hypothetical existence of carbides the phenomena of the diffusion of carbon into solid iron, both in the case (used in the process of cementation) where the diffusion takes place by contact of the free carbon with the iron and in the case where the diffusion is effected between more highly carburized iron and that less carburized, placed in contact. He maintains that the same phenomena are explained very simply by the passage of the carbon "from the molecules which are richer in it to those which contain a smaller amount," by a process entirely analogous to that of diffusion in saline solutions.

CHAPTER III

STUDIES ON THE PROCESS OF CEMENTATION DURING THE FIRST SEVEN YEARS OF THE TWENTIETH CENTURY

The last period of scientific studies on the process of the cementation of steel is clearly distinct from the preceding one, being characterized by the fact that the experimental researches comprised within it were almost always carried out with new and more accurate means of investigation, and interpreted on the basis of the new theories of physical chemistry.

Another fact characteristic of this period, which includes the first decade of our century, is the renewed activity in scientific researches on the cementation of steel, a fact which, however, is explained quite easily by the recent rapid development of the mechanical industries (and especially of the automobile industry) for which (as we shall see later) the process of cementation is becoming every day a more valuable and necessary aid.

The period with which we are now dealing can be divided into two well-defined parts:

In the first, which includes the first seven years, many of the old problems which we have seen in the preceding chapters studied and discussed for many years back, are subjected to new, ample and accurate investigations, carried out with new experimental methods and interpreted according to the new physicochemical doctrines. But the work of these first years, while preparing new and valuable experimental material, does not lead yet to the sure and complete solution of the problems studied so many years; among these it suffices to mention that of the definition of the function of solid cements and of gaseous cements, and that of the limits of temperature between which the process of cementation is effected.

In the second part of the same period, including approximately the last four years, several of the fundamental questions of the theory of cementation are completely solved in definite form, various important technical improvements of the process of cementation being based on their solution.

In the present chapter I shall limit myself to setting forth objectively the results of the experimental researches carried out during the first part of this last period, reserving the discussion of the possible theoretical and practical conclusions for one of the following chapters, together with those from the earlier investigations, summarized in the first two chapters, and of the later, more important ones, summarized in the fourth chapter.

Leaving aside some works of entirely secondary importance or of exclusively technical character (of the latter we shall speak later), the first important scientific investigations on cementation carried out during the last decennium are due to G. Charpy.

Charpy's studies mark the beginning of the new period of active scientific investigation on the process of cementation.

The first paper on cementation by Charpy was published under the title: *Sur la cémentation du fer.*[1] In it the author begins by pointing out how, notwithstanding the great number of previous *qualitative* investigations on the process of cementation, the only *quantitative* determinations on this process are those carried out by Mannesmann who (as we have already seen) had tried to establish the content of carbon which limits, at various temperatures, the cementation of the iron. But the series of temperatures determined by Mannesmann certainly contain inexact data, since in them the temperature of fusion of iron is put at 2000° C.

Charpy then reports briefly his results obtained by cementing iron filings, turnings and wires by means of a series of different cements: graphite, wood charcoal (ignited or fresh, pure or mixed with alkaline earth carbonates), animal charcoal, illuminating gas, carbon monoxide, cyanogen, potassium cyanide. The experiments were carried out under well-defined conditions, using, for the heating, an electric furnace with which it was possible to keep the temperature very constant, and measuring the latter very accurately by means of a LeChatelier thermo-electric pyrometer.

On the basis of his experiments Charpy maintains that he has proved that the cementation is not limited by the solubility of the carbon in iron, whatever may be the cement used or the temperature at which the cementation is effected.

"When the metal subjected to experiment is saturated with carbon, which happens after an interval of time which is a function of the dimensions of the specimen of steel, of the nature of the cement (which furnishes more or less carbon in the unit of time), and of the temperature (rises in which increase the velocity of diffusion of the carbon), crystals of cementite, or carbide of iron, can separate at certain points of the metal; they develop gradually on account of the inevitable oscillations of the temperature, which is kept *physically* constant.

"It is possible, therefore, even though the solubility of carbon in iron corresponds to a very low content, to completely transform the metal into carbide of iron, containing 6.67% of carbon . . . ."

I have quoted Charpy's words literally because, as is easy to verify on the basis of what we have already seen in the preceding pages, the observations to which they refer constitute a confirmation, based on accurate experimental data, of the considerations already developed before by Osmond,[2]

[1] *Comptes Rendus de l'Académie des Sciences*, 1903, 1st sem., Vol. CXXXVI, p. 1000.
[2] *The Journal of the Iron and Steel Institute*, 1897, Vol. II.

and therefore lead to conclusions essentially different from what all previous investigators had thought they were able to demonstrate with certainty.

These first experimental results of Charpy have given rise recently[1] to various interesting considerations on the conditions of the formation and of the equilibrium of cementite in the system iron-carbon.

Among the experiments on which he founds his assertions, Charpy cites the following: fillings of soft iron were kept *at a temperature of about* 650° in fused potassium cyanide, portions being analyzed from time to time.

After 48 hours' heating the filings contained 4.50% of carbon
After 86 hours' heating the filings contained 6.72% of carbon
After 110 hours' heating the filings contained 6.72% of carbon

After eighty-six hours the iron was therefore totally transformed into carbide, nor did it undergo any further transformation; the carbide obtained was completely soluble in acids and did not contain a trace of free carbon.

In view of the slowness with which the diffusion of the carbon proceeds at the relatively low temperature (around 650°), "if a piece of metal of considerable size is treated under the same conditions, it is observed that on its surface is formed a layer of iron carbide, almost pure, which cracks at many points when the metal is bent; then comes a layer of variable cementation which is but a few hundredths of a millimeter thick."

Working at higher temperatures, Charpy observed that the iron carbide decomposes, giving graphite. Thus, a piece of steel 3 mm. in diameter, heated for sixty-four hours at 1000° in a current of illuminating gas, gave a product containing 8.32% of carbon, 7.66% of it in the state of graphite. And steel filings heated at 1000° C. in *carbon monoxide* contained after thirty-six hours 9.27% of carbon, 8.27% of it in the state of graphite.

Charpy concludes that ". . . the cementation is not limited by the solubility of carbon in iron. It is possible to obtain by means of it either (when working under given conditions, and especially at low temperature) the transformation of the iron into iron carbide, or (under normal conditions) the indefinite transformation of the carbon into graphite by means of a limited quantity of iron acting as an intermediary."

We shall see later the great importance of the observations contained in this first work of Charpy.

About a month after the presentation of Charpy's Note, a preliminary note was presented by Guillet before the same Academy of Sciences.[2] In

[1] See Benedicks, *Ueber das Gleichgewicht und die Erstarrungsstrukturen des Systems Eisen-Kohlenstoff* (*Metallurgie*, 1907, Nos. 12–14).
[2] *Sur la cémentation des aciers* (*Comptes Rendus de l'Académie des Sciences*, 1903, 1st sem., Vol. CXXXVI, p. 1319).

this Guillet summarizes the first results of some investigations undertaken by him on the cementation of carbon steels and of special steels, using as cements: potassium cyanide, a mixture of potassium ferrocyanide and bichromate, wood charcoal, a mixture of wood charcoal with 5% of potassium carbonate, various mixtures of wood charcoal and barium carbonate, illuminating gas, animal charcoal.

For carbon steels Guillet reaches the following conclusions:

The velocity of penetration of the carbon is independent of the initial content of carbon in the steel, at least for hypo-eutectic steels, increases very rapidly with the temperature, varies for different cements, reaching, however, for many of these, the same limit as is reached, in general, after eight hours of heating at 1000° C. The effectiveness, which we have already seen was observed by Caron, of the addition of potassium carbonate (about 5%) to the wood charcoal is confirmed; this effectiveness Guillet attributes, as had already been done by Caron, to the formation of potassium cyanide by the action of the nitrogen of the air contained in the cementation boxes.

The brittleness of cement steels is due, in part, to the action of the prolonged heating on the "heart" of the steel, in part to the presence of cementite in the cemented zone.

As far as concerns the limit of concentration of the carbon obtained at various temperatures with different cements, Guillet observes that by cementing a fine wire of soft steel at 1100° C., after eight hours about 1.9% of carbon is obtained and the steel has a uniform structure, characterized by the usual network of cementite of highly carburized steels.

On repeating the cementation, the cementite of the network agglomerates and the absorption of the carbon begins again, proceeding, however, very slowly.

Passing then to the study of the cementation of special steels, Guillet communicates two very interesting observations.

1. The simple cementation of steels of considerably high nickel content (more than 7%) makes it possible, when it is continued until there is obtained in the cemented zone quite a high carbon content, in general above 0.8%, to obtain samples of steel, the center of which preserves the structure of tempered carbon steel, while the external layer assumes, *without tempering*, the martensite structure and the hardness of tempered steel;

2. γ-Iron steels (for example, a steel with 30% of nickel) are cemented at temperatures considerably lower than those below which carbon steels no longer undergo any modification.

To these results of the first investigations of Guillet we shall very soon have occasion to return.

A few months later Charpy presented before the Academy of Sciences[1] a new Note "Sur l'action de l'oxyde de carbone sur le fer et ses oxydes," the

[1] *Comptes Rendus*, 1903, 2nd sem., Vol. CXXXVII, p. 120.

first part of which contains some data, the importance of which, when completed and interpreted more rationally, we shall see later.

Charpy experimented by heating iron wire in a slow current of carefully purified carbon monoxide, and determined, in every experiment, the increase in weight of the metal and the quantity of carbon dioxide evolved; then he heated the metal (freed from any deposit of pulverulent carbon) in a current of oxygen to determine the quantity of carbon absorbed by this metal.

Charpy was able to observe that *above* 750° C. no deposit of pulverulent carbon is formed and the metal is sharply cemented, remaining perfectly polished and brilliant. In this case the values of the carburization deduced from the increase in weight of the metal agree with those obtained by the combustion of the metal and with those deduced from the weight of the carbon dioxide evolved during the cementation.

At temperatures below 750° C. a deposit of pulverulent carbon is formed, while the metal is carburized. Charpy maintains that he already obtains a true cementation proper at 560° C.

I reproduce herewith the table of numerical data reported by Charpy, as we shall have to refer to some of these data in what follows.

Temperature	Length of heating	Carbon fixed on the metal		
		Deduced from the increase in weight of the metal	Determined by combustion of the metal	Deduced from the weight of carbon dioxide evolved
560°	8 hrs.	0.10	0.09	Deposit of carbon
600°	8 hrs.	0.22	0.17	Deposit of carbon
715°	8 hrs.	0.26	0.28	Deposit of carbon
825°	3 hrs.	0.56	0.57	0.60
925°	2 hrs.	0.69	0.72	0.60
935°	2 hrs.	0.41	0.41	0.49
1025°	2.5 hrs.	0.60	0.58	0.58
1050°	2 hrs.	0.44	0.47	0.44
1085°	2 hrs.	0.53	0.53	0.58
1125°	2 hrs.	0.46	0.50	0.47
1175°	2 hrs.	0.47	0.47	0.51
1185°	2 hrs.	0.53	0.53	0.47
1190°	2 hrs.	0.30	0.36	0.33

From these data, Charpy maintains that we can at once infer that *the velocity of cementation* does not increase appreciably for temperatures higher than 900°. We shall see later how this assertion, not entirely exact, is due to the fact that in the experiments of Charpy it was not possible to take into account the practically most important factor in the velocity of *cementation*, that of the velocity of *penetration* of the carbon, taken as the depth to which the carbon penetrates into the mass of the iron in a given time. This factor, as well as the distribution of the carbon in the cemented zone, which we shall see is no less important, Charpy could not take into account on account of the shape—fine wires—in which he used the iron subjected to the action of the carbon monoxide.

Charpy observes that this fact can not be due to a phenomenon of saturation, for, as he himself showed in an earlier note, just reviewed, by sufficiently prolonging the contact of the iron with the carbon monoxide the separation of graphite in the metal can be secured. He adds that "the cementation will, on the contrary, be limited if, instead of working in a current of gas, the steel is heated in the presence of a limited quantity of carbon monoxide; under these conditions, the carburization ceases when the proportion of carbon dioxide formed reaches a certain value."

I will note here, since I shall make use of this observation later, how all the experiments carried out by Charpy at temperatures above 900° C. were limited to a duration of two hours (a single one barely extended two hours and a half), so that, a *slow* current of carbon dioxide always being used, all the cementations above 900° C. were in reality carried out with a limited quantity of carbon monoxide.

Charpy's note ends with some brief observations on the action of carbon monoxide on the oxides of iron; interesting observations which, however, bear only indirectly on the processes with which we are dealing.

In the meanwhile Guillet was continuing, from a standpoint somewhat different from that of Charpy, his investigations on the cementation of carbon steels and of special steels; investigations the results of which he had already, in part and succinctly, made known in the preliminary note summarized in the preceding pages. The definite results of this first series of researches are collected into a memoir presented by Guillet before the "Société des ingénieurs civils de France."[1] This it is well to review here somewhat in detail, for, although some of the data and deductions contained in it have been modified by the results of later investigations, nevertheless it has been the starting point of a series of researches and discussions fruitful in useful practical results.

Starting with some considerations on the great importance of the process of cementation and of the empirical data which in general guide and regulate its industrial application, Guillet proposes to "study this process by scientific methods," making use especially of the methods of microscopic metallography, and to "establish for it simple rules, easy to put into practice."

He considers it certain that cementation is produced only with γ-iron, the only one which can dissolve carbon, and that all carbon steels (whatever their content in carbon may be) are susceptible of "taking cementation."

[1] Léon Guillet, *La cémentation des aciers au carbone et des aciers spéciaux* (*Mémoires et compte rendu des travaux de la Société des Ingénieurs Civils de France*, Series VI, Year LVII, No. 2, February, 1904).

According to Guillet, the course of the cementation is regulated by four factors:[1]

1. The nature of the steel;
2. The nature of the cement;
3. The temperature of heating;
4. The length of contact.

These factors he proposes to study separately.

Beginning with the study of the cementation of the carbon steels, Guillet premises that in the final result of this process two things only can vary:[2]

1. The penetration of the carbon, which may be more or less deep;
2. The concentration of the carbon in the peripheral layer.

The first datum can be determined by means of the microscopical examination of a section of the cemented specimen, suitably polished and etched; and here the author dwells on the explanation of such an examination, recalling the distinction of carbon steels as hypo-eutectic, eutectic and hyper-eutectic,[3] and reproducing four microphotograms of cemented steels.

As to the second datum—the carbon content of the surface zone of the cemented cylinders—it is necessary to determine it by gravimetric analysis (by combustion) of the material obtained by removing on the lathe a surface layer of the metal about a quarter of a millimeter thick.

Guillet always carried out his experiments by cementing, in boxes 8 cm. in internal diameter, cylinders of steel 20 mm. in diameter and introducing the cold boxes into the furnace. He begins by proving, on the basis of a series of experiments carried out with a cement, the nature of which he does not indicate, on cylinders of steel of varying carbon content, that "up to a carbon content equal to at least 0.510%, the velocity of penetration of the carbon is independent of the initial content of this element in the steel."

Then, on the basis of a second series of experiments, also performed with a cement which he does not indicate, the author establishes "that the penetration increases with the time, but it is impossible—at least for the cement used in these experiments—to affirm that the velocity of penetration is constant." He concludes that in practice "it is necessary to test well the cement which is used and to make preliminary experiments as a basis, in order to obtain a definite penetration."

A third series of experiments shows that, all other conditions being equal, the velocity of penetration varies greatly with variation in the temperature,

[1] We shall have occasion to see, in what follows, that these factors are, in reality, more than four. Thus, for example, we shall see that to the factors indicated by Guillet it is necessary to add the pressure of the carburizing gas, the manner of the cooling of the cemented pieces, etc.

[2] We shall see later that here, too, other variations can present themselves. It suffices to mention, for example, the *distribution* of the carbon in the cemented zone.

[3] As I have already remarked, I must assume that the reader is well informed on what concerns the metallography of steels.

so that in certain cases a difference of 100° C. can double the velocity of penetration. The exact determination of the temperature of the cementation box is therefore of the greatest importance.

Finally, Guillet devotes a last series of experimental researches to the study of the influence of the nature of the cement on the course of the process of cementation.

After having noted the necessity of using only cements composed of chemical products of definite composition, so as to be always in a position to reproduce them exactly, and after having given a list of some cements satisfying such conditions, the author examines separately the mechanism of their action, distinguishing, from this point of view, six different cases:

1. As regards cements composed of carbon alone (such as sugar carbon, graphite and wood charcoal), Guillet affirms that important experiments recently completed have permitted him to establish that they *can not act by simple solution of the carbon by the iron placed in contact with them. Pure carbon does not cement in a vacuum.*

2. A cement containing carbon can act by means of the carbon monoxide formed by the action of the air contained in the box. But carbon monoxide *acts slowly*, giving $2CO = C + CO_2$. Moreover CO_2 has, on the contrary, a decarburizing function. In this way will act sugar carbon, washed animal charcoal, etc. To the statements of fact contained in this passage I shall have occasion to refer later.

3. Cements which contain a cyanide (such as potassium cyanide) act by means of the cyanogen group $(CN)_2$, which decomposes, liberating carbon.

4. In many cements the *formation* of a cyanide takes place. Such, according to Guillet, is the case with potassium ferrocyanide (which gives potassium cyanide and cyanate, together with iron oxide), with the mixture of potassium ferrocyanide and bichromate (which gives rise to a mixture of cyanate and cyanide, diluted in a mass of iron oxide and chromium oxide), with the mixture of carbon and barium carbonate (which, in the presence of the nitrogen of the air, gives barium cyanide and carbon monoxide, both active), and finally with ordinary wood charcoal, which owes its activity, above all, to the formation of potassium cyanide by the action of the nitrogen of the air on the potassium carbonate which is always contained in it.

To these considerations also (which are but the confirmation of those which we have already seen developed by Caron) we shall return later.

5. In cements which contain, together with carbon, carbonates which are dissociated at the temperature of cementation (especially calcium carbonate) there is formed carbon monoxide, which reacts, although very slowly.

6. Hydrocarbons, sometimes used in the cementation of large pieces, *certainly act by dissociation.* We shall have occasion, in what follows, to examine this last assertion, which, thus isolated, is not very clear.

On the basis of these considerations, Guillet classifies the cements in the following way:

1. Cements whose activity is due to carbon monoxide;
2. Cements whose activity is due to a cyanide (of potassium, of barium, of ammonium);
3. Cements whose activity is due to hydrocarbons.

The results, reproduced in the two accompanying diagrams (Figs. 15 and 16) taken from the data of Guillet, of a series of cementation tests performed with various cements under varying conditions, show that beyond a certain duration of the operation (about eight hours at 1000°) the velocity of penetration of the carbon is about the same for all cements, while this velocity varies widely from cement to cement at the beginning of each operation.

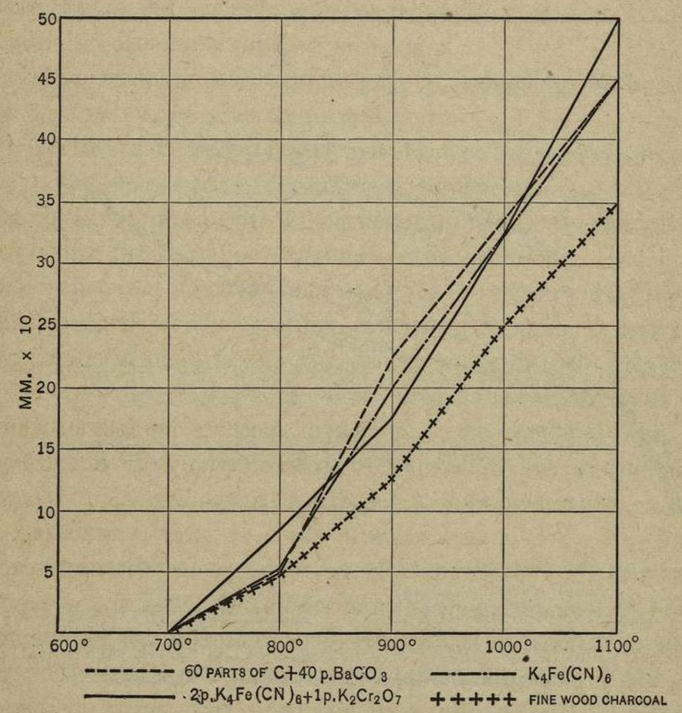

FIG. 15.—Variations in the velocity of penetration of the carbon with variations in the temperature and in the cements. (*Guillet.*)

An exception to the first part of this rule is wood charcoal which (as can also be seen from the two diagrams reproduced herewith) shows the smallest penetration after eight hours' heating at 1000°, while it gives a normal penetration after one hour.

Guillet explains this fact by assuming (as Caron had already assumed) that the carburizing activity of wood charcoal is due to the potassium cyanide which is formed by the action of the nitrogen of the air contained in the cementation boxes on the potassium carbonate always contained in ordinary wood charcoal. The course of various cementations carried out with mixtures of wood charcoal and potassium carbonate successively in a current of nitrogen, in a current of gaseous ammonia, and simply in the presence of the air contained in the boxes, showed that the *exhaustion* of the cement composed of carbon and potassium carbonate is due to the volatilization of the alkali cyanides and not to the exhaustion of the nitrogen contained in the cementation boxes.

In fact, the penetration is the same in the presence of air as in the presence of nitrogen. In a current of ammonia the penetration is continuous and always the same with any cement whatever; which, according to Guillet, is explained by assuming that in every case there is formed ammonium cyanide, to which the carburization is always due.

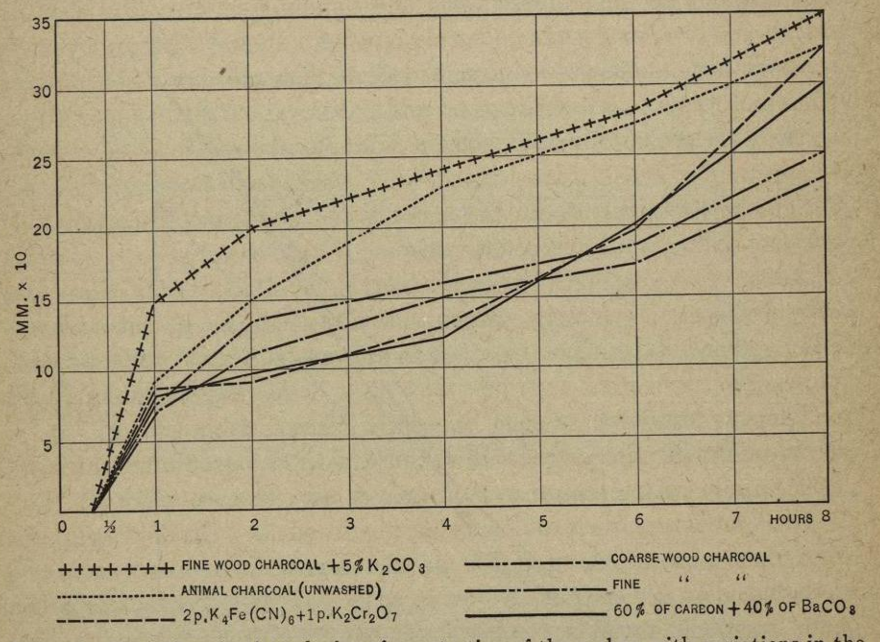

Fig. 16.—Variations in the velocity of penetration of the carbon with variations in the cements and in the length of heating. (*Guillet.*)

This last series of experimental researches on carbon steels concludes with some experiments which show the *influence of the cement on the carbon content of the surface layer*. The results of these experiments are collected in the following table:

Cements used	Carbon content: In 1st layer (1/4 mm. thick)	Carbon content: In 2nd layer (1/4 mm. thick)
80 C + 20 $BaCO_3$	1.14	0.75
60 C + 40 $BaCO_3$	1.32	1.19
40 C + 60 $BaCO_3$	0.94	0.77
$K_4Fe(CN)_6$	0.98	0.81
2 parts $K_4Fe(CN)_6$ + 1 part $K_2Cr_2O_7$	1.06	0.82

At this point Guillet, considering that he has solved with these experiments all the problems which relate to the properties of the cemented zone, passes at once to the study of the effect of the heating which accompanies the cementation on the mechanical properties, and especially on the brittleness, of the part of the cemented pieces ("core" or "heart") to which the carburization does not extend. He concludes (which could easily have been foreseen) that to reduce the brittleness to a minimum it is necessary to cement a steel containing the least possible amount of carbon during the shortest possible length of time and at the lowest possible temperature.

On the basis of various practical considerations, Guillet holds that the best carbon steel for cementation should contain from 0.10% to 0.15% of carbon and *a minimum quantity of manganese.*

A steel containing *more than* 0.35% *of manganese exfoliates* easily on quenching, when it is highly carburized.

We shall see later that the principal cause of the *exfoliation* of cemented steel is quite different from that indicated by Guillet.

The best temperature for the cementation is 850° C., being that which does not make the "core" of the cemented pieces brittle.

Guillet then lays much stress on the great importance of trying to obtain cemented zones in which the carbon concentration of the peripheral layer is exactly that of the eutectic, 0.90%. In this way only is one sure to avoid the presence of needles of cementite, which often do not disappear in quenching and are the cause of very great brittleness in the cemented zone.

We shall see later how this direction of Guillet has an importance even considerably greater than that attributed to it by its author.

It is necessary, then, to avoid "sudden cements," that is, those which in a short time give a surface layer rich in carbon. To this end Guillet recommends a cement, already recommended (as we saw) by Caron since 1861, composed of carbon (60 parts) and barium carbonate (40 parts).

The author then advises making the cementation boxes in such a way that there shall be around the pieces of steel a uniform layer of cement, about 5 cm. thick.

Finally Guillet characterizes as ridiculous the custom, common to almost all works, of quickly quenching the cemented pieces as they are removed from the boxes, for in this way the temperature at which the hardening is done can in no wise be controlled. He advises, instead, letting the cemented steel cool, to bring it to about 800° C., leaving it for the necessary length of time in a furnace heated to this temperature, and then to harden it. We shall see later how this procedure also presents serious disadvantages, and how the most rational process, and the one capable of furnishing the best and surest results, is a combination of that criticised by Guillet with the one recommended by him.

Having exhausted this first part of his investigations relative to the