THE POSITION OF MANGANESE IN MODERN INDUSTRY.

By M. V. DESHAYES.

No body among the metals and the metalloids (silicium, titanium, tungsten, chromium, phosphorus, etc.) has occupied a more prominent position in modern metallurgy than manganese, and it is chiefly due to its great affinity for oxygen. When this substance was discovered, more than a century ago (1774), by the celebrated Swedish chemist and mineralogist, Gahn, by treating the black oxide of manganese in the crucible, no one would have thought that the new element, so delicate by itself, without any direct industrial use, would become, in the middle of the nineteenth century, one of the most powerful and necessary instruments for the success of the Bessemer process, as well for its deoxidizing properties as for the qualities which it imparts to steel, increasing its resistance, its durability, and its elasticity, as has been shown elsewhere.

Without entering into a complete history (for it is beyond the task which we have here assumed),* it will not be without interest to recall how, when manganese was first obtained in a pure state, that it was supposed that it would remain simply an object of curiosity in the laboratory; but when its presence was proved in spiegeleisen and when it came to be considered an essential ingredient in the best German and English works for cutlery steel (where it is thrown into the crucible as the peroxide), then we find that its qualities become better and better appreciated; and it is surprising that no technologist ever devoted his attention to the production of manganese alloys.

It was not till after the investigations of Dr. Percy, Tamm, Prieger, and Bessemer, who employed crucibles for the production of these alloys, that Hendersen received the idea of utilizing it in the Siemens furnace. So important a compound could not remain unemployed. The works at Terre Noire produced, by the Martin furnace, for a number of years, ferro-manganese of 70 to 80 per cent. Shortly afterward, when competition in the market was established, the works at Carniola and at Carinthia, some English factories, and more especially the works at Saint-Louis, near Marseilles, of Terre Noire, of Montluçon, etc., successfully adopted the manufacture of ferro-manganese with the blast furnace, which is without doubt the method best adapted for the reduction of metallic oxides, as well in consideration of the reactions as from an economical point of view. Before very long it was possible to produce, by the blast furnace, alloys of 40, 60, 80, and even 86 per cent., in using the hot air apparatus of Siemens, Cowper, and Witwell, with the employment of good coke, and principally by calculating the charges for the fusion in such a manner as to obtain an extra basic and refractory slag.

Following in the same path, the Phoenix Co., of Ruhrort, sent, in 1880, to the Metallurgical Exposition of Dusseldorf, samples of ferro-manganese obtained in a blast furnace, with an extra basic slag in which the silica was almost entirely replaced by alumina. The works of L'Esperance, at Oberhausen, exhibited similar products, quite pure as to sulphur and phosphorus, and they had a double interest at the exhibition, in consideration of the agitation over the Thomas and Gilchrist process (see the discussions which were raised at the meeting of the Iron and Steel Institute). This process unfortunately requires for its prompt success the use of a very large quantity of spiegel or of ferro-manganese, in order to sufficiently carburize and deoxidize the burnt iron, which is the final product of the blowing.

The production of ferro-manganese by the blast furnace depends upon the following conditions.

1. A high temperature.
2. On a proper mixture of the iron ores and the manganese.
3. On the production of slag rich in bases.

These different conditions may be obtained with but slight variations at the different works, but the condition of a high temperature is one of the most important considerations, not only for the alloys of manganese, but equally as well for the alloys of iron, manganese, silicium, those of chromium, of tungsten, etc. It is also necessary to study the effects produced either in the crucible or in the blast furnace, and to examine the ores which for a long while have been regarded as not reducible.

The works of Terre Noire especially made at the same time, in the blast furnace, ferro-silicon with manganese, alloys which are daily becoming more important for the manufacture of steels tempered soft and half soft without blowing.

These alloys, rich in silicon, present the peculiarity of being poor in carbon, the amount of this latter element varying with the proportions of manganese. In addition to the alloys used in the iron and steel industry, we shall proceed to relate the recent progress obtained in the metallurgy of other materials (especially copper) by the use of cupro-manganese:

	Mn. per cent.	C.	Si.	S.	P.	
A	18 to 20	2 to 3	10 to 12	Traces scarcely perceptible.	About 0.100.	Extra quality for soft metals.
B	15 to 18	3.00	10 to 8			Medium qualities.
C	15 to 10	3.25	8 to 6			
D	5 to 10	3.50	4 to 6			Ordinary for hard metals.

The first alloys of manganese and copper were made in 1848, by Von Gersdorff; soon after Prof. Schrötter of Vienna made compounds containing 18 or 20 per cent. of manganese by reducing in a crucible the oxides of copper and manganese mixed with wood charcoal and exposing to a high heat.

These alloys were quite ductile, very hard, very tenacious, and capable of receiving a beautiful polish; their color varies from white to rose color, according to the respective proportions of the two bodies; they are particularly interesting on account of the results which were obtained by adding them to certain metallic fusions.

It is well known that in the refining of copper by oxidation there is left in the refined metal the suboxide of copper, which must then be removed by the refining process, using carbon to reduce the copper to its metallic state. M. Manhès, taking advantage of the greater affinity of manganese for oxygen, found that if this last element was intro-

duced into the bath of copper during the operation of refining, the copper suboxide would be reduced and the copper obtained in its metallic condition. For this purpose during these last years real cupro-manganese has been prepared, occupying the same position to copper as the spiegel or the ferro-manganese does toward the manufacture of steel. M. Manhès used these same alloys for the fusion of bronze and brass, and recommended the following proportions:

3 to 4 kilog. of cupro-manganese for 100 kilog. of bronze.				
0.250 to 1	do.	do.	do.	brass.
0.150 to 1.2	do.	do.	do.	copper.

In every case the alloy is introduced at the moment of pouring, as is the case in the Bessemer or Martin process, taking care to cover the fusion with charcoal in order to prevent the contact with air, together with the use of some kind of a flux to aid in the scorification of the manganese.

According to M. Manhès a slight proportion of manganese added to bronze appears to increase its resistance and its ductility, as is shown in the following table, provided, however, that these different alloys have been subjected to the same operations from a physical point of view; that is, pouring, rolling, etc.

	Cu.	Sn.	Mn.	Weight of fracture.	Elongation.
Ordinary Bronze.....	90	10		20 kil.	4.00
Bronze with Manganese, A,	90	10	0.5	24 "	15.00
Do. do. B,	90	10	1.0	26 "	20.00

The White Brass Co., of London, exhibited at Paris, in 1878, manganese bronzes of four grades of durability, destined for different uses and corresponding to about 20 to 25 kilos of the limit of elasticity, and 36 to 37 kilos of resistance to fracture; the number 0 is equivalent after rolling to a resistance to fracture of 46.5 kilos, and 20 to 25 per cent. of elongation.

Such results show beyond contradiction the great interest there is in economically producing alloys of copper, manganese, tin, zinc, etc. In addition, they may be added to metallic fusions, for deoxidizing and also to communicate to the commercial alloys (such as bronze, brass, etc.) the greatest degree of resistance and tenacity.

While many investigators have tried to form alloys of copper and manganese by combining them in the metallic state (that is to say, by the simultaneous reduction of their oxides), the Hensler Bros., of Dillenburg, have found it best to first prepare the metallic manganese and then to alloy it in proper proportions with other metals. Their method consisted of reducing the pure pyrolusite in large plumbago crucibles, in the presence of carbon and an extra basic flux; the operation was carried on in a strong coke fire, and at the end of about six hours the crude manganese is poured out, having the following composition:

Manganese.....	90 to 92
Carbon.....	6 to 6.5
Iron.....	0.5 to 1.5
Silicon.....	0.5 to 1.2

By refining, the manganese can be brought up to 94 to 95 per cent. of purity. It is from this casting of pure manganese that is obtained the substance used as a base for the alloys. This metal is white, crystalline, when exposed to the damp air slowly oxidizes, and readily combines with copper to form the cupro-manganese of the variety having the composition—

Copper.....	70
Manganese.....	30

Cast in ingots or in pigs it becomes an article of commerce which may be introduced in previously determined proportions into bronze, gun metal, bell metal, brass, etc. It may also be used, as we have already mentioned, for the refining of copper according to Manhès's process.

Tests made from this standpoint at the works of Mansfield have shown that the addition of 0.45 per cent. of cupro-manganese is sufficient to give tenacity to the copper, which, thus treated, will not contain more than 0.005 to 0.022 of oxygen, the excess passing off with the manganese into the scorias.

On the other hand, the addition of cupro-manganese is recommended, when it is desirable to cast thin pieces of the metal, such as tubes, caldrons, kitchen utensils, which formerly could only be obtained by beating and stamping.

The tenacity obtained for tubes of only three centimeters in diameter and 1.75 millimeters in thickness is such that they are able to withstand a pressure of 1,100 pounds to the square inch.

The manganese bronze, which we have previously referred to, and which is used by the White Brass Company of London, is an alloy of copper, with from one to ten per cent. of manganese; the highest qualities of resistance, ductility, tenacity, and durability are obtained with one to four per cent. of manganese, while with twelve per cent. the metal becomes too weak for industrial uses.

Manganese bronze.	Copper.	Manganese.	Weight of fracture in kilos per square mm.	Elongation.
A.....	96.00	4.00	19.00	14.60
B.....	95.00	5.00	20.62	10.00
C.....	94.00	6.00	20.80	14.60
D.....	90.00	10.00	16.56	5.00

The preceding table gives some of the experimental results obtained with the testing machine at Friedrich-Wilhelms-hütte on the crude cast ingots; the resistance is increased, as with copper, by rolling or hammering.

The manganese German silver consists of

Copper.....	70.00
Manganese.....	15.00
Zinc.....	15.00

But as this alloy often breaks in rolling, the preference is given to the following proportions:

Copper.....	80.00
Manganese.....	15.00
Zinc.....	5.00

This results in a white, ductile metal, which is easily worked and susceptible of receiving a beautiful polish, like the alloys of nickel, which it may in time completely replace.

The bronzes of manganese, tin, and zinc were perhaps the first upon which important investigations were made; they were obtained by adding to an alloy of copper, zinc, and tin (ordinary bronze) a definite quantity of the cupro-manganese of the type indicated above (Cu 70, Mn 30). By this means the resistance is increased fully nine per cent., probably in the same way as the copper, that is, by the deoxidizing effect of the manganese, as both the copper and the tin are always more or less oxidized in ordinary bronzes.

Manganese combines with tin just the same as it does with copper, and the proportion which is recommended as giving the highest resistances is three to six per cent. of cupro-manganese.

However, notwithstanding the use of cupro-manganese, the tin, as in ordinary bronzes, has a tendency to liquefy in those portions of the mould which are the hottest, and which become solid the last, especially in the case of moulds having a great width.

From a series of experiments made at Isabelle Hütte, it has been found that the metal which has the greatest resisting qualities was obtained from

Copper.....	85.00
Tin.....	6.00
Zinc.....	5.00

5 per cent. of cupro-manganese = manganese 1.00 remaining in the metal.

The best method of procedure is first to melt the copper in a crucible, and then to add the tin and the zinc; finally the cupro-manganese is added just at the moment of pouring, as in the Manhès process; then the reaction on the oxides is very effective, there is a boiling with scintillation similar to the action produced in the Bessemer and Martin process when ferro-manganese is added to the bath of steel.

The following are some of the results obtained from thirteen alloys obtained in this manner. These samples were taken direct from the casting and were tested with the machine at Friedrich-Wilhelms-hütte, and with the one at the shops of the Rhine Railroad. Their resistance was considerably increased, as with the other alloys, by rolling or hammering.

Numbers.	Nature of mould.	Copper.	Tin.	Zinc.	Cupro-manganese.	Limit of elasticity in kilos per mm.	Weight of fracture in kilos per mm.	Elongation, percentage.
1	Sand	85.00	6.00	5.00	—	11.30	16.00	—
2	—	85.00	6.00	5.00	4.00	13.00	16.10	2.00
3	Cast.	87.00	8.70	4.30	4.00	—	19.40	—
4	—	85.00	6.90	5.00	6.00	—	18.80	6.00
5	—	85.00	6.00	5.00	6.00	—	19.75	7.00
6	—	85.00	6.00	5.00	10.00	—	17.15	5.00
7	Sand	87.00	5.20	4.33	3.47	—	19.70	8.70
8	—	87.00	5.20	4.33	3.47	—	19.70	8.90
9	—	85.00	6.00	5.00	3.00	16.80	22.00	—
10	—	74.00	10.00	5.00	3.30	13.80	18.70	—
11	—	78.70	8.00	(7.66 Pb) (8 Pb)	3.30	13.80	20.70	—
12	—	82.00	9.80	4.90	3.30	14.75	19.75	—
13	—	86.20	16.50	—	3.30	14.30	24.70	—

The results of the tests of ductility which are here given, with reference to the cupro-manganese, manganese bronze, the alloys with zinc and tin, are taken from M. C. Hensler's very valuable communication to the Berlin Society for the Advancement of the Industrial Arts.

These various alloys, as well as the phosphorus bronze, of which we make no mention here, are at present very largely used in the manufacture of technical machines, as well as for supports, valves, stuffing-boxes, screws, bolts, etc., which require the properties of resistance and durability. They vastly surpass in these qualities the brass and like compounds which have been used hitherto for these purposes.—Bull. Soc. Chim., Paris, xxxvi. p. 184.

THE ECONOMICAL WASHING OF COAL GAS AND SMOKE.

In a recent number of the *Journal des Usines à Gaz* appears a note by M. Chevalet, on the chemical and physical purification of gas, which was one of the papers submitted to the Société Technique de l'Industrie du Gaz en France at the last ordinary meeting. This communication is noticeable, apart from the author's conclusions, for the fact that the processes described were not designed originally for use in gas manufacture, but were first used to purify, or rather to remove the ammonia which is to be found in all factory chimneys, and especially in certain manufactories of bone-black, and in spirit distilleries. It is because of the success which attended M. Chevalet's treatment of factory smoke that he turned his attention to coal gas. The communication in which M. Chevalet's method is described deals first with chimney gases, in order to show the difficulties of the first class of work done by the author's process. Like coal gas, chimney gases contain in suspension solid particles, such as soot and ashes. Before washing these gases in a bath of sulphuric acid, in order to retain the ammonia, there were two problems to be solved. It was first of all necessary to cool the gases down to a point which should not exceed the boiling-point of the acid employed in washing; and then to remove the solid particles which would otherwise foul the acid. In carrying out this mechanical purification it was impossible, for two reasons, to make use of apparatus of the kind used in gas works; the first obstacle was the presence of solid particles carried forward by the gaseous currents, and the other difficulty was the volume of gas to be dealt with. In the example to which the author's attention was directed he had to purify 600 cubic meters of chimney gas per minute, or 36,000 cubic

* See *Engineering*, May 27, 1881