

which I have already summarized on p. 45, *viz.*, those consisting in cementing pieces of wire and filings of soft steel at various temperatures, in a current of pure carbon monoxide.

The author, however, reports two new experiments, in which he subjected to the action of carbon monoxide soft steel in the form of cylinders 10 mm. in diameter, then determined the carbon in two concentric layers 1 mm. thick. Although this evidently does not allow him to draw any conclusion as to the *distribution* of the carbon in the cemented zone (as follows clearly from what I have said relative to my experiments of the preceding year¹), it at least furnishes him some information regarding the *concentration* of the carbon.

In the specimen cemented for 60 hours at 1000° in a "slow" current of carbon monoxide,² the external layer contained 0.63% of carbon, while the second layer contained but 0.5%. On the other hand, the external layer of an identical specimen, cemented under identical conditions but without allowing the carbon monoxide to "circulate," contained only 0.20% of carbon; the second layer of this specimen contained 0.15% of carbon; while the original metal contained 0.12%.

It is clear that these last experiments, with the few conclusions which can be drawn from them, cover but a very small part of those published in the preceding year by me and my collaborators; which latter, being supplemented by analyses of many thin successive layers of each cemented zone, had already led to useful conclusions on the operation of the cementation, especially as concerns a question of capital practical importance—the *distribution* of the carbon in the cemented zones.

In the third part of his memoir, Charpy studies the action of carbon monoxide at high temperatures on various metals and on some special steels. By causing carbon monoxide to react at 1000° and at ordinary pressure on chromium, on ferro-chrome with 88% of chromium, and on manganese, he observed the oxidation of the metal and the simultaneous decomposition of the carbon monoxide, with formation of free carbon.

It is well known that this phenomenon had already been studied exhaustively by Schenck in a series of works published, considerably before Charpy's work, in the *Berichte der deutschen chemischen Gesellschaft*. Schenck had, moreover, shown that this phenomenon manifests itself between limits of temperature and pressure well defined for each metal, and had also shown the precise significance of these limits. I will later offer more precise data on this point—the results of recent experimental investigations.

The experiments performed by Charpy with nickel and with tungsten

¹ I have already shown (see p. 95) the necessity of analyzing layers not thicker than 0.1–0.2 mm.

² Charpy does not indicate the velocity of the current of carbon monoxide, on which, however, the concentration of the carbon in the cemented zone essentially depends.

show that carbon monoxide (at 1000° C. and under ordinary pressure) carburizes the first metal only very slightly, while it carburizes the second strongly. Finally, by making carbon monoxide pass at 1000° over filings of various chromium steels or chromium-nickel steels of different composition, Charpy observes that, contrary to what he has shown to occur with iron,¹ the data relative to the carburization of the metal, deduced on the basis of the increase in weight of the filings, of the analysis of the metal and of the evolution of carbon dioxide, are here so different as to show that a considerable proportion of the carbon monoxide oxidizes the chromium. If, instead of using chrome-steel in the form of filings, pieces of considerable dimensions are used, the oxidation of the chromium is limited to the surface layer, while below this the cementation proceeds regularly by diffusion.

These results, of themselves incomplete and inconclusive, show clearly that a complete study of the cementation of special steels, carried out along the theoretical lines so clearly developed by Schenck, would without doubt furnish results of great practical interest.²

In the fourth part of his memoir, Charpy reports the results of some cementation experiments carried out on a large scale with three of the cements most frequently used in practice: wood charcoal, a mixture of wood charcoal and barium carbonate, and animal charcoal. He did not in these observe the formation of the slightest traces of cyanides, either in the gases or in the solid materials taken from the cementation boxes. This confirms the results of the earlier experiments published in 1865 by Cailletet (see p. 23). Only with the intimate mixture of carbon and barium carbonate do cyanides begin to appear, at about 1050°, but the cementation is already intense at considerably lower temperatures (900°–1000°).

Charpy shows, moreover, that the cementation is somewhat more intense when wood charcoal is used as cement in an atmosphere of carbon monoxide than when it is employed in the presence of its own occluded air. The first precludes the formation of cyanides which, in the second, might be formed (according to the hypothesis of Caron) merely by the action of the nitrogen of the air.

These experiments show that cyanides are not necessary for cementation, and that under the conditions under which cementation is ordinarily effected "the transport of the carbon to the metal is effected, at least for the most part, by the action of the carbon monoxide." The author adds that all the observations of Caron on the influence of alkalis on cementation with wood charcoal are explained just as well by the intervention of carbon monoxide as by

¹ See p. 45.

² Such a study, evidently very long and difficult, I began a couple of years ago, as I have had occasion to announce in various publications. A part of the first results has already been published, and will be given briefly in the following pages; others will be published shortly, but I of course make no pretense of exhausting so vast a subject.

that of cyanides. This last assertion has been confirmed by other, considerably more direct, experiments, but not all of the other remarks made by Charpy on this subject are correct.

About two months later I sent to the Editor of the *Gazzetta Chimica Italiana* a paper¹ containing the results of three series of investigations, carried out in collaboration with Doctor Astorri, designed to determine with great precision the specific action of carburizing gases and the way in which this action "adds itself" to that of the solid cements or of those cements (such as ethylene) which, although gaseous, owe their carburizing action essentially to the solid carbon which is formed by their decomposition in contact with the iron.

The first of these series of investigations comprises various cementations carried out under conditions analogous to those described in the preceding papers, using as cement carbon monoxide mixed with benzene vapor in various well-defined proportions.

The experimental conditions adopted in the various tests, together with the results obtained, are shown in the table which follows, as also data relative to the concentration and distribution of the carbon in the cemented zones.

Number	Temperature °C.	Length of cementation (hours)	Quantity and composition of gaseous cement used: gaseous CO (liters) and liquid benzene (c.c.)	Thickness of the zone			Remarks
				Hyper-eutectic (mm.)	Eutectic (mm.)	Hypo-eutectic (mm.)	
1	1000	4.0	{ 6 liters CO 2 c.c. C ₆ H ₆	0.2	0.6	0.2	Slight deposit of carbon on the steel. Concentration of C in hyper-eutectic zone, 1.1%.
2	1000	4.0	{ 6 liters CO 1 c.c. C ₆ H ₆	0.7	0.5	No deposit of carbon on the steel.
3	1000	4.0	{ 6 liters CO 1.5 c.c. C ₆ H ₆	0.2	0.6	0.2	Very slight deposit of carbon. Concentration of C in hyper-eutectic zone, 1.1%.
4	1000	4.0	{ 6 liters CO 15 c.c. C ₆ H ₆	0.7	0.4	0.4	Abundant deposit of powdery carbon.
5	1000	2.0	{ 3.75 l. CO 19 c.c. C ₆ H ₆	0.7	0.4	0.4	Very abundant deposit of carbon.
6	1000	2.5	{ 19 c.c. C ₆ H ₆	0.7	0.6	0.5	Deposit of compact carbon about 1 mm. thick.

¹F. Giolitti and L. Astorri, *Ricerche sulla fabbricazione dell'acciaio cementato*, IV: Sulla funzione specifica dei cementi gassosi e dei cementi solidi nel processo della cementazione (*Gazzetta Chimica Italiana*, 1910, Vol. XL, p. 1).

This Note, sent to the Editor of the *Gazzetta Chimica* July 30th, 1909 (as is seen from the statement printed as subtitle by the Editor), was published only six months later.

These results, compared with those carried out with pure carbon monoxide reported further back, show that the addition of small quantities of volatile hydrocarbons to carbon monoxide merely raises the concentration of the carbon in the external layers of the cemented zones above the value which would result from the use of pure carbon monoxide under identical experimental conditions. This increase is greater the larger the proportion of the hydrocarbon contained in the gaseous mixture, as long as this proportion does not reach a value such that the velocity with which the free carbon is formed by the decomposition of the hydrocarbon does not surpass the velocity with which this carbon passes through the stage of carbon monoxide into solution in the iron. From this limit (about 1.8 c.c. of liquid benzene to six liters of CO) the excess of carbon which is liberated begins to deposit on the steel and the concentration of the carbon in the external layers of the cemented zone reaches the maximum value corresponding to that which is obtained by cementing with solid cements, or with cements which behave as such, and from this point on, the concentration and the distribution of the carbon in the cemented zones no longer vary markedly, even if the proportion of the hydrocarbon increases greatly.

From what precedes it is evidently possible to obtain, by means of mixtures of carbon monoxide and vapors of volatile hydrocarbons, cemented zones in which the maximum concentration of the carbon in the external layers has a definite value, lying between a minimum corresponding to that which would be obtained by working under the given conditions with pure carbon monoxide, and a maximum which would be obtained by working with the vapors of the hydrocarbon alone. This is achieved simply by using gaseous mixtures containing a proper proportion of hydrocarbon varying with the conditions under which the cementation is to be effected, such as temperature, pressure, relation between the velocity of the gaseous current and the surface of the steel to be cemented, etc.

The practical importance of these observations is evident, widening, as they do, the field of application of carbon monoxide in the cementation of steel, and making it possible to combine the advantages of the use of this gas with those of the other cements and of "graduating" the concentration of the carbon in the cemented zones.

The second series of experiments covers cementation effected by using simultaneously carbon monoxide and wood charcoal.

The steel cylinders were placed, coaxially, in the usual porcelain tube, now set vertically and, together with them, the usual smaller porcelain tube to protect the thermo-electric pyrometer couple. The space still remaining free in the larger tube was filled with a granular wood charcoal, washed with hydrochloric acid and then ignited, using only the portion which passed through a sieve of 49 mesh per sq. cm., and was held by a sieve of 169 mesh per sq. cm.

A current of pure carbon monoxide of definite velocity was admitted at the lower end of the tube.

In the table reproduced below are reported the results of four of the many experiments carried out by this practically important process.

Number	Temperature °C.	Length of cementation (hours)	Volume of CO used (liters)	Thickness of the zone			Remarks
				Hyper-eutectic (mm.)	Eutectic (mm.)	Hypo-eutectic (mm.)	
1	900	4	2	0.4	0.9	Comparative cementation carried out under the conditions which most frequently manifest themselves in practice: with ordinary wood charcoal, simply ground (not washed nor sifted), and without a current of carbon monoxide.
2	1000	4	2	1.0	0.6	
3	1000	4	6	1.0	0.7	
4	1000	4	0	0.7	0.6	0.2	

It appears from the examination of the results of the first three operations, especially if these results are compared with those of the fourth cementation, carried out under the conditions which are usually found in practice, that the characteristic of the cemented zones which are obtained with "granular" carbon in a current of carbon monoxide is the absence of the external hyper-eutectic zone. This characteristic, which we shall see always manifests itself when working within certain limits of temperature, pressure and length of the operation, is easily explained when we take into account the characteristic function of the carbon monoxide as an "equalizer" of the concentration of the carbon in the cemented zones. In fact, as I have already explained, the mixture of carbon monoxide with small quantities of carbon dioxide (in our case, the mixture which is in equilibrium with the free carbon) acts, by its rapid diffusibility, as "carrier" for the carbon which burns at the points of the cemented zone where it is more concentrated, while it again sets it free where the concentration of the latter is smaller; in this way the accumulation of the carbon in the external zones of the steel is impeded.

In other words, in this case also the specific action characteristic of carbon monoxide, as I have previously defined it (p. 87), superposes itself on the specific action of the solid cement, long since known, which follows from the fourth experiment of the table reproduced above, giving a cemented zone of a *type intermediate* between the two which I have described on pages 82 and 84.

Finally, the third series of experiments relates to the study of cementation by pure solid carbon in a vacuum, or in the presence of gases other than carbon monoxide.

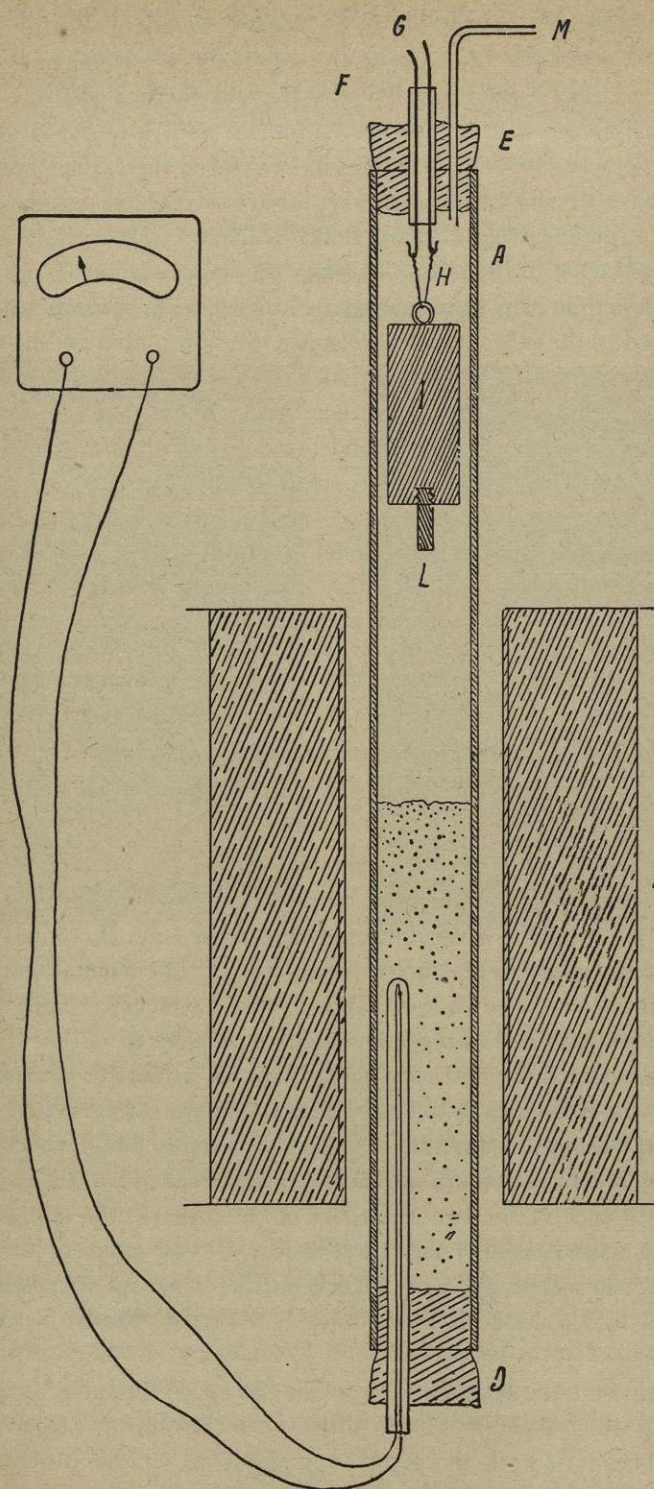


FIG. 48.

For the study of cementation in a vacuum, we adopted, after various unsuccessful attempts, the following experimental arrangement. The usual tube of glazed porcelain (*A*), the Heraeus furnace (*B*) and the Le Chatelier pyrometer with its porcelain protector were arranged as indicated in Fig. 48. In the lower half of the tube we placed the carbon, washed in the way I have already mentioned and reduced to a very fine powder, because the earlier experiments had shown that "granular" carbon does not give sufficient contact with the iron. Through the upper stopper *E* passed, besides the glass tube *M*, a porcelain tube *F*, 15 cm. long, through which ran, from one end to the other, two large copper wires, insulated and fastened in the tube by means of an insulating cement poured into it.

The lower ends of the two wires, bent into a hook, were connected by a fine iron wire, from which was suspended a steel cylinder *I*, 30 mm. in diameter by 150 mm. in height.

In the center of the lower base of this cylinder was bored a threaded hole into which was screwed the cylinder of soft steel *L* (10 mm. in diameter and 30 mm. high), the head of which was likewise threaded. The composition of the steel of the cylinder was as follows:

Carbon.....	0.09 percent.
Manganese.....	0.72 percent.
Silicon.....	traces
Sulphur.....	0.04 percent.
Phosphorus.....	0.08 percent.

Having heated to 1100° the lower half of the tube *A*, containing the carbon, while the cylinders *I* and *L* remained in the cold upper part of the apparatus, we produced a vacuum by means of the tube *M*, connected to a mercury pump, until the pressure in the interior of the cementation chamber was permanently reduced to less than 0.5 mm. of mercury. Then we filled the apparatus with pure nitrogen and again evacuated it.

Having repeated the operation three times, in order to be sure of having eliminated the last traces of oxygen which could form carbon monoxide, and keeping the vacuum at less than 0.5 mm. of mercury, we connected for a moment, by means of conductors, each of the external ends of the two copper wires *G* with each of the two electrodes of the furnace; the current which in this way passed through the fine iron wire *H* was sufficient to melt it, and the system of two cylinders *IL* fell on the carbon powder, which was compressed by the base of the cylinder *I*, while the cylinder *L* penetrated into it.

We then kept the temperature constant at 1000° for three hours and a half, during which time, in order to always keep the pressure below 0.5 mm., it was sufficient to work the pump very slowly to remove the very small quantities of air which penetrated at the high temperature through the por-

celain walls. These minimum quantities of air have no influence on the process of the cementation. The air leak was due to the slight permeability which the porcelain assumes at a very high temperature, and not to imperfect closing of the connections of the apparatus, as was proved by the fact that when the experiment was finished the external pressure no longer increased (from 0.4 mm.) during the twelve succeeding hours in which the cold apparatus was allowed to stand without working the pump.

Having removed the steel from the tube, we noted that carbon adhered to the whole surface of the smaller cylinder, except the last half centimeter,

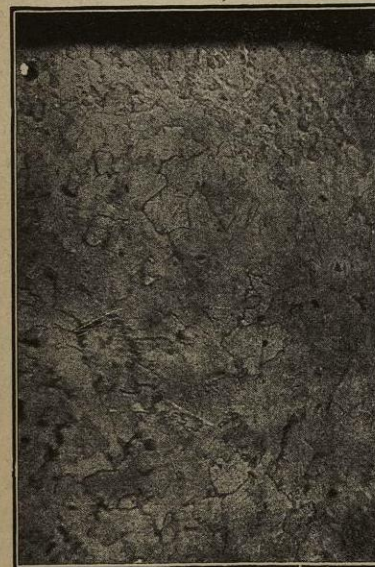


FIG. 49.



FIG. 50.

and to the bottom of the large cylinder, forming a friable crust half a centimeter thick, an evident proof of immediate contact.

On examining under a microscope the section corresponding to the point at which the carbon did not adhere, we could detect no increase in the proportion of pearlite toward the external edge; this is plainly evident in the photogram of Fig. 49.

If, instead, the sample was cut at one of the points at which the carbon had adhered, and examined in the same way, we noted an appreciable cementation, as appears in the photogram of Fig. 50.

The cemented zone, hypo-eutectic but considerably richer in pearlite than the original steel before the operation (see the deep zones in Fig. 49), is uniform along the whole external edge partially reproduced in Fig. 50, and has a thickness of about 0.15 mm.

These observations confirm fully what I had asserted before, that solid

carbon also, heated above 800° in contact with iron, dissolves in it, cementing it, even without the intervention of gaseous substances.

In fact, if the cementation, observed in our last experiment only at those points at which the solid carbon had come into direct contact with the surface of the iron, had been due to the intervention of the small quantities of gas which the action of the mercury pump had not succeeded in eliminating, this cementation ought to have been produced in the contiguous zones also; that this did not occur is proof that the very small quantities of gases remaining in the tube exercised no appreciable action, while the solid carbon exercised such an action directly, as was shown by its "localization" at the points in most intimate contact with the carbon.

From the present experiments, and from those described before, it follows that although gaseous cements have a preponderant action in the process of cementation, solid carbon also, when it is in intimate contact with β -iron and with γ -iron, dissolves in it, cementing it. And it is quite probable that the results apparently contradicting this assertion, obtained previously by some experimenters (for example, by Guillet; see p. 63), are due to the lack of sufficiently intimate contact between the iron and the carbon.

We used the same apparatus, just described, to investigate the course of the cementation by solid carbon and pure nitrogen, adding through the lower stopper *D* a second glass tube through which we admitted nitrogen. The carbon was the same as that used in the preceding experiments.

The pure nitrogen (prepared from ammonium nitrite) passed through a drying apparatus and a glass tube 40 cm. long containing metallic copper heated to redness, to eliminate oxygen completely, before reaching the cementation chamber.

The cementation apparatus was first emptied of air and then filled with nitrogen, the same operation being repeated several times; finally, having again evacuated it, we brought it to 1000° C., keeping in it for about an hour the minimum obtainable pressure (about 0.4 mm. of mercury) to make sure of having eliminated practically all the gases contained in the tube and occluded in the carbon. We then filled the apparatus with nitrogen and connected the exit tube *M*, which before communicated with the pump, with a mercury valve so as to prevent the possibility of the entrance of air into the apparatus owing to a diminution in the volume of the gas due to accidental cooling.

Having done this, we allowed the two cylinders of steel to fall upon the carbon and began to circulate nitrogen through the apparatus. The temperature was kept constant at 1000° C. for four hours, during which 2.5 liters of nitrogen passed through.

We obtained in this way a cemented zone which, as appears from the photogram reproduced in Fig. 51, is entirely similar to those which are ob-

tained by cementing with pure carbon monoxide at 1000° C.¹; it consists, in fact, of a single hypo-eutectic layer 1.8 mm. deep, in which the concentration of the carbon does not surpass, even at the external edge, the value 0.3%, then decreasing slowly and continuously toward the interior, finally reaching (at a depth greater than 1.8 mm.) the value which it had in the original steel. The photogram of Fig. 52 represents the center of the section examined.

The results of this experiment do not confirm those obtained by other experimenters (for example, by Guillet; see p. 49), showing, on the contrary,



FIG. 51.



FIG. 52.

that the carburization which is obtained by making nitrogen act on iron at a high temperature in the presence of solid carbon must be due to a reaction analogous to that on which is based the cementation by means of carbon monoxide. And here, too, there must be reached a state of equilibrium, as occurs with carbon monoxide, defined not only by the partial pressures of the various gases in the carburizing atmosphere which is formed by the said reactions, but also by the concentration of the carbon in the γ -iron of the cemented zone.

The note which I have just reviewed, although presented to the editor of the *Gazzetta Chimica Italiana* on July 30, 1909 (as seen from the subtitle added by the editor and from the fact that this work was presented by Doctor Astorri as a thesis for his doctorate in chemistry, taken at the University of Rome in June, 1909), was not published until six months later. To this delay is due the fact that two other experimenters, Guillet and Grif-

¹ See Fig. 27.

fith, not knowing of the results already obtained by us on cementation with solid carbon in a vacuum, repeated our experiments, although with different experimental arrangements.

However, the fact that two series of experiments executed absolutely independently gave identical results is the best proof of the correctness of these results.

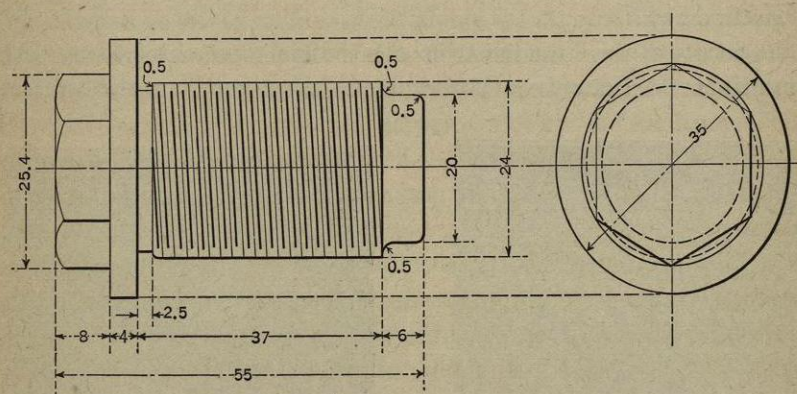


FIG. 53.

A record of the experiments of Guillet and Griffith appears in the October, 1909, number of the *Revue de Métallurgie*.¹ The article begins with a historical review of the question of the intervention of gases in cementation, laying special stress on the discussions between Caron and Margueritte,

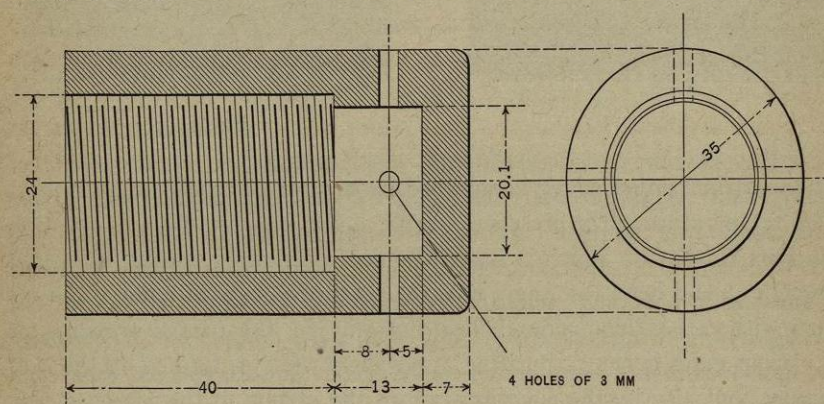


FIG. 54.

and between Guillet and Ledebur, of which I have already spoken at length. Then follows a description of the new experimental researches, designed to find whether pure carbon can cement in a vacuum either without pressure or under pressure sufficient to insure contact between the carbon and the iron.

¹ See also the "*Berichte der Abteilung für theoretisches Hüttenwesen*" in the "Proceedings of the Congress of Metallurgy of Düsseldorf" (1910).

The metal used was extra-soft steel in the form of wires, sheets and fragments of bars. The carbon (from sugar) had been heated at 1000° , first in a current of chlorine and then in a vacuum. The apparatus (consisting essentially of a long tube of glazed porcelain) was entirely similar to that used by me and Astorri. Guillet and Griffith took (as we did not) the precaution of eliminating the gases from the carbon and from the steel by long ignition in a vacuum, but not that of avoiding (as we did) exposure of the steel and the cement (even for a fraction of a second) to the action of the air or of any gas whatever, before coming in contact with each other.

A first experiment, "without pressure," consisted of igniting iron wires, simply placed in a porcelain boat filled with sugar carbon, in a vacuum for five hours at 1000° C. This did not give rise to the slightest trace of cementation.

A second experiment was carried out by igniting, also at 1000° for five hours, sugar carbon kept in contact with a small plate of soft steel by the pressure of a piece of steel of a few grams in weight. This also gave completely negative results.

Finally, a third series of experiments was carried out by means of the apparatus shown in Figs. 53 and 54. This consists of a hollow steel cylinder closed at one end with a screw plug, which makes it possible to compress strongly the substances contained at the other end of the cylinder, which, closed at the bottom, forms the cementation chamber.

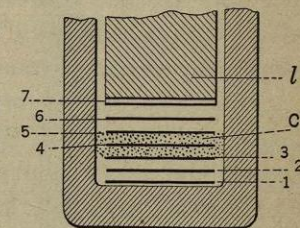


FIG. 55.

The cementation chamber has four lateral holes to allow of its evacuation. The experiments were executed by placing in the cementation chamber sheets of extra soft steel (with 0.08% of carbon), alternating with layers of the usual powdered sugar carbon, as indicated in Fig. 55. A first test was made by heating the apparatus for five hours at 1000° after having tightened the screw plug only very slightly; the concentration of the carbon in the central lamina increased to 0.15%. In a second test, made under conditions identical to those in the preceding one but after having tightened the screw plug as much as possible, so as to strongly compress the carbon against the steel sheets, the concentration of the carbon in the central sheet rose to 0.32%.

As is seen, these experiments confirm my conclusions concerning the possibility of cementing iron with solid carbon without the intervention of gases, and concerning the necessity of an intimate contact between the carbon and the metal in order that such a process may be effected; they further establish the fact that an increase in the pressure which produces such a contact gives rise to an increase in the cementation.

These conclusions, thus formulated by Guillet, have a special probatory value, as with them their author comes practically to a recognition of the incorrectness of his earlier opinion (see p. 63) as to the necessity of the intervention of gases in cementation; this he would not have done if the results of his last experiments had not appeared absolutely unassailable to him.

Weyl, of Aachen, published a paper more than six months after the note of Guillet and Griffith and that by myself and Doctor Astorri,¹ in which are reported with the most minute particulars the results of a large number of experiments carried out with the greatest care and accuracy for the purpose of establishing if pure carbon can cement in a vacuum. It does not seem necessary to review here the memoir of Weyl, as the experiments reported in it are performed along lines absolutely identical with, and with experimental arrangements very similar to (though more perfect than), those forming the subject of the two preceding papers. The conclusion which Weyl draws from his experiments are identical with those formulated by Guillet and Griffith and by me and Astorri. However, there is no doubt that the confirmation of the earlier conclusions by Weyl's experiments, made on materials of exceptional purity and with truly extraordinary accuracy, has great scientific value.

Conclusions contradictory of those of the three last papers were reached by Charpy and Bonnerot.² By heating for a long time in as perfect a vacuum as possible, at 1000° C., soft steel in contact with carbon (graphite, diamond or sugar carbon), after first having separately ignited the two substances at 1000° C. for a long time in a vacuum, they were unable to detect the slightest trace of cementation. They conclude that "solid carbon outside of a fragment of steel can not penetrate into it without the intervention of a gaseous vehicle," and they attribute the different results obtained by other experimenters to the insufficient elimination of the gases occluded in the carbon and in the steel used.

However, the decision whether the direct action of the carbon is extremely small (as the experiments of Guillet and Griffith and of myself and Astorri would indicate) or *nil* (as the experiments of Charpy and Bonnerot would seem to show) is a matter which is at most one of theoretical interest. Both series of experiments show with entire certainty that the direct action of the carbon ("by contact"), whether it is *nil* or only very small, is certainly such that it can be considered as *absolutely negligible* in any technical process of cementation.³ The question thus loses practical interest.

¹ Fritz Weyl, *Ueber Zementation im luftleeren Raum mittels reinem Kohlenstoff* (*Metallurgie*, July 22, 1910, Vol. VII, pp. 440-456); and "Proceedings of the International Congress of Metallurgy" held at Düsseldorf in June, 1910 (*Berichte der Abteilung für theoretisches Hüttenwesen*, p. 178).

² *Comptes Rendus de l'Académie des Sciences*, January 17, 1910, Vol. CL, p. 173.

³ In either case, the hypotheses of Mannesmann, Roberts-Austen, Ledebur, etc., which attribute the carburizing action of the solid cements used industrially to the *direct* action of the carbon are certainly shown to be false.

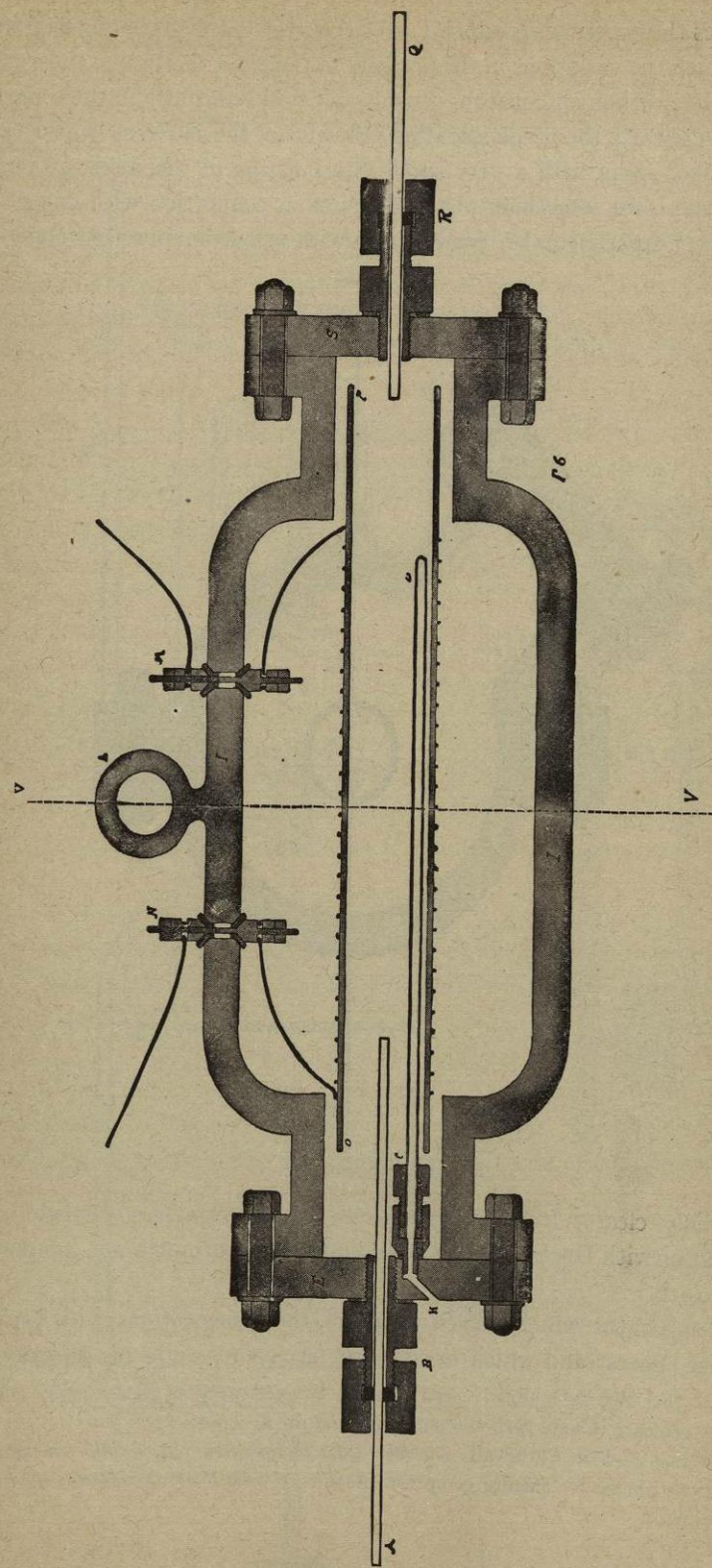


FIG. 56.—(Scale 1:5).

Besides the experiments which I have reported in the preceding pages, the effects which the variations in the pressure of the gases produce in those cases in which free carbon and gaseous cements act simultaneously in the cementation prove clearly the preponderating influence of the gases in the process of cementation, along with a very small direct action of the solid carbon. I have already said something of these effects in connection with one of my first series of experiments on cementation with ethylene,¹ but they come out

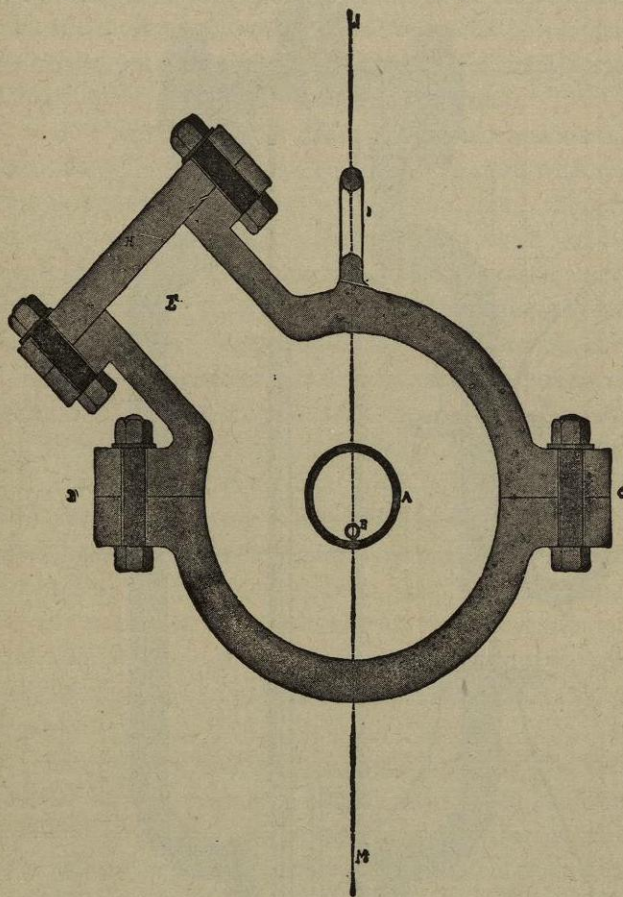


FIG. 57.—(Scale 1:5).

considerably clearer from another series of investigations carried out in collaboration with Doctor Carnevali and published (although not completely) early in 1910.²

The apparatus which served to effect the cementations with strongly compressed gases (and which we still use, except for slight modifications, in

¹ See p. 78. We have already seen that in the cementation with ethylene, the gas acts in the presence of solid carbon separating from the first portions of it.

² F. Giolitti and F. Carnevali, *Ricerche sulla fabbricazione dell'acciaio cementato*, V: Cementazione con gas fortemente compressi (*Rendiconti della Reale Accademia delle Scienze di Torino*, 1910).

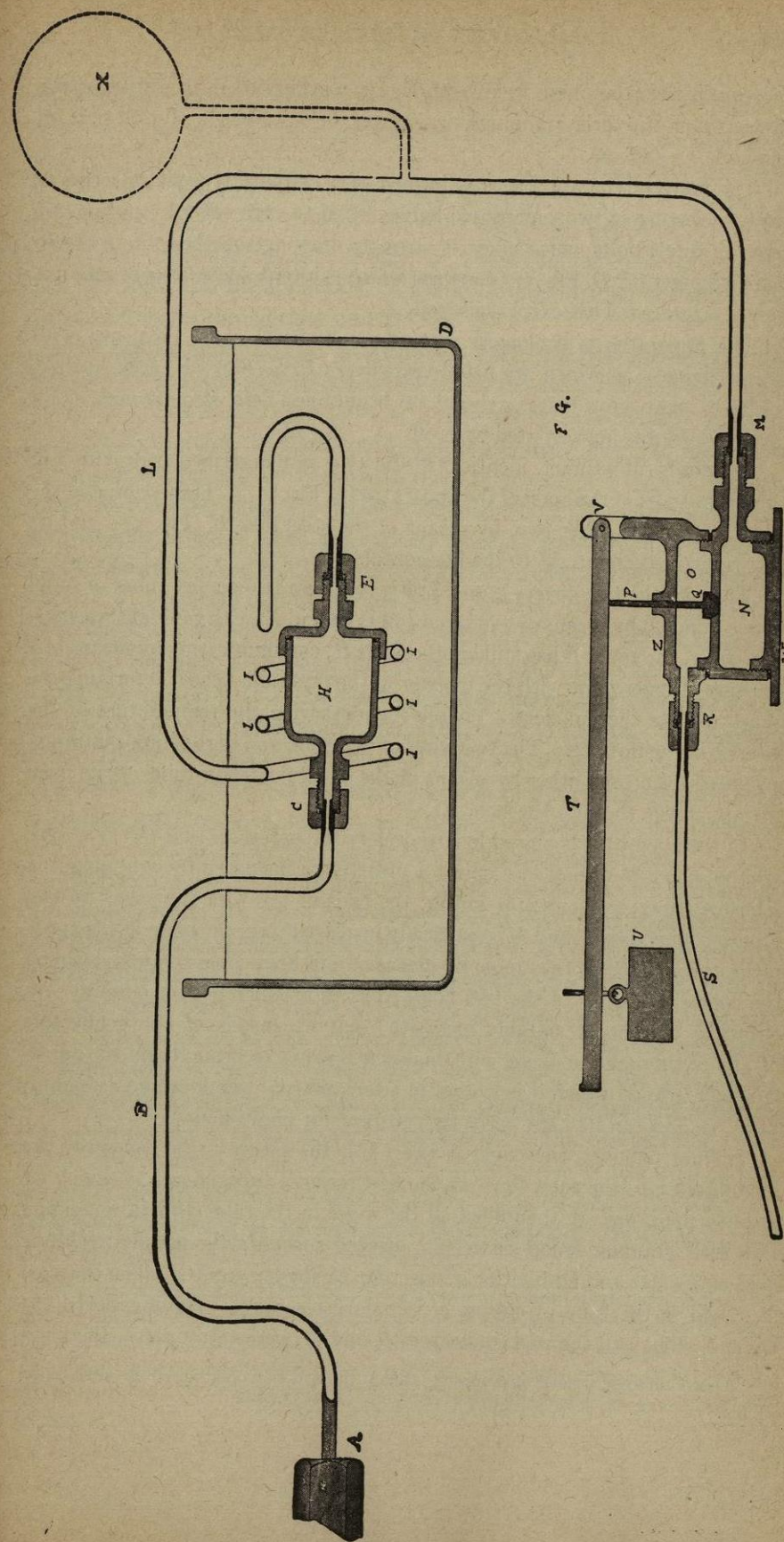


FIG. 58.—(Scale 1:4).

the continuation of these investigations) is represented in its various parts in section in the three accompanying figures (on a scale of 1:5 and 1:4; see Figs. 56, 57 and 58).

The body of the apparatus is formed of a cylindrical vessel of crucible steel, consisting of two superposed halves fitted to each other by means of a series of screw bolts which allow of strongly drawing together the two well-planed flanges (*C, D*, Fig. 57), between which is interposed a layer of asbestos board saturated with extra dense oil.

The apparatus is prolonged into two cylindrical ends, furnished with planed flanges, on which are fitted two covers *E, S* (Fig. 56), each held by means of eight screw bolts; a good joint is obtained here, also, by means of a layer of asbestos impregnated with oil.

A cylindrical adjunct, identical to the two just described, is provided in the central part of the body of the apparatus (*E*, Fig. 57). This is closed in the same way as the other two, by means of the steel disk *H* (Fig. 57), and its axis is inclined about 45° to the horizontal.

Through the two covers *E* and *S* (Fig. 56) pass two copper tubes of small bore (*A* and *Q*) by means of two screw joints (*B* and *R*) with gas-tight washers. Moreover, the cover *E* has still another hole *H*, communicating by means of a pressure-stopper joint with the interior of the porcelain tube *CD* forming the guard for the thermo-electric couple for measuring the temperature of the interior of the furnace. The two wires of platinum and of rhodium-platinum, insulated from each other by means of the usual porcelain tubes, issue from the apparatus through the hole *H*.

In the apparatus is placed longitudinally the porcelain tube *OP* (Fig. 56), around which is wound in a spiral a nickel wire insulated by wrapping it in asbestos paper and asbestos string; the ends of the wire are joined to two bronze connectors, *N* and *M*, electrically insulated from the body of the apparatus, through which they pass, by means of four fiber cones screwed down on the conical openings of the two holes so as to produce perfect closing. An electrical current of suitable intensity, sent by means of the connectors *M* and *N* through the nickel wire, makes it possible to bring it and the porcelain tube around which it is wound to a temperature which can go as high as 1200° C. and can be kept perfectly constant for many hours.

Having removed the cover *S* (Fig. 56), the pieces to be cemented are introduced into the tube *OP*. In the first series of experiments, of which we are now speaking, we then filled all the space in the tube *OP* still remaining free with granular wood charcoal,¹ washed successively with hydrochloric acid and water and ignited for a long time at about 1300° C. The charcoal was held in the tube by means of two asbestos plugs. Having closed the cover *S* (Fig. 56), the two connectors *N* and *M* were set in place, the hand

¹ Passed through a sieve of 16 mesh to the sq. cm. and held on a sieve of 81 mesh to the sq. cm.

and the key being introduced through the opening *E* (Fig. 57); by means of this same opening, all the space between the porcelain tube and the steel wall was filled with asbestos fiber so as to protect the latter from the effect of the high temperature to which the porcelain tube must be raised. Finally the cover *H* was replaced, the bolts being well tightened.

Having connected the tube *A* with the vessel containing the compressed gas, this is let into the apparatus, circulates through it from one end to the other, and issues through the tube *Q* (Fig. 56).

The copper tube *Q* (Fig. 56), through which the gas issues from the furnace, is connected with an apparatus which regulates the pressure, represented in section in Fig. 58 (scale, 1:4). This apparatus consists of a bronze chamber *H*, in which the slowing of the gaseous current owing to the widening of the section and the cooling obtained by means of a bath of running water *D*, condense the less volatile substances which are sometimes formed in large quantities, as when the vapors of certain heavy hydrocarbons are used as cements. The gases having been further cooled in the copper tubing spiral *I, I*, penetrate into the bronze box *N*, from which they can issue only by raising the polished bronze valve *Q*, weighted by means of the weight *U* sliding on the lever *T*. Along the course of the tube *L*, connecting the refrigerating apparatus with the box *N*, a manometer is inserted by means of a small copper tube, schematically indicated by *X* in Fig. 58. The washers of the various screw joints were made of rings of pure tin.

I report a single one of the series of experiments carried out with the apparatus just described, working at different temperatures and pressures and using various carburizing gases, *viz.*, cementations effected at 1100° C., using carbon dioxide under different pressures in the presence of granular carbon prepared in the way I have already described. Various experiments showed that carbon dioxide reacts with carbon at 1100° C. with such velocity that it is sufficient that the carbon dioxide, passing in quantity of 15 to 20 liters per hour, should traverse a layer of granular carbon only 6-7 cm. thick before arriving at the steel cylinders, to insure that the conditions of equilibrium of the two gases with free carbon at the given temperature shall have been reached. We can therefore practically consider that, knowing the concentrations at equilibrium of the two gases at 1100° C., the cementations of our first series are effected as if we had used carbon monoxide directly instead of carbon dioxide. Assuming this, the following table gives the results of the first series of experiments,¹ carried out with steel cylinders of the following composition:

¹The thicknesses indicated for the various zones are the mean of micrometric measurements made at many points of each specimen and not differing from each other by more than 0.05 mm. The thickness of the hypo-eutectic zones is measured from the point where the edges of primary cementite begin to the point where the concentration of the carbon is reduced to about 0.3%; there is possible, therefore, in this group of zones, an error of even 0.1 mm.

Carbon.....	0.14 percent.
Manganese.....	0.80 percent.
Silicon.....	0.03 percent.
Sulphur.....	0.05 percent.
Phosphorus.....	0.02 percent.

Number	Temperature	Pressure (kg. sq. cm.)	Time of cementation (hours)	Thickness of hyper-eutectic zone (mm.)	Thickness of eutectic zone (mm.)	Thickness of hypo-eutectic zone (mm.)	Total thickness of cemented zone (mm.)
1	1100° C.	9.5	2	1.3	0.6	1.2	3.1
2	1100° C.	ord. press.	2	0.0	0.5	1.1	1.6
3	1100° C.	15.0	1	0.8	0.7	1.0	2.5
4	1100° C.	6.0	7	2.0	1.1	2.0	5.1
5	1100° C.	ord. press.	7	0.0	1.6	1.8	3.4

The table at once clearly places in evidence the marked effect of the pressure of the cementing gas on both the velocity of the cementation and the concentration of the carbon in the cemented zones.

As regards the first point—the velocity of the diffusion of the carbon into the steel—it is enough to compare the results of the first experiment with those of the second to see how, all other conditions remaining constant, the increase in pressure from one to over nine atmospheres almost doubles the total thickness of the cemented zone obtained in two hours, raising it from 1.6 mm. to 3.1 mm.

The fourth and fifth experiments show that for a cementation of seven hours at 1100° C. the increase in pressure from one up to six atmospheres increases the total thickness of the cemented zone in the ratio of 3 to 2 (from 3.4 mm. to 5.1 mm.).

Finally, a comparison of the third experiment with the second shows that working at ordinary pressure it takes two hours to obtain a cemented zone whose thickness is less than two-thirds of that which can be obtained in one hour under a pressure of 15 kg. per sq. cm.

The effect of the pressure of the gas on the concentration of the carbon in the cemented zones follows clearly from a comparison of the first experiment with the second and of the fourth with the fifth. These comparisons show that while in the cemented zones obtained at ordinary pressure the hyper-eutectic zone is missing and the concentration of the carbon can not therefore exceed in them 0.9%, the zones obtained by cementation at pressures between 6 and 9.5 kg. per sq. cm. always contain well-developed hyper-eutectic zones.

It is self-evident that the strong influence which the pressure of the carburizing gas exercises on the depth of the cementation and on the concentration of the carbon in the cemented zones, while solid carbon is simultaneously present, is a sure proof of the preponderating activity of the gas in the cementation process over that of the solid carbon.

Moreover, a further proof of the diffusion of the carburizing gases into the mass of the steel during the process of cementation is furnished by a comparative study of the cementation of steels of different original content of carbon. I reported several series of experiments of this nature, carried out in collaboration with Dr. Carnevali, in a paper published at the beginning of 1910.¹ The following table gives one of these series, carried out by cementing for three hours, at 1100° C., but with various cements, two steels of the following composition:

	Steel A	Steel B
Carbon.....	0.18 percent.	0.94 percent.
Manganese.....	0.35 percent.	0.90 percent.
Silicon.....	0.05 percent.	0.17 percent.
Phosphorus.....	0.07 percent.	0.04 percent.
Sulphur.....	0.05 percent.	0.02 percent.

The following table shows that the cemented zones, all other conditions being equal, are deeper the higher the carbon content of the steel used.² It is clear that the contrary should manifest itself if the cementation were

Number	Cementing gas	Pressure (mm.)	Steel A				Steel B	Quantity of gas passed during 3 hours into cementation chamber (liters)
			Thickness of hyper-eutectic zone (mm.)	Thickness of eutectic zone (mm.)	Thickness of hypo-eutectic zone (mm.)	Sum of the three thicknesses (mm.)	Thickness of hyper-eutectic zone (mm.)	
1	Ethylene...	760	1.8	0.6	0.4	2.8	4.7	5
2	Ethylene...	458	0.9	0.4	0.4	1.7	2.6	5
3	Methane...	757	1.5	0.5	0.5	2.5	3.2	5
4	Methane...	463	1.1	0.4	0.3	1.8	3.1	5
5	Carbon monoxide ³	762	3.2	3.2	4.1	5
6	Carbon monoxide	461	3.0	3.0	3.8	5
7	Ethylene...	762	0.8	0.5	0.4	1.7	2.4	1
8	Ethylene...	759	1.9	0.6	0.5	3.0	4.5	15

¹F. Giolitti and F. Carnevali, *Ricerche sulla fabbricazione dell'acciaio cementato*, VI: Cementazione di acciai ad alto tenore di carbonio, con gas alla pressione atmosferica e a pressione ridotta (*Rend. della Reale Accademia delle Scienze di Torino*, 1910).

²I call attention to the fact that this result does not harmonize with those obtained a few years before by Guillet (see p. 47).

³The increase in the concentration of the carbon which is obtained by cementing with carbon monoxide at temperatures higher than 1000° C. is quite small (see *Gazz. Chim.* 1908, p. 341, *et seq.*).

In these cementations, small quantities of carbon dioxide (0.5–0.2%) mixed with the carbon monoxide are sufficient to “invert” the reaction, substituting a process of refining for that of cementation. Such an inversion is evidently impossible in cementations carried out with hydrocarbons.