

# Studies on the Determination of Non-Metallic Inclusions in Iron and Steel. I : Determination of Non-Metallic Inclusions in Plain Carbon Steel and Silicon Steel

著者	GOTO Hidehiro, WATANABE Toshio
journal or publication title	Science reports of the Research Institutes, Tohoku University. Ser. A, Physics, chemistry and metallurgy
volume	5
page range	505-512
year	1953
URL	<a href="http://hdl.handle.net/10097/26603">http://hdl.handle.net/10097/26603</a>

# Studies on the Determination of Non-Metallic Inclusions in Iron and Steel. I

## Determination of Non-Metallic Inclusions in Plain Carbon Steel and Silicon Steel\*

Hidehiro GOTÔ and Toshio WATANABE

*The Research Institute for Iron, Steel and Other Metals*

(Received August 17, 1953)

### Synopsis

Non-metallic inclusions in iron and steel are usually determined by hot nitric acid, electrolytic or chlorine methods. The present authors studied the adaptabilities of these three methods in the analyses of plain carbon steel and silicon steel, and obtained the following results:

In plain carbon steel, these methods were easily carried out but hot nitric acid method gave a lower value for silica than other methods, and electrolytic method gave a higher value for ferrous oxide and manganese oxide than other methods.

After all, chlorine method was most convenient and accurate. Hot nitric acid and electrolytic methods gave somewhat higher value for silica in silicon steel, but if more chlorine would be passed than in the usual case, chlorine method would give correct results.

### I. Introduction

Recently we are in a real need of an accurate and rapid method of determining the non-metallic inclusions in steels. For this purpose, the hot nitric acid method, electrolytic method and chlorine method are mainly used at present. In the present work, the non-metallic inclusions in plain carbon steel and silicon steel were determined by these methods and their advantages and disadvantages were investigated.

### II. Apparatus and analytical procedure

#### 1. Hot nitric acid method

There have been many reports concerning the hot nitric acid method, but in the present experiment "the analytical method for the determination of sand in cast iron" by Maekawa and Ebihara<sup>(1)</sup> was followed and the apparatus prescribed by J. S. P. S.<sup>(2)</sup> was used. The outline of this method is as follows:

After the sample is dissolved with nitric acid (1:3) and heated at 90°C, the non-reacted part of the sample is separated and this part is treated with 30 ml of the saturated potassium permanganate solution in order to decompose the

---

\* The 732nd report of the Research Institute for Iron, Steel and Other Metals. Published in the Journal of the Japan Institute of Metals 16 (1952), 274.

(1) Maekawa, Ebihara, Reports of The Japan society for the Promotion of Scientific Research, 19th committee, No. 1815.

(2) The Japan society for the proportion of Scientific research: *Rapid Method for the Analysis of Iron and Steels*. 2nd Ed. 139, (1949).

carbides and successively with hydrochloric acid, sodium hydroxide, and hydrochloric acid. Then the residue is ignited and weighed. By weighing, the percentage of the inclusion in sample is determined. The method of the determination of its constituents will be described later.

## 2. Electrolytic method

Concerning the electrolytic method, we find a report by Wada and Ishii.<sup>(3)</sup> In the present experiment their method was followed, that is, the sample rod serves as the anode and the copper plate as the cathode in the electrolytic solution which is composed mainly of ferrous sulfate. The sample is brought into solution by means of an electrolytic current. After electrolysis, the residue is treated with iodineferrous iodide solution in order to decompose carbides and then the inclusions are determined.

## 3. Chlorine method

Concerning the chlorine method, we find the reports by Wösmuht et al.,<sup>(4)</sup> Colbeck et al.,<sup>(5)</sup> and Moriwaki.<sup>(6)</sup> The apparatus employed in the present work was constructed on the basis of their apparatus and some improvements were made so that it might be suitable for industrial works. Its schematic diagram is illustrated in Fig. 1. It consists of a chlorine gas bomb, a nitrogen gas bomb, wash-bottles containing concentrated sulfuric acid for drying gases, a three-way stopcock, a tube containing sugar charcoal for purifying the chlorine gas, the electric furnace, U-tubes containing calcium chloride and phosphorus pentoxide for re-drying and a quartz boat in the quartz reaction tube in the electric furnace. The parts improved for the present apparatus were mainly as follows: the nitrogen gas inlet was installed by Colbeck et al between the electric furnace A and U-tube

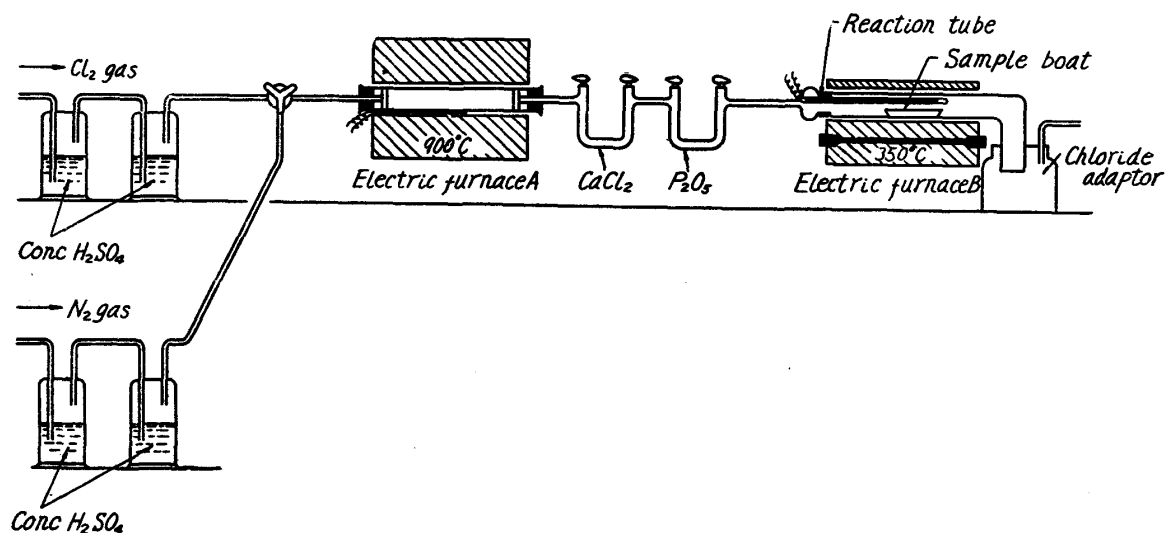


Fig. 1. Apparatus of chlorine method.

(3) Wada, Ishii, Reports of J. S. P. S., 19th committee, No. 1752.

(4) Wösmuht, Oberhoffer, Arch. Eisenhüttenwes., 2 (1929), 829.

(5) Colbeck, Craven, Murray, J. Iron and Steel Inst., 134 (1936), 251.

(6) Moriwaki, Jour. Iron and Steel (Japan) "Tetsu to Hagane", 27 (1941), 965.

containing calcium chloride, and so the oxygen contained in nitrogen gas could be removed by passing it through the alkaline pyrogallol solution. In the present apparatus it is installed as in Fig. 1 for the purpose of simplification. Usually the ring type electric furnace is used for heating the reaction tube, but with such a type considerable time is required for heating and cooling and, therefore, the furnace of split type equipped with the silicon carbide ("Erema") was used in the present work. By this device the chlorination could be done faster than before by about one hour. The procedure is as follows: first the sample<sup>(7)</sup> is placed in a boat and inserted in the reaction tube. Then the three-way stopcock opened nitrogen gas is introduced into the system to replace air in the whole apparatus (for about 15 minutes). The tube containing sugar charcoal is heated at 900°C (this temperature is maintained until the completion of chlorination). When the temperature attains to 900°C, the stream of nitrogen gas is stopped and the chlorine gas is introduced by turning the stopcock. After 15 minutes the temperature of electric furnace B is raised to 350°C until the chlorination is completed. During the chlorination, iron volatilizes as ferric chloride which condenses in the chloride adapter. After the completion of chlorination the electric furnace B is switched off and the stream of chlorine gas is stopped and the tube is cooled to room temperature by introducing nitrogen gas. After cooling, the boat is taken out and the residue is treated with hot water (at this time take out the non-reacted sample) and immediately filtered and then sufficiently washed several times in the following order: hot water, 100 ml of hot hydrochloric acid (5 per cent), 100 ml of sodium carbonate solution (5 per cent), hot water, 100 ml of hot hydrochloric acid (5 per cent) and hot water. The residue is transferred to a platinum crucible and ignited to ashes. After weighing, the percentage of the inclusions is determined. The method for the analyses of constituents will be described later.

In addition to the above, some remarks on the chlorine method will be given here. In this method, as the metallic elements are made to react with chlorine and are removed as chlorides, only the oxides are separated and determined. Silica and alumina are not affected by other elements and stable up to 550°C, but ferrous oxide and manganese oxide react with chlorine as follows:



That is to say, the oxygens in ferrous oxide and manganese oxide are quantitatively retained as  $\text{Fe}_2\text{O}_3$  and  $\text{Mn}_3\text{O}_4$ . Therefore, the actual amounts of ferrous oxide and manganese oxide will be obtained, if the amounts of iron and manganese determined by the analysis of the residue are multiplied respectively by 1.9277 and 1.7218. Also it has been reported that when  $\text{Fe}_3\text{C}$  and  $\text{Fe}_3\text{P}$  exist in such

(7) The references show that the samples used for the chlorine treatment are either chips or rods, but from the results of experiments it was found that the separation of the non-reacted part of the sample after the completion of chlorination was difficult when the chips were used. Accordingly, the block samples were used in the present work.

amounts as are usually contained in plain carbon steel, they are decomposed to ferric chloride, carbon and phosphorus by the treatment of chlorination. As the chlorine gas may contain  $O_2$  and CO, it is passed over the sugar charcoal heated at  $900^\circ C$  in order to remove  $O_2$ . It has been reported by Moriwaki<sup>(8)</sup> that by this process  $O_2$  can be completely converted to CO and the resulting CO cannot cause the decrease in the amounts of inclusions.

#### 4. Methods for the analysis of the constituents of inclusions

Many methods have been reported concerning the analysis of the residue, but the following method was used as the most accurate and simplest one. The residue ignited in a platinum crucible is fused with 2 g of sodium carbonate. The cooled melt is treated with hot water and sulfuric acid (1:5) is slowly added until the solution becomes acidic, and further 10 ml of sulfuric acid (1:1) are added. The resulting solution is evaporated on a sand bath to white fumes. After cooling 30 ml of water is added to the residue and heated to dissolve salts. Then the residue is immediately filtered and sufficiently washed and transferred to a platinum crucible. After igniting to ashes and weighing, silica is removed with hydrofluoric acid and sulfuric acid. By re-ignition and re-weighing, the amount of silica is determined. The residue in the determination of silica is fused with 1 g of  $K_2S_2O_7$  and extracted with hot water. The extract is added to the filtrate obtained when the separation of silica was done. The total volume of this combined solution is brought to 100 ml. After neutralization with sodium hydroxide solution, it is boiled and poured with stirring into another beaker containing 20 ml of hot 6 N sodium hydroxide solution. After boiling for about 30 minutes, the solution is allowed to stand. After cooling the precipitates are filtered and washed well with sodium hydroxide solution (1 per cent). The filtrate is used for the determination of aluminium and the precipitates are used for the determinations of iron and manganese.

The filtrate is neutralized with hydrochloric acid (1:1) using phenolphthalein as an indicator, and 3 g of sodium acetate or ammonium acetate and 4N acetic acid is added to it. This solution is heated to  $60^\circ C$  and add 10 ml of the acetic acid solution of oxine, keeping the pH at 4.8 to 5.0. The precipitate is filtered through a glass filter and washed first with hot water and then sufficiently with cold water. The precipitate is placed in an air bath and dried to a certain constant weight at 105 to  $110^\circ C$ . After weighing as  $Al(C_9H_6ON)_3$ , the amount of  $Al_2O_3$  is calculated.

The precipitates reserved for the determination of iron and manganese are dissolved on the filter paper with hot sulfuric acid (1:1) and hydrogen peroxide, and washed well. The solution is transferred to a 250 ml measuring flask and brought up to the mark with water. Two 100 ml portions of this solution are taken and both are boiled to decompose hydrogen peroxide. After cooling to one portion is added 5 ml of ammonium persulfate solution (20 per cent) and 10 ml of potassium thiocyanate solution (10 per cent), and then ferrous oxide is determined by colorimetry.

(8) Moriwaki, Jour. Iron and Steel (Japan) "Tetsu to Hagane", 27 (1941), 969.

To another portion, of which concentration of sulfuric acid was brought to 2 N, is added with 3 ml of 1/10 N silver nitrate solution and 10 ml of ammonium persulfate solution (20 per cent). After boiling it is cooled to room temperature with cold water and manganese oxide is determined by colorimetry.

### III. Experimental results and discussion

#### 1. Plain carbon steel

The constituents of the samples and the experimental results are shown in Table 1. As each method has been well investigated with regard to the plain carbon steel, there was no obstacle from the viewpoint of the procedure. The results obtained by the respective methods were previously inspected, comparing with those obtained by three methods, and it was seen that the reproducibilities of the hot nitric acid method and chlorine method were good but that of the electrolytic method was not good. This might be explained as follows: as the electrolytic method was carried out with a rod sample, the condition of sampling changed from outer to inner side with the repetition of the electrolysis, as actually seen in Table 1, that is, in this sample the outer surface contains inclusions of the form of aluminates, whereas the inner part contains mainly silicates.

Table 1. Results of non-metallic inclusions in plain carbon steel. Constituents of sample C 0.25%, Mn 0.49%, Si 0.224%, P 0.014%, S 0.024%.

Method	Sample taken (g)	Ignite residue (%)	SiO <sub>2</sub> (%)	FeO (%)	MnO (%)	Al <sub>2</sub> O <sub>3</sub> (%)
Hot nitric acid method	58.20	0.0065	0.0017	0.0014	trace	0.0040
	58.35	0.0060	0.0014	0.0015	trace	0.0044
	68.00	0.0080	0.0009	0.0011	trace	0.0060
Electrolytic method	out-side 14.5	—	0.021	0.0072	trace	0.0067
	13.0	—	0.022	0.0080	trace	0.0055
	inner 16.0	—	0.015	0.0150	0.0010	0.0105
	side 16.0	—	0.015	0.0230	0.0012	0.0060
	inner 16.4	—	0.019	0.0014	0.0010	0.0020
side 12.5	—	0.039	0.0180	0.0011	0.0028	
Chlorine method	17.0	0.020	0.011	0.0014	0.0006	0.0070
	14.0	0.016	0.013	0.0013	0.0006	0.0060

From the comparison of the results for each constituent obtained by three methods, it was seen that both the electrolytic method and chlorine method gave a consistent value for silica while the hot nitric acid method gave considerably low values. This seems to confirm that some parts of the silicates are attacked by hot nitric acid as Moriwaki<sup>(9)</sup> reported. With regard to ferrous oxide, the results obtained by the hot nitric acid method and chlorine method were consistent with each other, while those by the electrolytic method were of considerably high. The results of ferrous oxide by the electrolytic method are questionable, because

(9) Moriwaki, Jour. Iron and Steel, (Japan) "Tetsu to Hagane" 27 (1949), 151.

the behaviors of phosphide and sulphide are not sufficiently elucidated. The manganese oxide was determined by electrolytic and chlorine methods. This seems to confirm the fact described by Klinger<sup>(10)</sup> that these two methods only gave a satisfactory result for manganese oxide. For the determination of alumina chlorine method, hot nitric acid method and electrolytic method showed no great difference, and so it could be realized how stable the aluminate was. The time required for the separation of inclusions by each method was as follows: it required seven days with the hot nitric acid method, which could be shortened to 25 to 27 hours in haste., with the electrolytic method it required 24 hours per piece of rod sample and with the chlorine method it required two hours.

Judging from the above results and from the viewpoint of the procedure, it can be concluded that the chlorine method is the most accurate and rapid.

## 2. Silicon steel

The constituents of the sample and the results of analyses are shown in Table 2.

Table 2. Results of non-metallic inclusions in silicon steel. Constituents of sample C 0.08%, Si 4.06%, Mn 0.15%, P 0.021%, S 0.012%.

Method	Sample taken (g)	Ignite residue (%)	SiO <sub>2</sub> (%)	FeO (%)	MnO (%)	Al <sub>2</sub> O <sub>3</sub> (%)
Hot nitric acid method	45.1	0.179	0.150	0.0091	0.0012	0.014
	50.6	0.258	0.227	0.0087	0.0012	0.014
	*43.1	0.329	0.294	0.0120	0.0011	0.020
Electrolytic method	14.0	—	0.675	0.0710	0.0027	0.035
	12.0	—	0.837	0.0690	0.0024	0.033
	17.6	—	1.006	0.0290	0.0050	0.060
	12.3	—	0.502	0.0500	0.0050	0.060
Chlorine method	8.6	0.061	0.022	0.0090	0.0019	0.025
	13.4	0.058	0.018	0.0130	0.0017	0.022
	6.2	0.064	0.024	0.0140	0.0052	0.021
	5.4	0.073	0.027	0.0160	0.0049	0.022

\* Not treated with KMnO<sub>4</sub> solution.

With regard to the silicon steel, silica will give us the most difficult question. In the hot nitric acid method and electrolytic method the washing with alkaline solution must be done two or three times to remove the silica gel. In the chlorine method, the silicon volatilizes as silicic chloride at relatively low temperature (b. p. 57°C) and separates. But if it remains for some reason, the extractant ought to be made alkaline lest it should be hydrolyzed producing silica gel. Moriwaki<sup>(11)</sup> described that in his experiment on the ferrosilicon containing 40 to 70 per cent silicon the chlorination was carried out at 500 to 700°C and the extraction of the residue was made with sodium carbonate solution, and so the silica gel could be removed, on the other hand, the high value was obtained for ferrous oxide.

(10) P. Klinger, Arch. Eisenhüttenwes., 20 (1949), 151.

(11) Moriwaki, private communication, On the Determination of the Non-metallic Inclusions in Iron and Steel.

In the present investigation, however, the chlorination was carried out at 350°C as usual without raising the temperature, but a little more chlorine gas was passed through than in the case of the usual chlorination. The silicic chloride was perfectly volatilized and then the extraction was made with hot water as usual.

It was seen from the results that in the hot nitric acid method and electrolytic method the silica values were scattered and high. This was due probably to the fact that in both methods there was a question concerning the washing with alkaline solution. But in the hot nitric acid method and chlorine method the values except silica were consistent with one another and in the electrolytic method the high values were obtained in general. Further, as seen from Table 2, in the hot nitric acid method the same results were obtained even if the treatment with potassium permanganate solution was omitted. The time required for the analysis was not so much different from that in the case of plain carbon steel. Accordingly, it seems that the chlorine method is the most reliable one among them, because of a good reproducibility and an easy operation of the procedure.

### Summary

The non-metallic inclusions in plain carbon steel and silicon steel were determined by the hot nitric acid method, electrolytic method and chlorine method, and then the advantages and disadvantages of each method were elucidated.

(1) The apparatus of the chlorination method was improved as follows: (a) the bottles for the purification of nitrogen gas were improved and simplified, and (b) the furnace heating the reaction tube was improved so that the time required for chlorination was shortened by one hour.

(2) The simple and accurate method for the analysis of the constituents of the inclusions was established.

(3) The results obtained on the plain carbon steel by three methods were as follows: (a) The hot nitric acid method and chlorine method had good reproducibilities. (b) The results obtained by the electrolytic method were scattered, due probably to the change of sampling conditions at each time. (c) The hot nitric acid method gave the lower silica values than the others. (d) The hot nitric acid method and chlorine method gave the consistent values for ferrous oxide, whereas the electrolytic method gave the higher values. (e) Manganese oxide was determined only by the electrolytic method and chlorine method. (f) Method showed no great difference for alumina value. (g) Considering the above results and the time required for the separation of inclusions, the chlorine method was the most accurate and rapid.

(4) The results obtained with silicon steel were as follows: (a) The hot nitric acid method and electrolytic method gave the remarkably scattered and high values for silica. (b) In the chlorine method, in which a little more chlorine gas was passed through than in the case of the plain carbon steel and in which the residue was extracted with hot water, the good results including



the silica value were obtained. (c) The chlorine method and hot nitric acid method gave the consistent values for ferrous oxide; manganese oxide and alumina, whereas the electrolytic method gave generally high values. (d) With this sample, the chlorine method was also a simple and reliable one.