous impurities but also not liable to disintegrate spontaneously.

Class III., 35 to 60 per cent. silicon, containing, in most instances, a considerable proportion of poisonous impurities and in addition being more or less liable to spontaneous disintegration.*

Experiments to ascertain Effect of Exposure of Samples of Ferro-Silicon (1) *to Dry Air*, (2) *to ordinary Atmospheric Conditions.*

Quantities of 10 grammes of the powdered samples were weighed in watch-glasses, and (1) placed over sulphuric acid in a desiccator, (2) exposed to ordinary atmospheric conditions.

The results of these experiments may be briefly tabulated as follows:—

No. of Sample.	Percentage of Silicon.	Time of Exposure.	Volume of Poisonous Gases evolved by action of Water from 10 grammes ferro-silicon.		
			(*a*.) Before exposure.	(*b*.) After exposure to dry air.	(*c*.) After exposure to ordinary atmospheric conditions.
XXXV. ...	50 per cent.	9 days	1·11 cc.	0·96 cc.	0·18 cc.
LX. ...	52 ,,	14 ,,	3·7 ,,	3·7 ,,	2 9 ,,
LXI. ...	80 ,,	14 ,,	1 63 ,,	1·49 ,,	0·96 ,,

These experiments were only tentative. I was not able to make many, as I commenced them at a late stage of the work, but the conclusions to be drawn from them, so far as they go, are that in perfectly dry air little or no change occurs, while exposed to ordinary atmospheric conditions a varying loss of poisonous gas gradually takes place. It might be of advantage to pursue such experiments on a more extended scale.

* *Note.*—A summary of the quantities of poisonous gases found in these three classes is given in the Table on p. 80 in connection with the Preliminary Test for phosphoretted hydrogen.

In conclusion, I should like to express my indebtedness to Dr. Copeman for the great trouble he has taken in placing at my disposal a mass of information relating to the samples and to the literature of the subject, and for valuable suggestions as to the chief points to be elucidated in this enquiry.

I also take the opportunity of thanking my assistant, Mr. S. Bosworth, B.Sc., for the able help he has afforded me in preparing the figured diagrams, and especially in connection with the numerous details of this investigation.

H. Wilson Hake.

TABLE II.

Sources of Samples.

Identifying Number.	Percentage of Silicon.	Manufacturer.	Agent or Sender.
I.	10	Gjers Mills & Co., Middlesborough.	Per S. R. Bennett.
II.	13	" " "	" "
III.	14	" " "	" "
IV.	25	Not stated	Per G. G. Blackwell, Son & Co., Liverpool.
V.	27	" "	Per T. H. Watson, Sheffield.
VI.	50	" "	Per A. King.
VII.	50	" "	Per J. T. Dobb & Sons, Sheffield.
VIII.	50	" "	Per Birch & Co., London.
IX.	50	" "	Per G. G. Blackwell, Son & Co., Liverpool.
X.	50	" "	Per Board of Trade Surveyor, Middlesborough.
XI.	50	Société electro-metallurgique	Per T. H. Watson, Sheffield.
XII.	50	"From France"	" " "
XIII.	75	Not stated	Per G. G. Blackwell, Son & Co., Liverpool.
XIV.	92·5	" "	" " "
XV.	90	" "	Per C. Tennant & Sons, Newcastle.
XVI.	96	"Unknown"	Per G. G. Blackwell, Son & Co., Liverpool.
XVII.	10	Not stated	——
*XVIII.	24	" "	Per Robert Evans & Co.
XIX.	42	" "	Per G. G. Blackwell, Son & Co., Liverpool.
XX.	30	" "	Per Chalus & Sons, London.
†XXI.	30	" "	Per Willis & Co., Glasgow.
†XXII.	50	" "	Per G. G. Blackwell, Son & Co., Liverpool.
XXIII.	50	Cie electro-metallurgique Français Lapraz.	Per J. T. Dobb & Sons, Sheffield.

* Silico-manganese.

† Nos. XXI. and XXII. not included in Table I. owing to samples having been mixed in sending.

Identifying Number.	Percentage of Silicon.	Manufacturers.	Agent or Sender.
XXIV.	29	Not stated	Per T. H. Watson, Sheffield.
XXV.	60	" "	Per Chalus & Sons, London.
XXVI.	49	British Coalite Co., Wednesfield, Staff.	The Manufacturers
XXVII.	47	" " "	" "
XXVIII.	51	" " "	" "
XXIX.	52	" " "	" "
XXX.	·25	"La Volta," Soc. de l'Industrie electro-chimique St. Marcel.	" "
XXXI.	50	" " "	" "
XXXII.	50	Carbid Werk Deutsch-Matrei A. G., Meran, Autriche.	" "
XXXIII.	45	Soc. electro - chimique du Giffre St. Jeoire Hte. Savoie.	" "
XXXIV.	50	Carbid Werk Deutsch-Matrei A. G., Meran, Autriche.	" "
XXXV.	50	" " "	" "
XXXVI.	70	Soc. electro - chimique du Giffre.	" "
XXXVII.	75	Carbid Werk Deutsch-Matrei A. G., Jajce, Bosnie.	" "
XXXVIII.	90	" " "	" "
XXXIX.	48	British Coalite Co., Wednesfield, Staffs.	" "
XL.	25	Cie. Gle. d'electro chimique de Bozel.	" "
XLI.	50	" " "	" "
XLII.	75	" " "	" "
XLIII.	90	" " "	" "
*XLIV.	—	S.A. Electro-metallurgique, P. Girod, Ugine, Savoie.	" "
*XLV.	—	" " "	" "
*XLVI.	—	" " "	" "
*XLVII.	—	" " "	" "
XLVIII.	20	"La Volta" Soc. de l'Industrie electro - chimique (St. Marcel).	" "
XLIX.	24	" " "	" "
L.	28	" " "	" "
LI.	43	" " "	" "
LII.	46	" " "	" "
LIII.	48	" " "	" "
LIV.	50	" " "	" "
LV.	60	" " "	" "
LVI.	72	" " "	" "
LVII.	26·5	Keller Leleux & Cie., Cie electro-thermique, Livet, Isère.	" "
LVIII.	46	" " "	" "

* Nos. XLIV. to XLVII. not included in Table I. owing to the absence of any information relating to the percentage of silicon, &c. All four samples gave an immediate intense black coloration with silver nitrate paper. (*See* preliminary test, p. 78.)

Identifying Number.	Percentage of Silicon.	Manufacturers.	Agent or Sender.
LIX.	52	Keller Leleux & Cie., Cie electro-thermique, Livet, Isère.	The Manufacturers.
LX.	52	" " "	" "
LXI.	80	" " "	" "
LXII.	47	Soc. electro-chimique du Giffre.	" "
LXIII.	50	" " "	" "
LXIV.	62	" " "	" "
LXV.	75	" " "	" "
LXVI.	50	Kellner Partington Pulp Co., Sweden.	Per G. G. Blackwell, Son & Co., Liverpool.
LXVII.	45	S.A. electro-metallurgique, P. Girod, Courtepin Suisse.	The Manufacturers.
LXVIII.	45	" " "	" "
LXIX.	45	" " "	" "
LXX.	35	Maker unknown. "French"	Per G. G. Blackwell, Son & Co., Liverpool.
LXXI.	35	" " "	" "

H. W. H.

REPORT ON COMPOSITION AND STRUCTURE OF FERRO-SILICON.

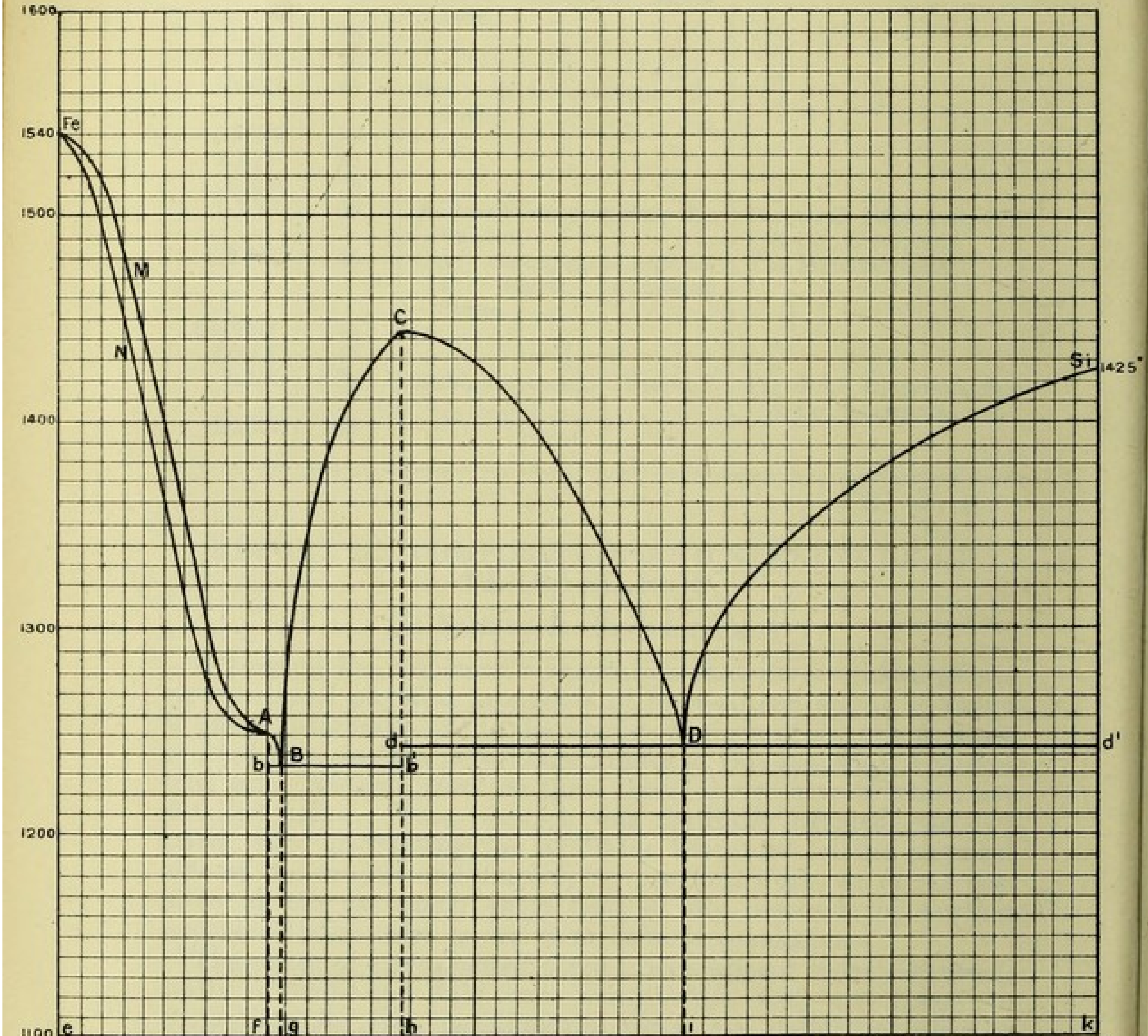
By Samuel R. Bennett, M.A.

Acting on Dr. Copeman's suggestion that investigation of the structure and physical properties of ferro-silicon might be found to afford information as to the source of origin of dangerous gases evolved from certain percentage grades of this material, I undertook some research work on these lines, the results of which are detailed below. This research was naturally divided into two parts, viz., abstracting the available literature on the physical side of the subject and amplifying previous work, as far as possible in the extremely short time at my disposal, by further experiments in order to arrive at definite conclusions.

The series of alloys called ferro-silicon appear to consist essentially of two—and only two—constituents, *i.e.*, are binary in formation, for even in industrial forms the impurities seem to exert but little influence on the microstructure. As a matter of fact, in ferro-silicon as at present manufactured the percentage of impurity is small compared with the early products of the electric furnace.

The first comprehensive investigation into the manner in which iron and silicon exist in the various grades of this alloy was made by Guertler and Tammann* with alloys prepared by melting together in the electric furnace almost pure constituents in varying

* W. Guertler and G. Tammann, "Über die Verbindungen des Silicium mit dem Eisen." Zeitschrift für anorganische Chemie 1905, Bd. 47, s. 163.
Paul Goerens, "Introduction to Metallography," translated by Fred. Ibbotson, B.Sc., A.R.C.S.I.



PERCENTAGES OF SILICON BY WEIGHT

FIG. 9.

(To face p. 91.)

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proportions as required. Figure 9 has been constructed from their original diagram in order to show more readily these results and compare the properties of the alloys as met with in use. In the figure ordinates represent temperatures, and abscissæ the percentages by weight of Si present. Transformations occurring in the solid state below 100° C. were not fully investigated. Corresponding to the maxima of the liquidus FeABCDSi two chemical compounds are shown—one Fe_2Si freezing at 1,251° C. with 20 per cent. Si by weight at the point A, and the other FeSi at C with 33·3 per cent. Si by weight and freezing at 1,443° C. Also two eutectics (alloys of maximum fusibility) are shown at B and D. B consists of Fe_2Si and FeSi—(21·6 per cent. Si)—and freezes at 1,235° C.; D consists of FeSi and Si, and freezes at 1,245° C.

Above the liquidus all the material is in a molten condition, whilst below the solidus $FeNAbBb^1dDd^1Si$ every alloy is completely solid. Between the liquidus and solidus the material will in each case be partly molten and in part solidified according to the temperature. For all alloys up to 20 per cent. of Si, Fig. 9, solidification begins by the formation of mixed crystals of Fe and Fe_2Si in the molten material in the region FeMAN. Below the solidus FeNA and in the region FeNAfe there is solid solution of Fe_2Si as primary crystallites. A 20 per cent. grade of ferro-silicon of this class consists of the compound Fe_2Si which solidifies wholly at the definite temperature 1,251° C., but the microstructure will depend on the subsequent rate of cooling. Alloys between 20 per cent. Si and 21·6 per cent. Si commence to solidify at the curve AB, and in the region ABb consist of Fe_2Si together with molten material. When the temperature 1,235° C. is reached, final solidification takes place of the eutectic Fe Si + FeSi round the primary crystals of Fe_2Si, and below this temperature in the region Bbfg this structure will be exhibited. Solidification commences on the curve BCD for all alloys between 21·6 per cent. Si and 60 per cent.; in the region $BCDdb^1$ any one will consist of primary crystals of FeSi in molten material. For alloys between 21·6 per cent. Si and 33·3 per cent. Si complete solidification takes place at the eutectic temperature 1,235° C., and below which in the area Bb^1hg the structure exhibited will be primary crystals of FeSi in a field of eutectic B. But alloys between 33·3 per cent. Si and 60 per cent. solidify completely at 1,245° C., and in the solid state in the region Ddhi consist of crystals of FeSi immersed in eutectic D of FeSi and Si. Finally alloys between 60 per cent. Si and pure Si begin to freeze at the curve DSi; in the region of $SiDd^1$ each will consist, according to concentration, of crystallised Si surrounded by molten material. At the eutectic temperature residual solidification takes place, and in the region Dd^1ki the structure will be crystals of Si in a ground of eutectic D.

Guertler and Tammann confirmed the form of their diagram from which Fig. 9 is deduced by microscopic examination.

It has been demonstrated also by experiment* that FeSi cannot enter into low grade ferro-silicons, being easily dissociated into Fe_2Si and Si according to the equation $2FeSi = Fe_2Si + Si$.

* Comptes Rendus, Vol. 133, No. 24, 1901.

Moissan* investigated the properties of the compound Fe_2Si, and isolated the silicide in small prismatic crystals possessing a high metallic lustre of density about 7·0 at 22° C. It is magnetic, but FeSi is non-magnetic. Hahn† has indicated the existence of an amorphous silicide Fe_2Si which treated with hydrofluoric acid leaves a residue of silky FeSi. FeSi has a density of 6·17 at 15° C., according to P. Lebeau.‡ Both Moissan and Lebeau claim to have isolated $FeSi_2$, while the existence of Fe_3Si_2 has also been asserted.

Experiments on Specific Volumes.

The work of E. Maey§ went to prove that for any binary alloy consisting of a mechanical mixture of its two constituents the specific volume follows the " mixture law " as calculated from the constituent specific volumes. If compounds or solid solutions existed in the alloy departures from the law resulted. The diagram in Fig. 9 shows that solid solutions are only found in grades below 20 per cent. Si by weight. Consequently departures from the " mixture law " above 20 per cent. can only indicate compounds. To get an indication as to whether more than the two silicides shown in Fig. 9 existed, experiments were made determining densities as functions of composition for various grades.

The densities of twenty-four samples of ferro-silicon ranging from 13·6 per cent. to 96 per cent. Si were determined in forty-six experiments. Although the various grades examined were by no means uniform in composition, the values given in the following table for the mean densities found are, in all probability, accurate within ±2 per cent. error.

Densities of Ferro-Silicon Alloys.

Percentages of Silicon.			No. of Samples.	No. of Experiments.	Mean Density.	Remarks.
Weight.	Volume.	Atomic.				
13·6	32·1	24	1	2	6·90	Temp. 65 deg. F. Bar. 29·7 in.
26·1	51·5	41·5	1	2	6·55	Mean throughout all experiments.
27·2	53	42·7	2	2	6·47	Variations from mean density range 0·15.
28	54	43·7	2	4	6·25	
29·5	55·7	45·5	2	4	6·17	
30·5	57	46·7	2	3	5·88	
33·3	60	50	1	3	6·10	
42	70	59	2	4	5·05	
50	75	66·6	4	7	4·68	
52·8	77	69	3	5	4·46	
58	80·5	73·5	1	3	3·90	
92·8	97·5	96	2	5	2·49	
96	98·5	98	1	2	2·46	

* Comptes Rendus, 1895.
† Annalen der Chemie und Pharmacie t. 129, p. 57.
‡ Comptes Rendus, Vol. 128, No. 15, 1899.
§ Zeitschrift f. Phys. Chem. Bd. 3.

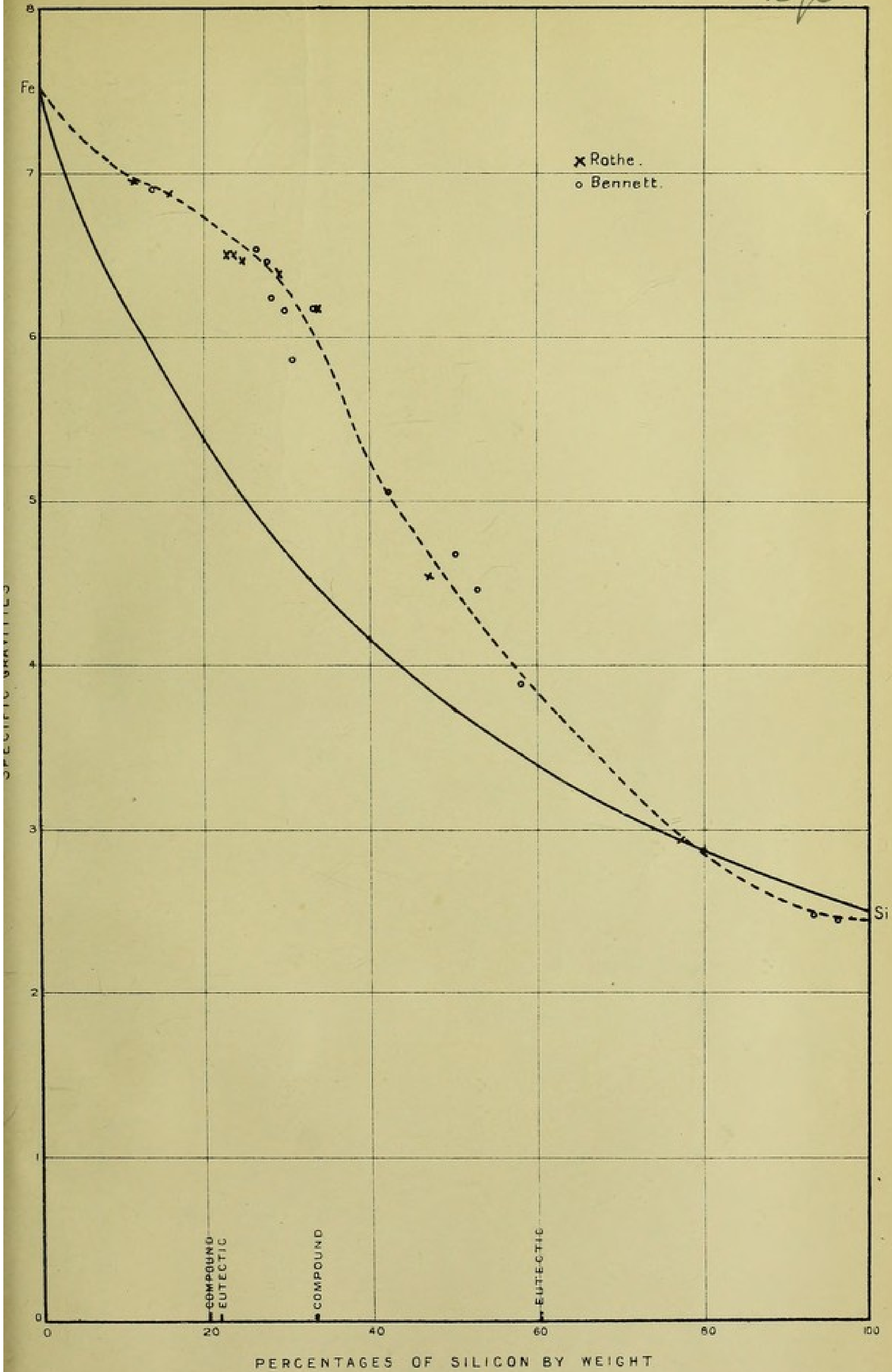

FIG. 10.

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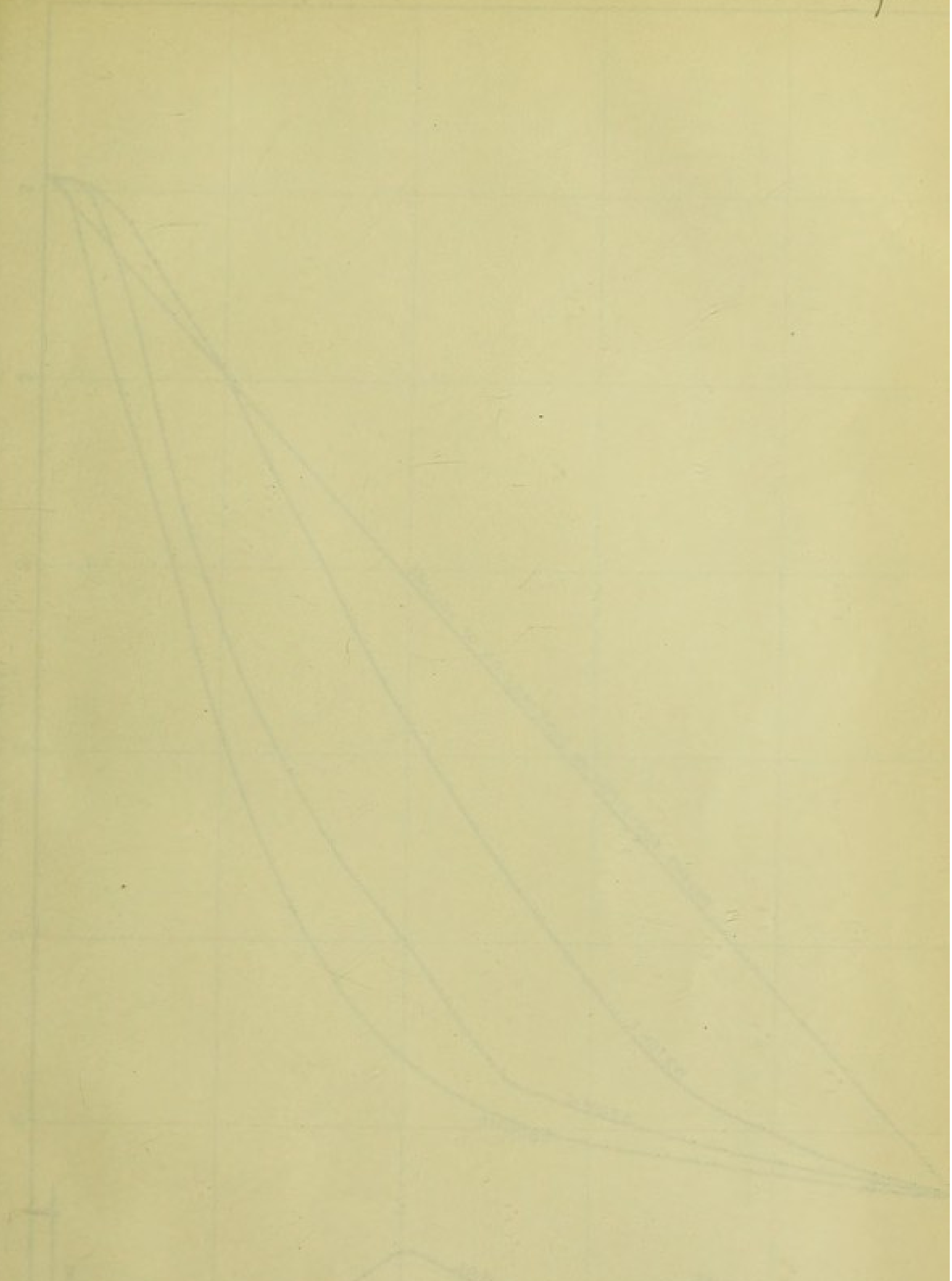
Compare with Figure 5. Showing Dr. Wilson Hake's experimental determinations.

(To face p. 92.)



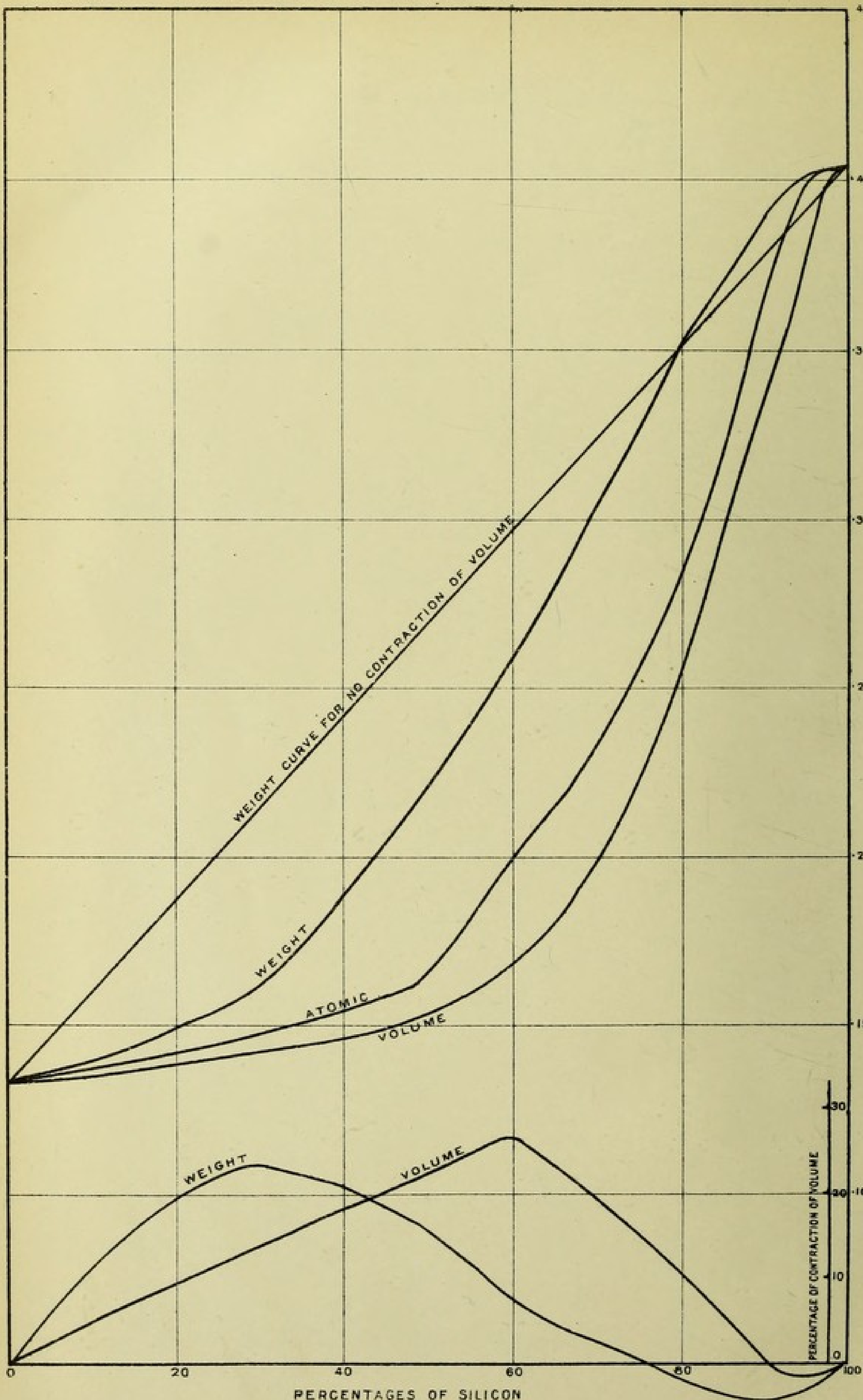


FIG. 12.

(To face p. 93)

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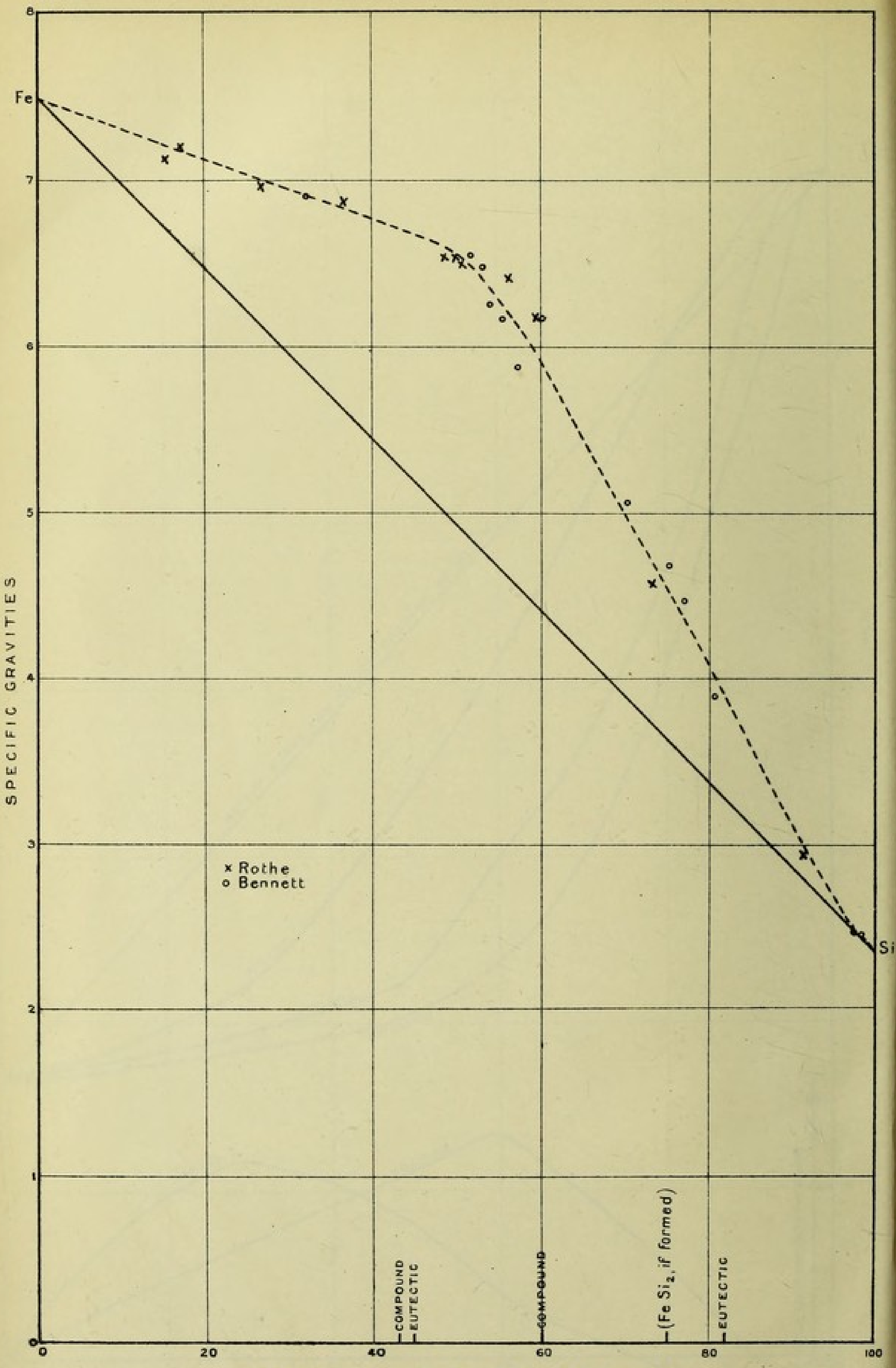

FIG. 11.

(To face p. 93.)

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Specific gravities of ferro-silicon alloys have also been determined by J. Rothe (Mitteilungen aus dem königlichen materialprüfungs amt zu Grosslichterfelde West) with the results set out in the following table:—

Test.	°/。 Si.	Sp. gr.	Temp., &c.
No. 1	11·58	6·96	20·3
„ 2	15·81	6·88	20·7
„ 3	22·83	6·51	17·3
„ 4	23·47	6·51	19·5
„ 5	24·26	6·48	17·2
„ 6	29·04	6·40	19·9
„ 7	32·05	6·18	16·7
„ 8	47·25	4·55	21·0
„ 9	77·29	2·93	19·6

The results of these density experiments when plotted against the percentages of silicon, as has been done in Figures 10 and 11, show complete accord with those determined by Rothe—in fact, the two sets supplement each other to a large extent, and are so used in what follows. In Figures 10 and 11 are also given as continuous lines the theoretical curves which the experiments would have given had there been no contraction or expansion of volume in the alloys.

These figures show, however, that a considerable contraction of volume occurs in the alloys, especially in the neighbourhood of the compounds Fe_2Si and FeSi.

Underneath the specific volume curves in Figure 12 are given curves showing percentage contraction of volume corresponding for the weight curve to percentages of silicon by weight, and for the volume curve to percentages of silicon by volume. From these curves, but perhaps more clearly from Figure 11, it will be seen that the presence of a silicide $FeSi_2$ is very unlikely in the case of the particular industrial alloys examined, although the peculiar physical properties of the 50 per cent. grade of ferro-silicon (corresponding to 75 per cent. by volume) would have inclined one to the view that perhaps it was a definite chemical compound, solid solution, or eutectic in structure.* Also the existence of Fe_3Si_2 is not definitely indicated in the specific volume curves, or at least it produces no further increase of variation from the "mixture law" than Fe_2Si and FeSi, of which it might presumably be composed.

Experiments on Micro-structure.

Very little work has been published on the micro-structure of ferro-silicons. Dr. Thomas Baker illustrated his paper on "The influence of Silicon on Iron"† with two micro-photographs, one of a 27 per cent. grade and the other 81 per cent. grade, but no corresponding complete analyses were given. Several difficulties are

* *Cf.* American Electrochemical Society's Transactions, 7, pp. 251–270, 1905. Article by A. B. Albro.

† Journal of Iron and Steel Institute, No. II., for 1903.

encountered in attempting to examine or photograph some specimens of this alloy under the microscope. One of these is, that of etching, and on this point I quote Mr. J. H. Wreaks, Demonstrator and Lecturer in Metallography and Metallurgy at the University of Sheffield, to whom also I desire to express my thanks for his kindness in examining samples of 27 per cent., 30 per cent., and 50 per cent. ferro-silicon submitted to him:—"The specimens were ground, polished, and cleansed with alkali in the usual manner, then immersed in cold, strong nitric acid. Hydrofluoric acid was then added drop by drop, say, one drop every half minute, until the polished surface presented a *slightly* frosted appearance. During the wet grinding (surfacing) of the samples an objectionable smell, faint but distinct, was observed. Each specimen also showed, when examined under the microscope, prior to etching, a pitted surface. These pits may be blowholes; they may be the holes from which some substance (*e.g.*, calcium phosphide, carbide? &c.) has been decomposed and removed by the water used during grinding operations, or from which a brittle material has fallen during preparation (general) for microscopic examination.

"The three ferro-silicons examined conformed in microstructure with the deductions to be expected from the curve of Guertler and Tammann. The 27 per cent. and 30 per cent. materials each showed a ground mass (presumably FeSi) upon which was scattered patches of eutectic (presumably $Fe_2Si + FeSi$)."

The difficulty of etching seems to have been overcome satisfactorily in Figures 13 and 14, which represent microphotographs of the same specimen of a fairly pure 27 per cent. ferro-silicon—the impurities being 0·38 to 0·4 per cent. carbon and 0·3 per cent. manganese, phosphorus less than 0·1 per cent., and only a trace of sulphur. In these figures the apparently octahedral crystals of FeSi are seen in similar orientation surrounded by the typical eutectic laminated structure. Fig. 15 gives a clue to the formation of these crystals, the mass of compound (FeSi) (indicated by the arrowhead) being seen in the act of breaking up at the moment when solidification occurred.

The preparation of a good specimen of approximately 50 per cent. ferro-silicon is almost impossible, as the material readily crumbles away. Mr. Wreaks suggests that comparison of an analysis of the finer detrital matter obtained by a process of selective attrition or cautious crumbling with that of the mass remaining should give some information as to the structure and the position occupied by impurities. He further suggests that the traces of impurities (Ca, Al, S, &c.) may be extruded from, and form exceedingly thin films around the primary crystals produced during freezing. A. B. Albro* says that under high magnification the extremely brittle ferro-silicon of about 50 per cent. Si has a characteristic structure of octohedra. However, the micro-sections I have examined agree apparently with the acceptance of this ferro-silicon as a binary alloy, in substantial agreement with Guertler and Tammann's curve.

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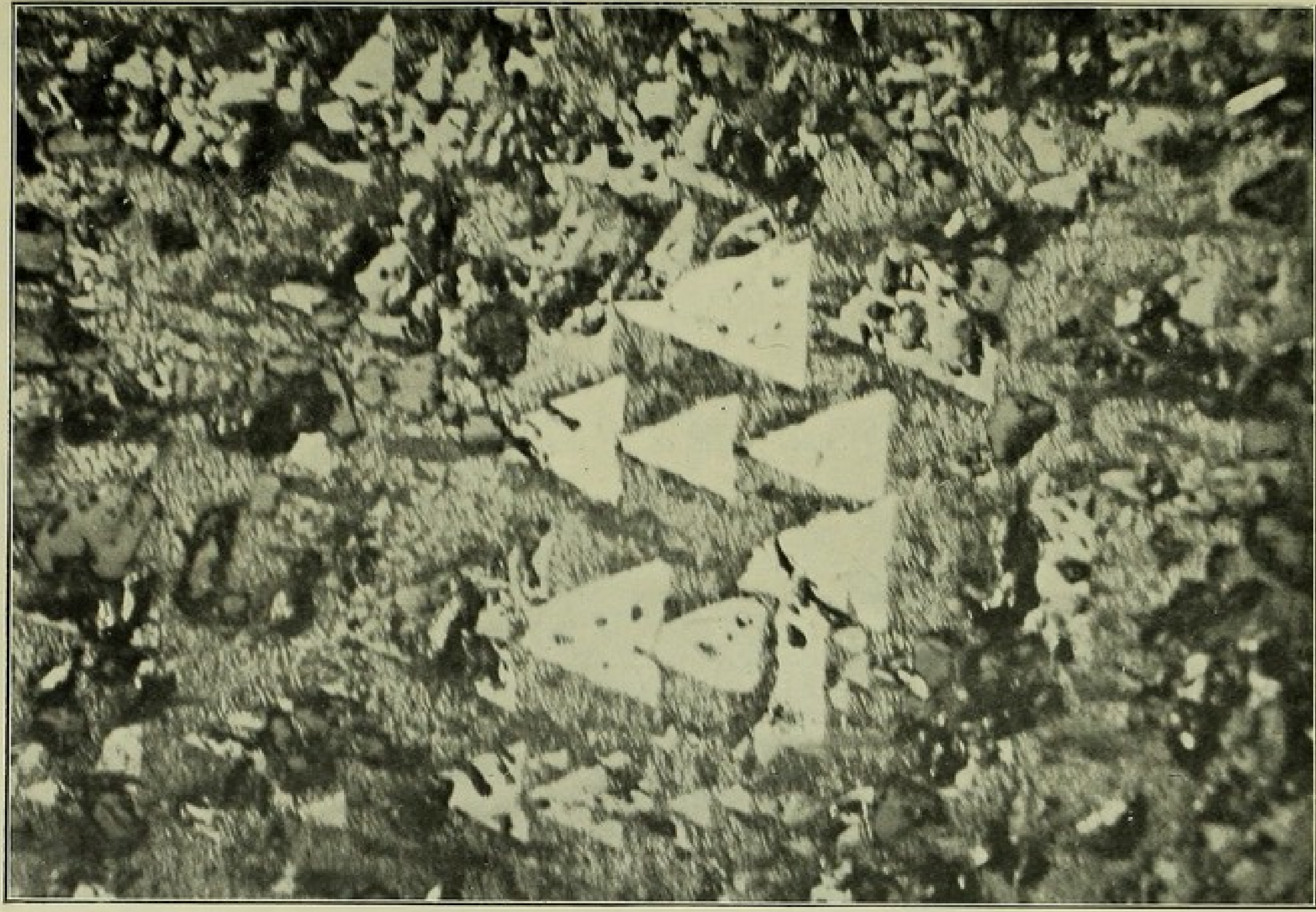
* Amer. Electrochem. Soc. Trans. 7, 1905.

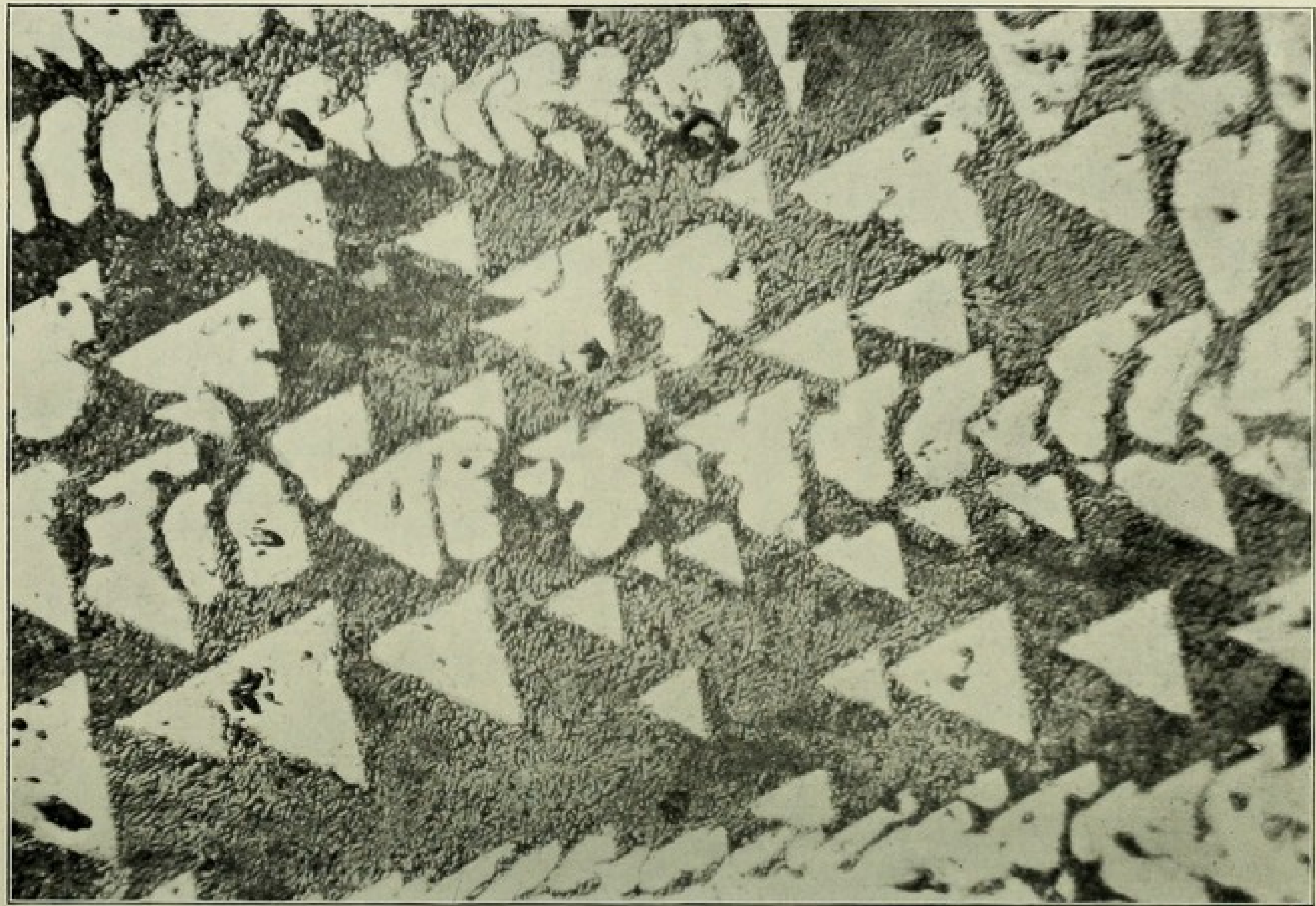
Fig. 13.



Micro-photograph of 27 per cent. ferro-silicon. Magnification 100 diameters. Specimen etched with aqua regia. Focussed for central crystals.

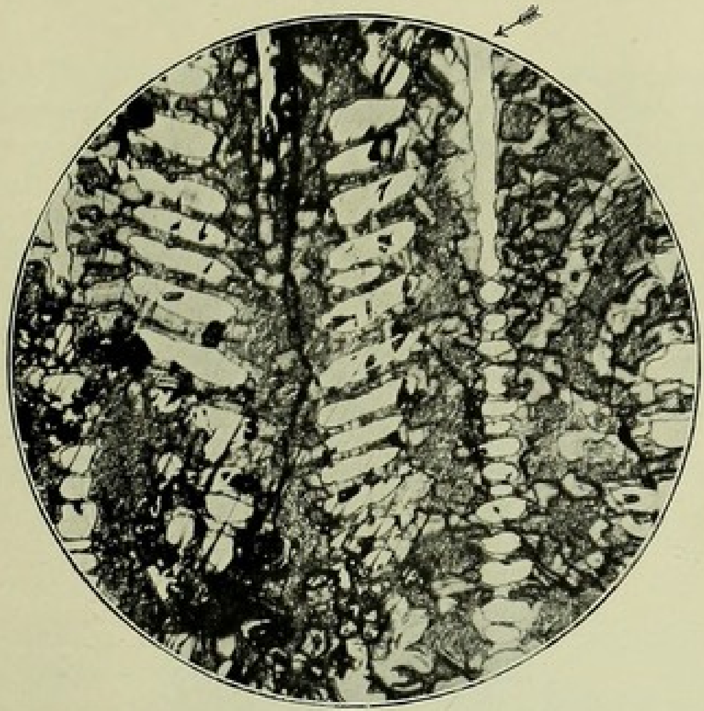
(To face p. 94.)

FIG. 14.



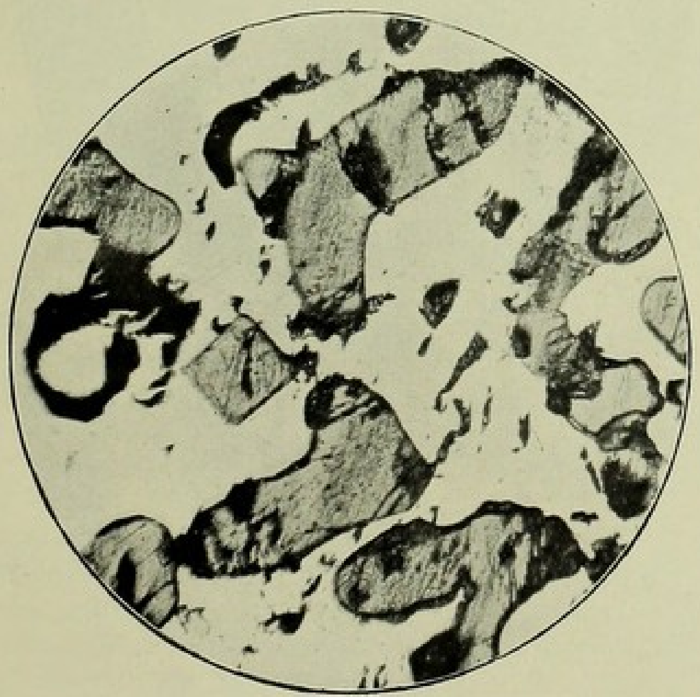
Micro-photograph of 27 per cent. ferro-silicon. Magnification 100 diameters. Specimen etched with aqua regia.

Fig. 15.



Micro-photograph of 23·1 per cent. ferro-silicon. Magnification 100 diameters.
Specimen etched with boiling hydrochloric acid.
For further description *see* page 94.

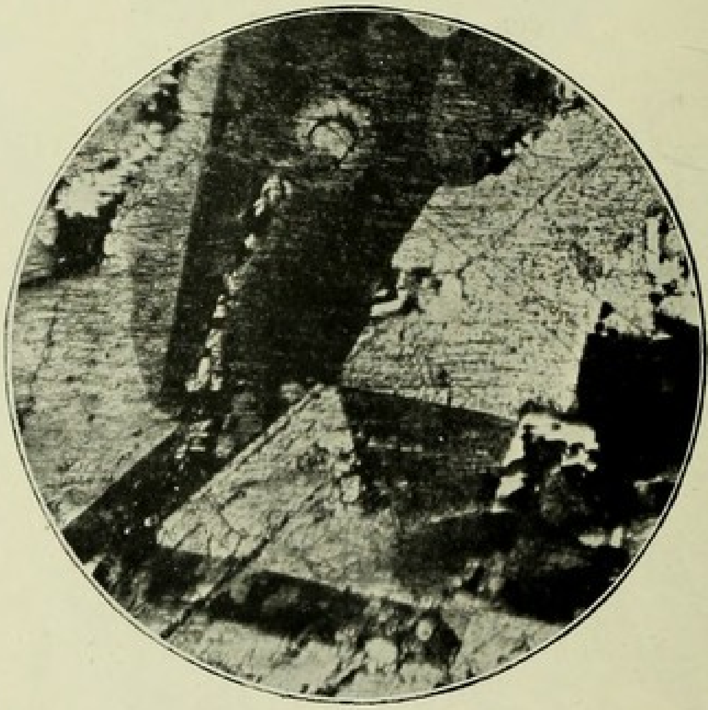
Fig. 16.



Micro-photograph of 50 per cent. ferro-silicon. Magnification 100 diameters.
Direct illumination. Etched with hydrochloric acid.

The black areas represent holes from which brittle material, almost certainly part of the eutectic, has been broken during preparation of specimen. The dark laminated areas represent eutectic (FeSi + Si) which has been acted on by the etching medium. The remaining field of white has not been acted on by the acid and simply shows a fine polished surface.

Fig. 17.



Micro-photograph of 92 per cent. ferro-silicon. Magnification 100 diameters. Etched with caustic soda.

The photograph (Fig. 17) shows clearly large octohedral crystals of silicon surrounded by eutectic (FeSi + Si) which has fallen out in many places. Comparison of this with the photograph of 81 per cent., given in Mr. Baker's paper, exhibits identity of structure in principle, there being (as is to be expected from Guertler and Tammann's curve) a greater proportion of eutectic in the latter. As regards the structure of approximately pure Silicon, Albro finds that the crystals fracture easily on planes that were vertical during solidification, this structure being unaffected by heat variations of temperature short of the melting point.

I may mention that all the microphotographs were taken under direct illumination.

Conclusions.

(1.) The various percentage grades of ferro-silicon are substantially binary alloys.

(2.) Two compounds, Fe_2Si and FeSi, exist; the former corresponding to 20 per cent. Si, and the latter to 33·3 per cent. Si, by weight. Microstructure also indicates the existence of two eutectics, one consisting of Fe_2Si and FeSi corresponding to 21·6 per cent. Silicon approximately, and the other consisting of FeSi and Si at 60 per cent. Silicon.

(3.) Investigation of the specific volumes of various grades of alloys does not indicate the presence of other compounds.

(4.) Up to 20 per cent. Si the alloys consist of solid solutions of Fe and Fe_2Si which are hard, firm masses giving off little or no gas. Alloys from 20 per cent. Si to 21·6 per cent. Si consist of primary crystals of Fe_2Si in ground of eutectic composed of Fe_2Si and FeSi; these alloys begin to get more brittle than the lower grades. From 21·6 per cent. Si to 33·3 per cent. Si the structure shows FeSi surrounded by eutectic Fe_2S and FeSi; from 33·3 per cent. to 60 per cent. Si there are crystals of FeSi in eutectic FeSi + Si; and above 60 per cent. Si crystals of Si in field of eutectic FeSi and Si.

(5.) The amount of gases given off by different grades of ferro-silicon depends not only on the impurities present in the materials used in the electric furnaces, but also on the physical properties of the alloys in consequence of which, in certain cases, access of moisture is afforded to a much larger extent of surface.

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S. R. Bennett.

TRANSPORT AND STORAGE OF FERRO-SILICON.

Action taken by Shipping and Railway Companies.

In this country, at any rate, attention was first directed to the possible danger incidental to the transport and storage of ferro-silicon, by the occurrence of a series of explosions at the Liverpool Docks in 1904, an account of which has been set out in an earlier section of this report (see pp. 11 and 12).

About that time, as I am informed by Mr. Beck, of the firm of Matthew Beck & Co., of Liverpool, who at that time represented the Compagnie Générale d'Electro-Chimie, of Paris, negotiations had been opened with various shipping firms for the carriage of this material to America viâ Liverpool. In view, however, of the facts disclosed by the report of Dr. Dupré, F.R.S., and Captain Lloyd, who investigated the circumstances attending the explosions at Liverpool, the various shipping companies included in what is known as the "Atlantic Combine," as well as a number of other companies, including practically all those owning vessels sailing from Liverpool, appear to have jointly undertaken an enquiry into the subject. Samples of ferro-silicon of all grades were obtained from several quarters and analysed by Mr. Norman Tate, of Liverpool, who reported that high-grade ferro-silicon gives off gases of a poisonous nature which cannot be detected altogether by smell.

In view of this report and of conferences with Professor Lewis, of the Royal Naval College, Greenwich, and with Dr. Dupré, the shipping firms concerned came to the conclusion that the material is dangerous to carry from the shipowners' point of view; and thereupon announced, in April, 1905, that they would only carry ferro-silicon, in bulk, which is the product of the blast-furnace, and the value of which does not exceed £12 per ton.

It may be mentioned that the "Atlantic Combine" includes the following Shipping Companies:—

White Star Line;
Leyland Line;
Red Star Line (to the Continent);
American Line;
Dominion Line;

other companies outside the "Combine," who decided also to decline consignments of ferro-silicon, included:—

Clan Line;
Hall Line;
Anchor Line;
Furness Allan Line;
Canadian Pacific Line;

while three Companies, whose vessels do not carry passengers:—

Johnston Line;
Manchester Line;
City Line (to the Bristol Channel);

agreed only to accept ferro-silicon for carriage (on deck), by special arrangement.

On learning of the decision arrived at by the "Atlantic Combine" and other shipping companies, Messrs. Beck & Co. at once communicated with the Compagnie Générale d'Electro-Chimie, expressing regret that the investigation instituted by the Combine had resulted so unfavourably, and adding that they would be glad to place in the right quarter any further information the Compagnie Générale should send, which might be likely to induce the Combine to modify, to some extent, the conclusion arrived at.

In reply, the Compagnie Générale, which by this time had adopted the title (by which it is still known) of the Comptoir International de Vente du Ferro-Silicium, forwarded a lengthy statement, in which, after referring to the chemical and physical properties and method of manufacture of ferro-silicon produced in the electric furnace, expressed the opinion, "without fearing contradiction," that "ferro-silicon is not any more dangerous or objectionable than many other chemicals . . . . which are accepted as freight without giving the matter a moment's thought."

They further asserted that they were "assured by numerous experts" that no reaction could take place "by coming in contact with other chemicals or sea-water so as to produce . . . phosphoretted hydrogen"; while as to arseniuretted hydrogen "there can be absolutely no question raised, as ferro-silicon positively contains no arsenic. Ferro-silicon is neither explosive, inflammable, poisonous, nor a dangerous substance." As regards the accidents at the Liverpool Docks, "we are creditably informed that the cause of the explosion was not due to the ferro-silicon but to the calcium carbide, which was accidentally intermixed at the ferro-silicon works."

These somewhat dogmatic statements did not, however, carry conviction in the desired quarter, as is evidenced by the fact that the shipping companies concerned apparently took no steps to reverse the decision at which they had previously arrived. It was not until three years (in April, 1908) later, so far as I have been able to learn, that any special action was taken by shipping companies other than those enumerated above. The information, however, having been afforded to me in confidence, I am, of course, unable to enter into details.

Much of the ferro-silicon coming to Sheffield was, until recently, at any rate, consigned viâ Antwerp and Grimsby, in vessels owned by the Great Central Railway. Acting on a report, supplied by the Superintendent of their Chemical Laboratory, to the effect that it is impossible to carry ferro-silicon on board ship without danger, the Company, under date November 26th, 1908, issued a notice to their Antwerp Agents, through Messrs. Sutcliffe & Son, their Agents at Grimsby, to the following effect:—

DEAR SIRS,

Ferro-silicon.

Please note that owing to the dangerous nature of this traffic, it must not be accepted for conveyance by the Great Central Railway Company's steamers trading between Grimsby and your Port.

Kindly acknowledge receipt and oblige—

Yours truly,

(Signed) JOHN SUTCLIFFE & SON.

According to custom, the Antwerp Agents, on receipt of this notice would, in turn, advise all other firms concerned. Under date December 23rd, 1908, Messrs. Thos. Wilson, Sons, & Co., Ltd., of Hull, issued a printed slip stating that "Ferro-silicon must not be put on board our steamers, unless on the open deck, and at its Owner's Risk." The issue of this notice was doubtless due to the fact that investigation of the circumstances attending the death of five Russian emigrants on the steamship "Ashton," in the course of that vessel's voyage to Grimsby where she arrived on December 13th, 1908, had already afforded reason for the belief that these deaths were to be attributed to poisoning by the fumes of ferro-silicon. And in this connection, it is of interest to note that the Antwerp Agents for the Great Central Railway, by whom this particular consignment of ferro-silicon had been accepted for shipment to Grimsby, are also Agents for Messrs. Thos. Wilson, Sons, & Co., Ltd. It appears that this lot of ferro-silicon was shipped, notwithstanding the notification of the previous month by Messrs. Sutcliffe & Son in their letter, owing to the fact that the firm from whom it was accepted had given a definite assurance that this particular consignment had been manufactured by a new and improved process which entirely obviated possibility of danger. Unfortunately, also, on account of the bad weather which had been experienced by the steamship "Ashton" on her passage *from* Grimsby, and the likelihood of its continuance, the ferro-silicon was packed in the vessel's hold, instead of on deck as originally had been intended.

In January, 1909, a Conference of Steamship Owners and Agents, representing a number of other East Coast Lines, adopted a unanimous resolution to the effect that "this traffic (*i.e.*, ferro-silicon) is not to be carried."

Messrs. Wilson, of Hull, in an explanatory letter to a correspondent, dated February 12th, 1909, defined their position with regard to the transport of ferro-silicon as follows:—"The only condition on which we can carry this article (ferro-silicon) is for the firms interested in same to convince the Board of Trade, by expert evidence, that ferro-silicon containing less than a certain percentage of silicon is entirely harmless, and to get the latter to issue a notice to shippers to this effect. In that case, of course, the packages would have to be marked to the effect that the contents are under a certain percentage of silicon." In this same letter, Messrs. Wilson express regret that, on the strength of their Analyst's report to the effect that ferro-chrome contains a certain percentage of silicon and arsenic, they could not continue carrying this article on their steamers, either below or on deck. This additional prohibition, however, was shortly afterwards withdrawn at the instance of the Board of Trade.

A month later, Messrs. Wilson, in forwarding me certain particulars which I had requested of them, stated that "At present we are declining to carry the article (ferro-silicon), and this is no doubt causing considerable inconvenience to manufacturers in this country."

In illustration of further action in respect of absolute refusal to accept ferro-silicon for transport by important shipping companies, the following notice, the issue of which promptly followed on recognition of the cause of the fatalities on the steamship "Ashton," may be cited:—

SPECIAL NOTICE TO SOUTH AND EAST AFRICAN SHIPPERS.

Dangerous Goods.

London, 6th January, 1909.

Having regard to the great danger to life and property attendant upon the conveyance in steamships of dangerous cargo, unless specially stowed, and owing to the growing tendency of shippers and suppliers to omit to obtain the shipowners' sanction for the shipment of such cargo before sending the same alongside, the undersigned steamship lines respectfully desire to call attention to the clauses of the "Merchant Shipping Acts," whereby shippers of dangerous goods are required, under heavy penalties, to mark the nature of the goods on the outside of the packages, and to give written notice of their contents and of the name and address of the senders to the owners of the vessel.

The special attention of shippers is also directed to the extremely dangerous nature of Ferro-Silicon (Pyrites Siliceuse), which is said to have recently caused the death of a number of passengers in a steamer carrying this article, and *notice is hereby given that* FERRO-SILICON *cannot be accepted for shipment under any circumstances.*

THE UNION-CASTLE MAIL STEAMSHIP COMPANY, LIMITED.
Donald Currie & Co., Managers.
THE CLAN LINE STEAMERS, LIMITED,
Cayzer, Irvine & Co., Ltd., Managers.
THE BUCKNALL STEAMSHIP LINES, LIMITED.
THE NATAL DIRECT LINE,
Bullard, King & Co.
THE ABERDEEN DIRECT LINE,
John T. Rennie, Son & Co.
THE ELLERMAN LINE } Joint Service.
THE HARRISON LINE }
THE HOUSTON LINE,
R. P. Houston & Co.
THE BRITISH INDIA STEAM NAVIGATION COMPANY.

Notwithstanding, however, that practically all the chief shipping companies have determined, under existing circumstances, to discontinue acceptance of consignments of ferro-silicon from abroad, a certain amount of the material continues to reach this country, owing to the fact that certain owners, in order to obtain trade, are willing to accept possible risk. As a consequence, what business remains has been transferred from East Coast to West Coast ports, and, at present, practically all consignments, comparatively small in amount, from France, Austria, and Italy to this country, are being shipped from Treport to Manchester. From Sweden, also, the traffic has now been diverted from Hull to Manchester, an alteration of route which is stated to have involved considerable pecuniary loss. At this latter port, as I learned, the cargoes are discharged into "flats," in which they are taken back to Liverpool, and from thence conveyed to Sheffield and elsewhere by rail. But owing to the fact that some, at any rate, of the high-percentage ferro-silicon still coming from abroad is consigned under the name of iron-ore or other similar designation, it is practically impossible for the port authorities to afford any reliable statistics as to the actual amount of this material imported.

There can, however, be no doubt that agents' and manufacturers' stocks are becoming depleted, and that, in consequence, especially as no electrically produced ferro-silicon is being produced in this country, considerable anxiety exists as to how future needs for this material are to be met.

OFFICIAL CIRCULARS, NOTICES, AND REGULATIONS, ISSUED IN THIS COUNTRY AND ABROAD, IN REFERENCE TO THE TRANSPORT AND STORAGE OF FERRO-SILICON.

Immediately on the occurrence of certain fatal accidents on board the steamship "Olaf Wyjk," of which an account is given in an earlier section of this report (see p. 15, *et. seq.*), the Swedish

Government instructed Professor A. Werner Cronquist, of Stockholm, to investigate the circumstances of the case. His report on this investigation, in which he was assisted by Dr. J. Petrén, Professor of Metallurgy in the Technical High School of Stockholm, was issued on May 7th, 1907.

The gist of this report was communicated in the form of a Memorandum to the British Home Office, by whom it was forwarded to the Board of Trade. This Department, in view of the importance of the results of Professor Cronquist's investigation, and of the conclusions arrived at, as to hitherto unrealised danger incidental to the transport and storage of ferro-silicon, and the consequent necessity for the observance of certain precautionary measures, issued and circulated a notice, in September, 1907, in the following terms:—

NOTICE TO SHIP-OWNERS, SHIP-MASTERS AND SHIPPERS.

Ferro-Silicon.

The Board of Trade have received from the Home Office the following Memorandum relative to the dangerous properties of ferro-silicon :—

"Professor Cronquist, of Stockholm, who was instructed to investigate the causes of the death of four of the passengers on board the Swedish steamer 'Olaf Wijk,' confirms the view that their death must be attributed to the gases given off by ferro-silicon contained in the hold under the cabins.

"High-grade ferro-silicon, although it has been known to chemists for many years, has only recently been prepared on a large scale for technical purposes ; *i.e.*, for adding to steel to increase the proportion of silicon ; in steel rails about 0·5 per cent. of silicon is required in the finished steel, and in high silicon castings about 0·25 per cent.

"It is made by heating together iron ore, quartz, coke and lime (as a flux) to an enormously high temperature in the electrical furnace ; the coke reduces the quartz and ore to silicon and metal, with the production of ferro-silicon containing up to 80 per cent. silicon. It is generally packed in iron drums or casks for export.

"Certain kinds of ferro-silicon seem to be decomposed, or rather disintegrated into powder by the action of moist air ; this apparently is not dependent on the proportion of silicon present, as specimens containing up to 80 per cent. silicon have been found to remain unchanged for weeks.

"Its poisonous properties can be simply explained by the fact that it is liable to evolve phosphoretted and arseniuretted hydrogen in contact with moisture. The iron ore and quartz often contain phosphates, which, in presence of carbon, and at the high temperature of the electrical furnace, would no doubt be converted into phosphides, combining with the lime to form calcium phosphide ; in the same way any arsenic present would yield calcium arsenide. These would be decomposed in presence of water and evolve phosphoretted and arseniuretted hydrogen, both of which possess powerful poisoning properties.

"The explosions that have occasionally occurred are more difficult to explain, and various theories have been put forward to explain them.

"These properties of ferro-silicon indicate that considerable danger is connected with its transport, not only to persons on the ship, but to dock labourers engaged in unloading it at docks.

"*Primâ facie*, it seems that the presence of moisture is the cause of the accidents, and every effort should be made to ensure that the material is in a dry condition when packed, and that there is no possibility of moisture gaining access to the receptacles containing it."

WALTER J. HOWELL,
Assistant Secretary.

Marine Department,
Board of Trade,
September, 1907.
M. 18898—1907.

The subsequent occurrence of further fatalities, especially those on board the steamship "Ashton," in December, 1908 (see p. 22, *et. seq.*), further aroused the apprehensions of various shipping and other transport companies to such an extent that in several instances, as previously stated, notices were issued by them that consignments of ferro-silicon would no longer be accepted under any circumstances. Refusal of transport for this material naturally gave rise to considerable loss of trade by the foreign firms producing high-grade ferro-silicon, and to much inconvenience among steel manufacturers and others by whom ferro-silicon is necessarily employed in various trade processes. And, in consequence, numerous requests were received by the Board of Trade that, in order to re-assure shippers and their agents, regulations should be issued by that Board governing the conditions under which this substance might be conveyed by sea or rail.

In view of these requests, and in order to meet the case so far as was possible pending the completion of my official investigation, the Board of Trade in March of this year (1909) issued a second notice in terms as follows, differentiating between the innocuous low-grade ferro-silicon made in a blast furnace, and the high-grade electrically-produced alloy:—

NOTICE TO SHIPOWNERS, SHIPMASTERS AND SHIPPERS.

Ferro-Silicon. (Second Notice.)

The Board of Trade are advised that after inquiry no facts have been ascertained indicating that low grade ferro-silicon made in a blast furnace is dangerous, and, this being so, they are not aware of any reason why it may not be safely carried on board ship as ordinary cargo without any special precautions.

Upon the information at present before the Board they think that no objection need be raised to the shipment of this kind of ferro-silicon provided each consignment is accompanied by a certificate from the maker or shipper to the effect that it is low grade ferro-silicon made in a blast furnace and contains not more than 15 per cent. of silicon.

WALTER J. HOWELL,
Assistant Secretary.

Marine Department,
Board of Trade,
March, 1909.

M. 5413—1909.

Four months later, in July, 1909, the following official regulations dealing with blast-furnace ferro-silicon, the terms of which are somewhat similar to those of the Board of Trade notice, was issued from the India Office:—

REGULATIONS TO BE OBSERVED IN CONNECTION WITH THE CARRIAGE OF FERRO-SILICON IN VESSELS CONVEYING STORES FOR THE GOVERNMENT OF INDIA

Ferro-Silicon will only be allowed shipment when in the form of pigs.

A certificate must be produced with each shipment, stating that the Ferro-Silicon does not contain more than 15 per cent. of Silicon, and has been made in a blast furnace.

The certificate should be obtained by the shipowner from the shipper, and sent with a notification of shipment to the Surveyor of Shipping, India Office, Royal

Albert Docks, if the shipment is made in London; to Messrs. Melly & Co., if made in Liverpool; and to Captain Livingstone, 35, Dunearn Street, Glasgow, if made in Glasgow.

The Ferro-Silicon should be stowed as far as possible from the crews' quarters.

W. G. BUTLER,
Director-General of Stores.

India Office,
1st July, 1909.

In Sweden, where, owing to abundance of cheap water-power, industries depending on the use of the electric furnace have been growing somewhat rapidly during the past few years, the report of Professor Cronquist, on the case of the "Olaf Wyjk," was speedily followed (in September, 1907) by the appointment of a Government Commission, composed of Professor Cronquist, his colleague in the original enquiry, Dr. Petrén, and Mr. T. A. Leffler, Expert Metallurgist of the Association of Swedish Ironmasters. The terms of reference of this Commission included the investigation of dangers incidental to the storage and transport of ferro-silicon, and the drawing up of "legal regulations in order to prevent accidents."

Application has been made, through the Foreign Office, to the Swedish Government for a copy of the Report of this Commission, which, however, up to the time of writing has not been received.

But in a paper read before the recent International Congress of Applied Chemistry (London, 1909), Professor Cronquist gave an account of the various accidents known to have been caused by ferro-silicon, and of certain investigations undertaken by the Commission to establish the conditions under which poisoning from ferro-silicon came about. In this paper he refers to the loss of 19 lives in persons of different nationalities, as follows:—

7 Russian and Finnish	On 8 ships, of which—
6 German	4 were sailing under the German flag
3 Swedish	2 ,, ,, ,, British ,,
2 British	1 ,, ,, ,, Swedish ,,
1 French	1 ,, ,, ,, Finnish ,,

Professor Cronquist's paper further records a series of experiments carried out with the object of determining the origin of the phosphoretted hydrogen derived from ferro-silicon, and the circumstances under which it is evolved; and concludes with certain suggestions for preventing such evolution.

As the result of the Commission's findings, of which Professor Cronquist's paper would appear to be, in some sort, a *resumé*, the Swedish Government issued certain provisional instructions for the storage and transport of ferro-silicon in the form of a Royal Ordinance, copies of which, accompanied by a translation, were forwarded to the Foreign Office, from the British Embassy at Stockholm on July 19th, 1908.

The covering letter states that the Ordinance was signed on June 17th, 1908, published on July 18th, and was to come into force immediately.

The terms of this Ordinance are as follows :—

Translation.

We Gustaf, &c., &c., considering it necessary that precautionary measures should be taken for the storage and transport of Ferro-Silicon (kiseljärn), have decided that provisional measures shall be taken, and have found good after consultation with our Board of Commerce and our Railway Administration to decree as follows :—

Par. 1.

By ferro-silicon is meant in this Ordinance iron ore treated electrically.

Par. 2.

If ferro-silicon is stored it must be in an open space or in a well ventilated place not situated in a building used for human habitation.

If the space be not covered, the ferro-silicon must be protected from wet by waterproof tarpaulins or other sufficient means.

Par. 3.

During transit from one place to another ferro-silicon must be stowed in well made and strong vessels allowing for the escape of gases.

On each vessel the word "Kiseljärn" (Ferro-Silicon) shall be clearly painted in red.

Par. 4.

The transport by railway of ferro-silicon may only take place in open goods waggons and the vessel shall be well covered with waterproof tarpaulins.

Par. 5.

Upon the export of ferro-silicon by sea care must be taken that the Bill of Lading always accompanies the goods.

Par. 6.

On board passenger steamers ferro-silicon may only be carried on the open deck and at a distance of at least half a metre from the exterior of the place destined for the housing of passengers.

Par. 7.

In *wholly* or *half decked* vessels not carrying passengers ferro-silicon may only be carried in the manner described in the foregoing paragraph, or in the cargo hold, this latter being separated from the space destined for the crew by strong, well caulked and tight bulkheads, decks or storerooms.

In such bulkheads, decks or storerooms there must be no openings.

Par. 8.

When carried in the hold of a *wholly decked* ship the following regulations are to be observed.

The cargo hold must be provided with at least two ventilating drums of about the same diameter which are to be situated near the fore and after ends of the hold either straight or diagonally opposite one another.

The united inner diameter of these ventilating drums must not be less than $\frac{1}{900}$ of the roof surface of the hold ; and no drums must have a less diameter than seven square deci-metres.

These drums must not be provided with dampers.

If the drums are two in number the foremost one shall start from the roof of the hold and the aftermost one shall open from 0·3 to 0·5 metres from the bottom of the hold.

Should there be more than two ventilating drums an equal number should be placed in the fore and after parts of the hold and their joint diameter in both places should be about equal. The drums in the fore end of the space shall start alternately one from the roof and one 0·3 to 0·5 metres from the bottom of the hold and those in the after end shall be arranged in a similar manner.

All ventilation drums are to be provided with movable heads. The lower edge of the opening of the head shall be at least 0·6 metres above the bulwarks.

Any shaft, tunnel, or other space adjoining the cargo hold, which is to be used by men shall be kept carefully baulked from the cargo hold and shall also be provided with ventilation drums, wind-sails or some other contrivance for obtaining sufficient ventilation. At every entrance to such shafts or spaces a notice enjoining precaution should be posted up.

Par. 9.

In transporting ferro-silicon in the hold of a *half decked* cargo ship care must be taken that sufficient ventilation is obtained by means of drums as described above or otherwise by permanently open hatches, empty spaces in the hold, or by wind-sails.

Par. 10.

In *undecked* vessels not carrying passengers ferro-silicon may only be carried in a cargo hold divided by strong well caulked tight bulkheads and storerooms from the crew space.

In such bulkheads, &c., there must be no openings.

Par. 11.

The captain is bound to take such other measures for ventilation as circumstances demand and the conditions on board permit.

Par. 12.

Offences against these regulations when ordinary law is not applicable are punishable with fines of from 20 to 500 kronor.

Par. 13.

Prosecution for disregard of this Ordinance is before the Common Court and is carried out by the Public Prosecutor.

Par. 14.

Fines inflicted under these regulations are payable as to two-thirds to the Crown and one-third to the prosecutor.

If there are no assets for the payment of fines cases are dealt with according to the ordinary penal code.

This Ordinance comes into force immediately after its issue.

Signed at the Palace at Stockholm,
17th June, 1908.

The following letter and notice explain themselves :—

British Legation, Stockholm,
January 5th, 1909.

SIR,

WITH reference to Mr. Dering's despatch No. 72, Commercial, of July 19th, 1908, I have the honour to inform you that Paragraph 4 of the regulations concerning the transport of ferro-silicon by railway has been amended and now reads as follows :—

" Ferro-silicon, on being conveyed by railway, must be transported in open trucks, the vessels containing it being well covered with water-tight tarpaulins, except in the following cases :—

" When the quantity does not exceed 2,500 kilograms it may be conveyed in closed waggons, but never in the same waggon as living animals or food stuffs ; nor may any person ride in the waggon containing ferro-silicon. On occasion of such transport no waggon shall be used unless provided with ventilation openings in the sides. Should such openings be provided with shutters, they must be opened and the air allowed free access to the waggon.

I have, &c.,
(Sgd.) CECIL SPRING RICE.

The Rt. Hon.
Sir Edward Grey, Bart.,
&c., &c., &c.

COPY OF NOTICE SENT BY BOARD OF TRADE TO THE "SHIPPING GAZETTE," 7th August, 1908.

Ferro-Silicon.

The Board of Trade have received through the Foreign Office a copy of a Swedish Ordinance containing provisional regulations for the transport and storage of ferro-silicon. The Ordinance which is now in force provides that ferro-silicon must be stored in an open or well ventilated place and must be protected from wet. During transit it must be packed in strongly made vessels which allow for the escape of gases, each vessel being clearly marked with the word "Kiseljärn" (ferro-silicon) in red. When it is carried by sea, the Bill of Lading must accompany the goods, and detailed regulations must be complied with for securing adequate ventilation and preventing the gases affecting passengers or crew. In passenger ships ferro-silicon may only be carried on deck and away from the cabins. In cargo ships ventilators of a prescribed area must be provided in the hold, and all adjoining living spaces must be separated from the hold by gas-tight bulkheads and be properly ventilated.

Up to the present, so far as is known, regulations dealing with the storage and transport of ferro-silicon have not been issued by any other Continental Government, but Professor Cronquist states, in his paper, that the "General Directory of German Railways" has decreed that all packing cases containing ferro-silicon shall be of iron or wood, and watertight.

If regulations in regard to the storage and transport of this substance are to be of real value, it is obviously desirable that there should be international agreement on the subject. And in the hope of such general agreement on the subject eventually being attained, the Swedish Government have recently made representations to other Powers, including the British Government, as to the desirability of holding a Conference for the purpose of formulating such rules and regulations as, by general consent, may be determined to be necessary.

CONCLUSIONS AND RECOMMENDATIONS.

Since attention has been directed to the dangers incidental to the transport and storage of ferro-silicon, evidence has been forthcoming as to no inconsiderable amount of illness, as well as a number of deaths, which must undoubtedly be attributed to the action of poisonous gases which, under certain conditions, are given off by this substance. In addition, some cases of bodily injury have been directly caused by explosion of gases evolved under pressure, as in the well-known Liverpool instance, where the ferro-silicon had been packed in hermetically sealed iron drums.

From the account of the accidents known to have been occasioned in one or other of these ways, which has been set out in an earlier section of this report, it will be seen that these untoward events have for the most part occurred during transport of consignments of ferro-silicon by water, either on sea-going vessels, or in barges and canal boats plying on rivers or other inland waterways. Moreover, they have occurred in various parts of the world, on vessels of different nationalities, and in connection with the transport or storage of the product of different manufactories.

So long as low grade blast-furnace ferro-silicon only was available, accidents of the kind referred to were unknown, and this material, generally known as "siliceous pig" from its similarity in appearance to pig-iron, and containing at the most 15 per cent. of silicon, cannot be regarded as in any sense constituting a "dangerous cargo," in view of which the Board of Trade have issued a notice (*q.v.*, p. 102) stating that it is not proposed to put in force special regulations as to its transport and storage.

With the advent, however, of electrically produced ferro-silicon of considerably higher silicon percentages than could be produced in the blast-furnace, and its increasing use commercially, transport to this country assumed larger dimensions, for the reason that the material, of which none is at present manufactured in the British Isles, was necessarily all consigned from abroad. But for some time a large proportion at any rate of this form of ferro-silicon, which was, of course, new to shippers and their agents, reached this country under designations such as "scrap-iron," "iron-waste," &c., these terms not improbably having been adopted with the object of obtaining more favourable freight rates than might otherwise have been possible.

The explosions which occurred at Liverpool in 1904, however, forcibly directed attention to the possible dangers of this material, which, so far as anything was known of it, had previously been considered to be perfectly innocuous. But even so, it was not until the occurrence, in December, 1908, of the fatalities on the s.s. "Ashton," in the course of her voyage from Antwerp to Grimsby, that the danger incidental to the transport of this material became fully recognised in this country. And, indeed, indications have been afforded, in the course of my investigation, that this material has caused many similar accidents, on a smaller scale, the true explanation of which has not improbably been overlooked. Lehnkering and Bahr in Germany have given expression to a similar opinion.

Enough evidence has, however, been forthcoming to prove the necessity, under existing circumstances, for stringent regulations, if possible of international character, in connection with the transport and storage of electrically-produced ferro-silicon, in order to ensure such precautions being observed as shall successfully obviate the occurrence of such distressing incidents in future.

It is not, of course, suggested that every batch of electrically produced ferro-silicon is potentially dangerous. Indeed, it is now well recognised, alike by manufacturers and users of this substance, that samples containing certain definite percentages of silicon, of which the 50 per cent. grade has come to be considered as specially open to suspicion, are more likely than others to give off those poisonous and explosive gases, to the evolution of which the occurrence of accidents, often fatal in their result, must be attributed.

Up to the present, however, transport agents have been afforded no means of gaining information as to the percentage grade of any particular consignment of ferro-silicon, no mention of this point being made on the contract note or "manifest," and somewhat naturally, therefore, have come to regard with equal suspicion every lot of this material they may be called upon to handle.

Consequently, being unable in any way to discriminate between such qualities as may be potentially dangerous or possibly quite innocuous, shipping and other transport companies have endeavoured to cut the Gordian knot by refusing to carry ferro-silicon on any terms whatever. Such action, if persisted in, must cause, as indeed it has already caused, serious injury to an important industry abroad, and at the same time to steel and iron makers in this country. For this reason the present investigation has been mainly concerned with determination, as precisely as possible, of the nature and extent of the danger incidental to the use of ferro-silicon; and with determination, also, of the conditions under which it may be handled and transported with a minimum of danger to those who may directly or indirectly be brought in contact with it.

A well recognized peculiarity of certain grades of ferro-silicon is shown in a tendency of the lumps of alloy to crumble or, using the term more generally employed, to disintegrate spontaneously, sometimes to such an extent that evenually the whole sample may become reduced to a comparatively fine powder. This tendency, which is accentuated in presence of moisture, is in all probability due to some unstable physical condition, the precise nature of which is not fully understood notwithstanding the attention that has recently been given by numerous investigators to the crystallographic and other physical attributes of the alloy which it was hoped might afford some clue.

Generally speaking it is found that this tendency to spontaneous disintegration is exhibited most markedly by ferro-silicon containing about 50 per cent., by weight of silicon, although certain examples, the silicon content of which, as shown by chemical analysis, ranges between 30 per cent. and 35 per cent. ? (actually 33·3 per cent.) have been found to undergo complete disintegration, as was the case with a particular sample of what was stated to be a 35 per cent. grade, recently forwarded to me for examination by Messrs. Blackwell, of Liverpool.

A similar condition is stated to have been observed in the case of certain samples of 60 per cent. ferro-silicon.

Provided that, as appears probable, a considerable proportion of the poisonous gases which, as Dr. Hake has demonstrated, can be obtained from all samples of ferro-silicon of about 50 per cent. silicon content, is present occluded in minute spaces with which the substance of the alloy is riddled, it is obvious that disintegration of the mass will cause their evolution more rapidly than otherwise would be the case, a condition which, accentuated as it would be by the presence of moisture and motion, may be considered as having important bearing on the special danger which, on occasion, has been shown to be incidental to its storage and transport on ship-board.

It is obviously desirable, therefore, unless strong reason to the contrary can be shown, that, for the future, the use of grades of ferro-silicon in the region of 50 per cent. should be entirely dispensed with, in metallurgical operations. No difficulty need, I think, be anticipated from the adoption of this suggestion, since, as I have previously stated, no governing necessity appears to exist demanding the employment of a so-called 50 per cent. grade, the only reason for the employment of which, so far as I have been able to learn, being found in the facility its use affords to the workman in calculating the quantity of silicon required as an addition to any particular "bath" of metal.

As regards the chemical composition of 50 per cent. ferro-silicon, it may be mentioned that in the course of an interview with Dr. Heroult, the managing director of the Société Electro-metallurgique Française, he expressed himself as being decidedly of opinion that the specially undesirable qualities exhibited by this particular grade—tendency to spontaneous disintegration and evolution of poisonous gases—were related to the amount of *aluminium* present in the alloy. He was unable however, so far as I could gather, to advance any definite reasons for the opinion he had formed. But I was specially interested when, later on, in the course of correspondence, Mr. Bennett, who, at the time was engaged on work in connection with this report, made the same suggestion, basing it on the fact that he had noticed that the amount of aluminium in samples of the consignment of ferro-silicon which had caused a series of explosions at Liverpool in 1904, was unusually high, as shown by chemical analyses made at the time.

It is noteworthy that in the various analyses of ferro-silicon of different percentage grades, supplied by manufacturers or their agents, the amount of aluminium present, in the 50 per cent. grade, is always about twice as much as that in the corresponding 75 per cent. grade, although the total amount present in each grade may vary considerably in the case of material produced by one or another firm. Unfortunately, however, analyses of other samples of ferro-silicon known to have given rise to accidents are not available for comparison, but in the possible event of any further accidents arising, this is certainly a point to which attention should be directed.

Mr. Bennett suggests that as the heat of formation of Al_2O_3 is very great—392,000 calories approximately—the presence of a large percentage of aluminium in ferro-silicon is indicative of very high temperature reactions having taken place in the electric furnace, and that these reactions are favourable to the formation of compounds which readily break up into poisonous and explosive gases.

Yet further evidence, in this case of an experimental nature, as to the possible influence exerted by the presence of aluminium in rendering ferro-silicon liable to disintegrate spontaneously has reached me, in a letter from Mr. Olsen, of Christiania, the representative of a firm engaged in the manufacture of this material. He informs me that he has carried out a number of experiments with the object of determining the reason why certain samples of ferro-silicon should disintegrate while others do not. As the outcome of these experiments he has found, as he informs me, that aluminium has "a great effect" in this connection. For if, in the course of manufacture, aluminium is purposely added, so as to raise the aluminium content of the final product, he finds that "at certain percentages" which however he does not explicitly indicate, "the ferro-silicon "can scarcely be kept for a few minutes without falling to "pieces." Mr. Olsen states in conclusion that he is still continuing his experiments.

The fact of the liability of certain percentage grades of ferro-silicon to disintegrate, whereas this peculiar property is not shared by samples of intermediate percentages, would seem to indicate that the special percentages (33·3 per cent., 50 per cent., and 60 per cent.) of ferro-silicon—certain samples of which have been observed to exhibit this tendency—may represent in each instance definite points of chemical or physical constitution, of which this special property may be a concomitant. And in this connection it is of interest to note that these three percentage grades of ferro-silicon would correspond with silicides of iron represented by the formulæ FeSi, $FeSi_2$, and $FeSi_3$ respectively.

Of these, the existence of the first named has been known for some considerable time, while more recently both Moissan and Lebeau claim to have isolated a definite crystalline silicide of the composition $FeSi_2$. But so far as I am aware, $FeSi_3$ has not been isolated. Even supposing, however, that definite silicides corresponding to all three formulæ had been isolated, that fact alone would not necessarily account for the instability of the particular alloys to which they correspond.

Neither is any complete physical explanation of the phenomenon afforded by the results of researches into the composition and structure of the various percentage grades of ferro-silicon, although, as discussed in detail in Mr. Bennett's special contribution to this report, *two* of the three percentages incriminated do correspond to critical thermic points, as also to equally definite points in the eutectic structure of the alloy. On the other hand, in neither of these respects is any indication afforded that a 50 per cent. grade of ferro-silicon corresponds to any such critical point, although the special characteristic referred to is, for the most part, far more accentuated than in the lower and higher grades (33·3 per cent. and 60 per cent., respectively), which, to some extent, as previously stated, are liable on occasion to exhibit a similar tendency to disintegration.

In this respect, however, as in the amount of poisonous gases (mainly phosphoretted and arseniuretted hydrogen) obtainable from particular samples of ferro-silicon, the amount of variation is very considerable, not only for any given percentage grade, but for the product, at one or another time, of different firms. In other words, although it is, of course, recognised that, as a general rule, the greater the chemical purity of the materials used, the greater will be likely to be the purity of the ferro-silicon produced; this, evidently, does not constitute the whole story, as certain firms of repute have occasionally found to their cost when regrettable accidents have occurred in connection with the transport of consignments of their particular brand of this alloy. Indeed, to so comparatively small extent has it hitherto proved possible to control the precise chemical composition of any given batch of ferro-silicon, that the representative of the Société Electro-metallurgique Française, whom I interviewed in Paris, informed me that, on occasion, of two samples of the alloy obtained from the *same* tapping, one may be found to give off gases in considerable quantity, while the other gives practically negative results in this respect. That this may be the case has since been confirmed as the result of examination of the large number of samples received from the various works visited in the course of my investigation.

As an illustration of a somewhat similar occurrence, I may mention that of two samples of ferro-silicon produced in the course of experiments conducted by the British Coalite Company from portions of the *same* lot of "charge" (which in their case undergoes much more intimate admixture than in the factories abroad) and in the *same* furnace, but made on different dates and under different electrical conditions, one working resulted in the production of an alloy containing 47 per cent. of silicon, the other an alloy of 51 per cent. Moreover, in the case of the first working (47 per cent.), the amount of alloy produced was greater than in the other, while, as determined by Dr. Wilson Hake, the proportion of poisonous gases was also considerably greater. Here, so far as is known, the only varying factor was the voltage and ampèrage of the electrical current supplied, of which, in the case of the more impure sample, the voltage was higher and the ampèrage lower than in the second working. In view of these facts it is of the utmost importance that further carefully controlled experimental work should be carried out, in order to determine whether or not precisely similar methods of working can, under proper conditions, be depended on to produce, with the same charge, ferro-silicon of identical percentage and of equal purity. It is, of course, possible that the instance recorded above, of varying results obtained from different samples of the same tapping, might be due to unobserved variations of electrical condition in the furnace during the particular "run" having given rise to varying reactions, the results of which evidence themselves in the different layers of an incompletely homogeneous molten alloy.

I have already suggested that further experimental work on a large scale is required in order to place the manufacture of ferro-silicon on a really scientific basis. For although it is, I think, undoubtedly the case that the ferro-silicon, produced by firms of repute at the present day, is, on the whole, of better quality than was the case a few years ago, especially for the reason that, under no circumstances are carbide furnaces now used for the production of this material, still the work is carried out largely on empirical lines, even so enlightened a manufacturer as M. Girod having informed me that, in the works under his control, no investigations as to the gases contained in the ferro-silicon there produced had ever been undertaken, for the reason that such estimations "had not been asked for by their customers"!

Dr. Wilson Hake has demonstrated, in the course of his chemical researches on the subject, that, contrary to the opinion usually held, as I found, among manufacturers at any rate, substitution of steel turnings and shavings for the iron-ore originally employed is not the only direction in which the composition of the furnace charge might theoretically, at any rate, be improved. For, as I have previously stated, Dr. Hake has shown that the coal, and even the siliceous material employed, is liable to contain such quantities of phosphates as, when converted, as they are, by the action of the electric furnace into phosphides, may be capable of giving rise to considerable quantities of phosphoretted hydrogen.

The use of a better quality of anthracite coal than is usually available locally would doubtless bring about a lessening of the amount of phosphide in the alloy produced, but whether the extra cost entailed would be sufficiently compensated for by the extra purity of the ferro-silicon produced is a question which can only be determined by the manufacturer.

But pending further knowledge of the whole subject than is at present available, what steps of a practical nature can be taken to avoid likelihood of further accidents in the future?

The Chambre Syndicale des Forces Hydrauliques et de l'Electro-Chimie, etc., of Paris, have, as I have shown, suggested in their report that manufacturers of ferro-silicon should in future restrict themselves to the production of certain grades only of this alloy; and, in addition to the firms represented by the four members of the Commission, a number of other firms have now given in their allegiance to the recommendations put forward in the report.

The findings of the Commission, however, are, apparently, supported by no published evidence, chemical or otherwise, and although action on the lines laid down in their report is probably that which is most likely to prove of value for the required object, the special research work which has been undertaken in this country indicates, as I think, the desirability of restricting still further the percentage range, as regards silicon content, in the manufacture of ferro-silicon.

The Commissioners, who are also all manufacturers of ferro-silicon, admit by implication the validity of my suggestion that there exists no special need for the employment of a 50 per cent. grade of this alloy (since they advise that it, and indeed every grade between 47 per cent. and 60 per cent., shall no longer be manufactured); and indeed they do not set out reasons for supposing that any particular grade is essential, while they admit that some grades are potentially dangerous.

Under all the circumstances reviewed in my present report, and especially in view of the scientific evidence brought forward, I am of opinion the conclusion is justified that the manufacture of ferro-silicon should, at present, be restricted to the production of percentage grades of 70 per cent. and upwards at one end of the scale; and, at the opposite extremity, up to and including 30 per cent., on the supposition that under certain circumstances the employment of a comparatively low grade may be desirable or necessary.

Although, in the event of these recommendations becoming universally accepted, the occurrence of further accidents may be regarded as, to say the least, improbable, it will necessarily happen for some time to come, at any rate, that ferro-silicon, of percentage grades other than those here suggested as permissible, will be ordered and consequently manufactured.

Consequently it will, in any case for the present, be essential to enforce such regulations as will be likely to encourage shippers and other transport agents to remove the existing boycott on the industry. To meet these requirements I have drawn up and submit, at the end of this Report, a draft of suggested regulations which I trust, without being too stringent in their requirements, may prove of service for the desired purpose.

SUMMARY OF CONCLUSIONS.

1. Numerous accidents, fatal and otherwise, have been caused within the last few years by the escape of poisonous and explosive gases from consignments of ferro-silicon, which, in every instance, have been found to consist of so-called high-grade ferro-silicon, produced in the electric furnace.

2. These accidents, for the most part, have occurred during transport of the ferro-silicon by water, whether in sea-going vessels or in barges and canal-boats plying on inland waters.

3. These accidents have occurred in various countries and on vessels of different nationalities, while the ferro-silicon carried has, in almost every instance, been the product of a different manufactory.

4. Ferro-silicon, especially of grades containing from 40 per cent. to 60 per cent. of silicon, is invariably found to evolve considerable quantities of phosphoretted hydrogen gas, and, in less amount, of arseniuretted hydrogen, both of which are of a highly poisonous nature. A certain amount of the gas evolved is present, as such, in the alloy, being "occluded" in minute spaces with which its substance is often permeated.

5. As the result of careful investigation, it has been shown that certain grades of ferro-silicon—notably such as contain about 33 per cent., 50 per cent., and 60 per cent. of silicon*—even when manufactured from fairly pure constituents, are both brittle and liable to disintegrate spontaneously, this latter characteristic being apt to be specially marked in the case of the 50 per cent. grade.

All these grades are commonly employed at the present time.

6. In the event of disintegration occurring, the amount of surface exposed will, obviously, be greater than if the mass were solid.

7. Evolution of poisonous gases is greatly increased by the action of moisture, or of moist air, under the influence of which phosphoretted hydrogen is generated from calcium phosphide, which, in turn, is formed, in large part, at any rate, from the calcium phosphate present in anthracite and quartz, at the high

* Corresponding possibly to the formulæ, $FeSi$, $FeSi_2$, and $FeSi_3$ respectively. Moissan and Lebeau both claim to have isolated the first two of these three silicides of iron in crystalline forms.

temperature of the electric furnace. If spontaneous disintegration of the alloy also occurs, much larger quantities of gas would be given off from such friable and unstable material, other conditions being equal. The greater or less tendency of a given sample to evolve poisonous gases, and even a rough estimate of their probable amount may be arrived at by the use of test-papers prepared with silver nitrate.

8. There is no evidence that low-grade ferro-silicon (10 to 15 per cent.), produced in the blast-furnace, has ever given rise to accidents of similar character to those known to have been caused by the high-grade electrically-produced alloy. Blast-furnace ferro-silicon does not evolve poisonous gases even in presence of moisture.

9. As regards ferro-silicon produced in the electric furnace, the evidence available goes to show that certain percentage grades are practically quite innocuous. This statement applies to grades of alloy of a silicon content up to and including 30 per cent., and probably also, though in considerably less degree, to those of 70 per cent. and over.

10. In view of the fact that the use of ferro-silicon of grades ranging between 30 per cent. and 70 per cent. apparently is not essential in metallurgical operations, with the possible exception of basic steel manufacture, it will be advisable that the production of this alloy of grades ranging between these percentages should be discontinued in the future.

11. The proprietors of iron and steel works making use of ferro-silicon will assist in the protection of their workpeople, and at the same time act for the public benefit by restricting their orders to grades of this material, either not exceeding 30 per cent., or of 70 per cent. and upwards, according to the special nature of their requirements.

12. But as, pending international agreement on the question, intermediate percentages of ferro-silicon will doubtless continue to be manufactured and sold, the issue, by the Board of Trade, of special regulations will be necessary in order to obviate, so far as may be possible, chance of further accidents during the transport of this substance.

Inter alia, these regulations should require a declaration of the nature, percentage, date of manufacture, and place of origin of any such consignment.

SUGGESTED REGULATIONS AS TO PRECAUTIONARY MEASURES IN CONNECTION WITH THE STORAGE AND TRANSPORT OF FERRO-SILICON.

1. Ferro-silicon should not be sent out from the works immediately after manufacture, but, after being broken up into pieces of the size in which it is usually sold, should be stored under cover, but exposed to the air as completely as possible, for at least a month before being despatched from the works.

2. Manufacturers should be required to mark in bold letters each barrel or other parcel of ferro-silicon with the name and

percentage grade (certified by chemical analysis) of the material; the name of the works where it is produced; the date of manufacture; and date of despatch.

3. The carriage of ferro-silicon on vessels carrying passengers should be prohibited. When carried on cargo boats it should, if circumstances permit, be stored on deck. If it be considered necessary to store it elsewhere, the place of storage should be capable of being adequately ventilated, and such place of storage should be cut off by airtight bulkheads from the quarters occupied by the crew of the vessel.

4. This regulation should apply to the transport of ferro-silicon on river or canal barges as well as on sea-going vessels.

5. Storage places at docks or at works where ferro-silicon is used should have provision for free access of air, and should be situated at a distance from work-rooms, mess-rooms, offices, &c.

In concluding this report, I desire to express my best thanks to all those—manufacturers and others—too numerous to mention individually, to whom I am so greatly indebted for facilities of one or another kind that have been so readily and so generously afforded me in the course of my investigation and in the preparation of this report. I desire, however, especially to express my indebtedness to Dr. B. A. Whitelegge, C.B., of the Home Office, H.M. Chief Inspector of Factories, and to Mr. C. Hipwood, of the Board of Trade, with both of whom I have had the benefit of frequent conference.

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1908–09.

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For 1908-09.

ON THE NATURE, USES, AND MANUFACTURE

OF

FERRO-SILICON,

WITH SPECIAL REFERENCE TO POSSIBLE DANGER ARISING FROM ITS TRANSPORT AND STORAGE.

Presented to both Houses of Parliament by Command of His Majesty.

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