CHEMICAL DETERMINATION OF NON-METALLIC INCLUSIONS IN IRON AND STEEL

By RAIZO ISHII
Professor of Chemistry

In this paper the method of analyzing non-metallic inclusions in iron and steel is discussed, and a new method based on electrolysis is proposed. In this new method, one applicable not only to carbon steel but also to pig iron, chromium steel, etc. is considered.

I

Iron and steel contain various elements, some of which exist in part in the state of oxides. These oxides are called non-metallic inclusions, commonly consisting of silica, alumina, ferrous oxide and manganous oxide. The presence of non-metallic inclusions debases the quality of iron and steel and degrade them, hence it is necessary in the examination of iron and steel to know how much of them is contained in iron and steel in question. The determination of total amount of each element present in iron and steel is of course carried out, but the determination of non-metallic inclusions has hitherto been neglected because of its difficulty. At present, various methods for their determination are being proposed but we have not yet to find a good one. The author has carried out some research as to this point and wishes to announce its result here.

II

As methods of determining non-metallic inclusions in iron and steel are proposed: (a) the method of using an acid, (b) that of using halogens and (c) electrolyzing method. The method of using an acid is to dissolve the sample in, for instance, nitric acid[1] and let non-metallic inclusions remain as residue, but by this method manganous oxide MnO and ferrous oxide FeO are dissolved, making the result of determination uncertain. Among the methods of using halogens, that which makes use of chlorine renders the value of ferrous oxide too large, while the method of using iodine is comparatively good but has the disadvantage of requiring much reagent. The author has, therefore, taken up the electrolyzing method. Thus he has carried out electrolysis

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[1] S. Dickenson, *J. Iron and Steel Inst.*, **113** (1926), p. 177.

in a certain electrolyte using the sample as anode and taking out non-metallic inclusions as residue.

It is G. Lippert[2] who applied the electrolyzing method for the first time to the extraction of non-metallic inclusions, and we have the report by F. Fischer.[3] No marked development has been seen in this direction since then till we come to H. Hertz[4] who has carried out fundamental research on electrolysis and has shown the possibility of applying this method to the analysis. Then Fitterer,[5] Scott,[6] Treje[7] and others have carried out extraction of inclusions by using, in each case, different electrolyte and different apparatus. The defect of electrolytic method lies in that the solution becomes alkaline with the progress of reaction producing ferrous hydroxide which mingles with the inclusions, and this should be avoided. Kippe[8] has compared various electrolyzing methods, discussing their advantages and disadvantages, and the researches of Bihet,[9] Styri[10] and Klinger[11] aim at removing the above-mentioned defect. Klinger's method is useful for extracting inclusions but has the disadvantages of the manipulation being too complicated and the reagents being required in large quantity.

The author wishes to establish a method in which the analytical equipment and operation are as simple as possible, the reagents easily accessible, and reliable values are to be obtained.

III

To prevent the solution from becoming alkaline in the course of electrolysis or to maintain the hydrogen-ion concentration in the electrolyte constant, the author tried to make the amount of iron deposited on the cathode by electrolysis equal to that dissolved at the anode, i.e. to prevent the hydrogen-ion in the solution from discharging at the anode. For this purpose the method of using the same electrolyte as is used in the preparation of electrolytic iron may be suggested, but the one commonly used for that purpose cannot be applied here, for it produces iron residue in the process of electrolysis. After various experiments the author has arrived at a method satisfying to some extent. Even with this method, the discharge of hydrogen-ion takes place, although to a slight extent, rendering the solution gradually alkaline. To

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[2] G. Lippert, *Z. analyt. Chem.*, **2** (1863), p. 39.

[3] F. Fischer, *Stahl u. Eisen*, **32** (1912), p. 1563.

[4] H. Herty & G.R. Fitterer, *Min. Metallurgy Invest. Bull.*, **44** (1929), *Stahl u. Eisen*, **50**, p. 601.

[5] G.R. Fitterer, *Trans. Amer. Inst. Min. Metal. Eng.*, *Iron & Steel Devision*, No. **44** (1931), p. 196.

[6] F.W. Scott, *Ind. Eng. Chem.*, *anal. Ed.*, **4** (1932), p. 121.

[7] R. Treje & C. Benedicks, *J. Iron & Steel Inst.*, **133** (1933), No. 2, p. 205.

[8] K.H. Kippe, *Arch. Eisenhüt.*, **10** (1936), p. 93.

[9] O.L. Bihet & F. Willems; *Arch. Eisenhüt.*, **11** (1937/38), p. 125.

[10] H. Styri, *Trans. Amer. Inst. Min. Metal. Eng.*, **105** (1933), p. 185.

[11] P. Klinger & W. Koch, *Arch. Eisenhüt.*, **11** (1937/38), p. 569 .

present this undesirable effect, dilute sulfuric acid is added drop by drop to the solution through the device of siphon and the pH-value of the solution being maintained constant.

The residue remaining after electrolysis contains, beside the desired non-metallic inclusions, iron carbide and sometimes minute iron pieces mingled with them. These must be removed, as they will be confused with the ferrous oxide present in the inclusions if the residue is analysed without this preliminary treatment. So they are dissolved away with a suitable reagent, which, of course, should not dissolve the inclusions themselves. For this purpose an aqueous mixed solution of iodine and ferrous iodide is used as reagent. By treating with this solution iron carbide and minute iron pieces are dissolved away while inclusions remain intact. The residue is then fused with sodium carbonate and from the fused mass silicon, aluminium, iron and manganese are determined respectively in accordance with the ordinary methods of analysis. The values obtained are then converted into those of SiO_2, Al_2O_3, FeO and MnO and from the total amount of the sample dissolved the percentage of respective non-metallic inclusion is calculated.

In case of carbon steel the above method is applicable in determining the inclusions, but in case of an alloy steel containing more than 1% of chromium a modification is necessary as the residue of electrolysis contains, beside iron carbide and minute steel pieces, minute particles of a compound of Cr-Fe-C which resist dissolving in the solution in the subsequent treatment with iodine-ferrous-iodide solution and remain till the last stage of analysis, making the value of inclused FeO too large. The author made various experiment to remove these contaminated particles, but in vain.

The residue after the treatment with iodine solution contains above-mentioned compound of Cr-Fe-C beside the desired SiO_2, Al_2O_3, FeO and MnO. The author has then sought a method of extracting FeO alone from this mixture, and after various experiments has decided to adopt hot oxalic acid solution as the reagent for the extraction. The substance dissolving in this solution is ferrous oxide only. By determining iron in the solution we get the amount of FeO, the amounts of other inclusions being determined from the residue of oxalic acid treatment.

In case of determining inclusions in pig iron, iron phosphide Fe_3P will remain in the final residue if the residue of electrolysis is treated as in the case of carbon steel residue, giving abnormally large value for ferrous oxide. The effect is similar to that of the compound of Cr-Fe-C in the residue of chromium steel. Iron phosphide does not dissolve practically in oxalic acid solution, hence the residue after iodine solution treatment is treated with oxalic acid solution to determine the value of ferrous oxide as in the case of chromium steel, and other inclusions are determined from the remaining residue.

With a sample containing much silicon such as pig iron, silica formed in the process of electrolysis by the oxidation of silicon and not that present as inclusion will attach to the final residue which must be removed by washing it with caustic alkali solution before fusing the same with sodium carbonate.

IV

(1) *Apparatus and reagents*

Electrolyte: 40 g of ferrous sulfate (crystal), 30 g of ammonium sulfate, 20 g of ferrous chloride (crystal) and 3 g of ammonium citrate are dissolved in water making the solution 1 L, and after letting it stand for a while the solution is filtered for use.

Sample: Pieces of suitable size are used, e.z. square or round bars of 15 cm in length and 1 cm in diameter. They are used as anodes.

Cathode: A piece of perforated copper plate is bent in the form of a cylinder, 10 cm in height and 9 cm in diameter, with a handle attached at the upper edge.

Dilute sulfuric acid: 2n-H_2SO_4 placed in a 3-L glass bottle and made to run into electrolyte through the device of siphon. When the current passed is 0.5 ampere, the acid is added at the rate of 3 drops per minute.

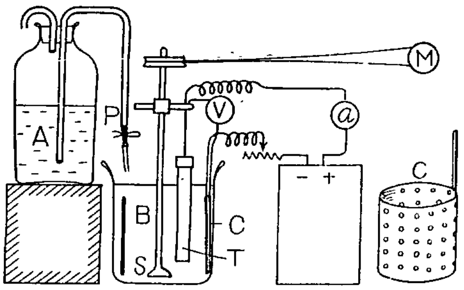
Stirrer: A glass rod with propellers at its lower end and driven by a small motor is used.

Battery: used as the source of electric current for analysis. The number of battery is increased in accordance with the number of samples to be used as anode.

Iodine-ferrous-iodide solution: 30 g of iodine, 5 g of pure iron, 4 g of ammonium citrate and 10 cc of water are placed in a conical flask, more water is then added and the solids are dissolved by shaking while being cooled. To this solution 30 g of iodine is again added, the solution is diluted with water to make it 75 cc and is used after filtration.

The arrangement of apparatus is shown in the following figure.

Arrangement of electrolyzing apparatus



A: sulfuric acid solution,
B: electrolyzing vessel,
C: copper plate for cathode,
T: anode test-piece,
S: stirrer,
P: pinch cock,
a: ammeter,
V: voltmeter.

(2) *Manipulation of analysis*

(a) Extraction of non-metallic inclusions. The case of carbon steel.

About 800 cc of electrolyte is placed in a 1-L beaker, copper cathode is inserted, a sample of known weight is placed in the solution which is made the anode, and the electric current is passed. One or several pieces of the sample are used at the same time. The current density is adjusted to 1A/100 cm^2. In the course of electrolysis pH of the solution is occasionally examined by means of test paper for hydrogen-iron concentration and pH value, of about 5 is maintained by adjusting the rate of addition of sulfuric acid through siphon. Time required for electrolysis may be shortened by increasing the number of pieces of the sample. To stop electrolysis the pieces of the sample forming the anode are raised from the electrolyte to disconnect the current and the cathode copper plate is then taken out of the solution. The residue of electrolysis remains attached to the sample, so it is carefully stripped off and dropped in the solution. If the upper surface of the solution is covered with brown coating of ferric hydroxide at the end of electrolysis, this must be removed by means of a piece of paper, before cutting off the current, 1-2 g of citric acid is then added to the solution, the whole is well stirred and the electric current is cut off after the solution has become clear. The residue is separated from the solution by filteration and is washed several times with 2% ammonium citrate solution.

The residue together with filter paper is now placed in a 100 cc conical flask with a glass stopper, to which is added 10 cc of iodine-ferrous-iodide solution and after shaking for about 1 hr. the mixture is left over night. The remaining residue is separated by filteration, washed with amonium citrate solution several times till the filtrate is colorless and does not show any reaction of ferrous ion.

The washed residue is placed in a platinum crucible together with the filter paper, the latter is burnt to ashes, 2 g of sodium carbonate is added, and after fusing and cooling Si, Al, Fe and Mn are determined in accordance with ordinary methods of analysis and amounts of SiO_2, Al_2O_3, FeO and MnO are calculated to find percentages of non-metallic inclusions in the sample.

In the case of chromium steel or any sample which contains chromium or in case when the sample contains much phosphorus such as pig iron, the residue is taken in about 50 cc of 1-n oxalic acid solution before fusing with sodium carbonate and after heating for 1 hr. on hot water bath is filtered, the filtrate is heated to distil off oxalic acid, the residue is then dissolved in acid and iron determined in accordance with the ordinary method. The residue remaining after oxalic acid treatment is fused with sodium carbonate to determine inclusions other than ferrous oxide.

In case of a sample containing much silicon such as pig iron, the residual inclusions are washed with 5% caustic potash solution before fusing them with sodium carbonate.

(b) Analysis of extracted inclusions. The ordinary analytical method has been used in the analysis. That which the author has adopted is as follows. The mass obtained by sodium carconate fusion is dissolved hydrochloric acid, the solution is evaporated to dryness and is dehydrated for 1 hr. in the air bath at 120°. After cooling, hydrochloric acid is again added, the mixture heated and the insoluble part filtered off, of which silicon is determined. The filtrate is divided into two equal parts, one part being used in the determination of manganese and the other in the determination of iron and aluminium. Thus, to the first portion 5 cc of sulfuric acid is added, the liquid evaporated and when white fume of sulfuric acid begins to appear small amount of nitric acid is added, the mixture heated and when white fume is again produced it is cooled. After this manganese is titrated by bismuthate method or is colorimetrically determined.

The other portion of the solution is diluted with water to about 50 cc, neutralized with 10% caustic soda solution and then about 5 cc more of it is added to produce the precipitate of ferrous hydroxide. The mixture is boiled for awhile and filtered after cooling. (The filtrate is reserved for the determination of aluminium.) The precipitate is dissolved away by pouring hot hydrochloric acid over the filter paper. Iron is then determined by Reinhardt method. The reserved filtrate is acidified with hydrochloric acid and aluminium is determined by phosphate method.

V

The results of the following experiments form the basis of the adopting of above-mentioned methods for extracting and treating inclusions.

As non-metallic inclusions are considered SiO_2, Al_2O_3, FeO, MnO or such substances as manganese silicate, ferrous silicate, manganese aluminate, etc. formed by the combination of oxides.

(1) In the first place non-metallic inclusions or substances related to them have been prepared, placed in 1 L of electrolyte and agitated for 6-24 hours to see to what extent they are dissolved, the results obtained being as follows:

Substance	Amount taken (in mg)	Time agitated (in hrs.)	Amount dissolved in electrolyte (in mg)
SiO_2	50	24	1.6
Al_2O_3	50	24	0.3
FeO	50	17	1.5
FeS	50	17	1.0
Fe_3C	867.0	8	610.3
Fe_3P	315.5	12	156.4
MnO	50	6	14.9
MnO (Silicate)	20	14	2.0
MnO (Aluminate)	20	14	2.7
MnS	28	20	27.9

From this result is seen that MnO is dissolved a little but other inclusions may be regarded as practically insoluble. The amount of these substances dissolving in the solution depends on the temperature at which they have been prepared. In actual cases they have undergone treatment at high temperature, hence should be far more difficult to solve than above-mentioned preparations.

As to iron carbide Fe_3C no pure sample was obtainable, hence an indirect method was resorted to. Thus a certain sample of carbon steel containing 1.45 % C was taken, electrolyzed following abovementioned directions for the determination of non-metallic inclusions. In the experiment 4.0 g of the sample was electrolyzed. The insoluble residue in the electrolyte was taken up on filter paper and, after washing with 2% ammonium citrate solution, iron was determined and the value of 240.7 mg obtained. On the assumption that no minute iron pieces existed in the residue and also that no ferrous oxide was present in non-metallic inclusions, this 240.7 mg of iron can be regarded as previously existed in the form of iron carbide, or we see on calculation that 256.7 mg of iron carbide was present in the residue of electrolysis. In 4.0 g of the sample (containing 1.45% C) 867.0 mg of iron carbide was present, hence we see that 610.3 mg of it was dissolved and 256.7 mg remained as residue. In this case, however, iron carbide was dissolved not only by the reaction of the electrolyte on it but also by the electrolysis itself.

Similar result may be stated as to iron phosphide. Thus, by electrolyzing 8.5 g of a certain sample of pig iron (containing 0.508% P) 24.7 mg of phosphorus was found in the residue. This shows that, of 315.5 mg of iron phosphide present in 8.5 g of the sample, 156.4 mg was dissolved while 158.1 mg of it was left in the residue. In this case also, more of the substance was dissolved by the electrolysis than that by the simple reaction of the electrolyte.

As to other substances it does not matter even if they were not dissolved at this stage, for they shall be subsequently treated with iodine solution.

(2) Behavior of various inclusions and related substances against 10 cc of iodine-ferrous-iodide solution is as follows:

Substance	Amount taken (in mg)	Time let alone after shaking (in hrs.)	Amount dissolved (in mg)
SiO_2	20	17	2.5
SiO_2	1.8	17	0
Al_2O_3	20	16	0
FeO	50	17	0.4
FeS	20	17	20
Fe_3C	107.5	17	106.5
Fe_3P	158.1	17	10.9
MnO	10	14	4.5
MnO (Silicate)	17	14	0 7
MnO (Aluminate)	15	14	1.3
MnS	28	14	27 7

Manganese oxide dissolved a little, but other non-metallic inclusions may be regarded as practically insoluble. If the temperature at the time of their preparation is higher, they ought to be more difficult to solve.

Again 500 mg of carbon steel ($C=1.45\%$) was taken, shaken for 1 hr. with 10 cc of iodine-ferrous-iodide solution, and after letting alone for 17 hrs. insoluble part was separated by filtration and iron was determined as to this residue, yielding the value of 0.9 mg as the amount of iron. The residue may have been ferrous oxide, but if we assume this to have consisted of iron carbide, the amount of residue was 1 mg. There was present 107.5 mg of iron carbide Fe_3C in 500 mg of this steel, so we see that nearly all of it was dissolved by the treatment with iodine-ferrous-iodide solution. A similar result has been obtained with a different sample of carbon steel. It is also seen from this experiment that metallic iron dissolves quite well in iodine solution.

Residue of electrolysis contains iron phosphide Fe_3P. By treating the residue obtained by electrolyzing a certain specie of pig iron with iodine solution, it was found that 10.9 mg of iron phosphide (1.7 mg as P) dissolved and 147.2 mg of it (23 mg as P) remained, showing that the substance is nearly insoluble. Also by treating 328 mg of a certain sample of grey pig iron ($P=0.221\%$) with iodine solution, it was seen that only 0.74 mg of P was present in the residue, showing that iron phosphide is totally insoluble in iodine solution.

Both MnS and FeS were dissolved well with this treatment.

(3) In order to see how inclusions and related substances would behave against oxalic acid solution, these substances were treated separately with 50 cc each of 1-n hot oxalic acid solution. The results obtained are as follows:

Substance	Amount taken (in mg)	Amount dissolved (in mg)
FeO	30	30
FeO (Silicate)	12	7.1
Fe_2O_3	30	28.2
SiO_2	20	0
Al_2O_3	30	0
MnO	20	0
Ferrophosphor $\left\{\begin{matrix}P=23.4\\ Fe=74.4\end{matrix}\right.$	200	2.3 (as Fe_3P)
Fe_3P	4.6	0.1
Cr-Fe-C	100	0
Ferrochrome $\left\{\begin{matrix}Cr=65.3\\ Fe=31.3\end{matrix}\right.$	30	0.1

From this we see that ferrous oxide was dissolved well while other substances were not. Even when ferrous oxide was present as ferrous silcate, we may say that it was practically soluble. Iron phosphide and the compound of Cr-Fe-C did not dissolve in oxalic acid solution.

(4) To a certain sample of carbon steel the method of determining non-

metallic inclusions was applied and the result obtained was 0.071% as the value of FeO in the sample. To the same sample the method of treating with iodine solution was applied and the residue was treated with oxalic acid solution to determine iron dissolving in the solution, the value of 0.071% FeO being obtained as the result which agreed well with the result of former determination. Again the treatment with oxalic acid solution was applied to another kind of carbon steel and non-mentallic inclusions in oxalic acid and in the residue were determined with the following results showing the dependability of the method of extraction with oxalic acid solution.

Trials	Inclusions in oxalic acid solution (%)				Inclusion in the residue (%)			
	SiO_2	Al_2O_3	FeO	MnO	SiO_2	Al_2O_3	FeO	MnO
1st	0	0	0.029	0	0	0.005	0.002	0.003
2nd	0	0	0.025	0	0	0.006	0.003	0.004
3rd	0	0	0.032	0	0	0.004	0.002	0.004

VI

Below are the examples of the results of analysis of carbon steel, special steel, pig iron, etc. carried out in accordance with above-mentioned method.

(1) Carbon steel (C=0.22%)

	SiO_2	Al_2O_3	FeO	MnO
Results obtained by author's electrolyzing method	0.005	0.005	0.012	0.009
Fesults obtained by a certain warm nitric acid method	0.005	0.005	0.001	0.001

(2) Silicon steel. The method for analyzing carbon steel was applied, except that the final residue was washed several times with caustic potash solution.

(3) Chromium steel. The final residue was treated with oxalic acid solution, and ferrous oxide was determined from the solution and other inclusions from the residue.

Cr-steel No. 1 (Cr=2.8%)

	From oxalic acid solution	From the residue
SiO_2	0	0.023
Al_2O_3	0	0.003
FeO	0.059	—
MnO	0	0.001

Cr-steel No. 2 (Cr=0.7%)

	From oxalic acid solution	From the residue
SiO_2	0	0.006
Al_2O_3	0	0.003
FeO_2	0.026	—
MnO	0	0.001

(4) Pig iron. Oxalic acid treatment was carried out, and the residue was washed with caustic alkali solution.

	From oxalic acid solution	From the residue
SiO_2	0	0.022
Al_2O_3	0	0.034
FeO	0.080	—
MnO	0	0.005

	From oxalic acid solution	From the residue
SiO_2	0	0.045
Al_2O_3	0	0.040
FeO	0.093	—
MnO	0	0.003

Summary

The electrolyzing method of determining non-metallic inclusions in iron and steel, viz. SiO_2, Al_2O_3, FeO and MnO is discussed. When a suitable electrolyte composed of 40g. $FeSO_4 \cdot 6H_2O$, 30g $(NH_4)_2SO_4$, 20g, $FeCl_2 \cdot 4H_2O$ and 3 g of ammonium citrate dissolved in 1 L of solution is used and its pH value maintained at about 5 during the electrolysis by regularly adding H_2SO_4 drop by drop, the inclusions are taken out as residue mixed with a part of Fe_3C and minute Fe pieces. By treating with I -FeI -solution, Fe_3C and Fe are removed and from the remaining residue the value of SiO_2, Al_2O_3, FeO and MnO are determined in accordance with the ordinary method of analysis. The presence of a compound of Cr-Fe-C or Fe_3P hinders the application of the method as such, due to their insolubility in iodine solution, but the difficulty may be overcome by treating the residue of the treatment with iodine solution with hot oxalic acid solution which dissolves FeO but not the compound of Cr-Fe-C nor Fe_3P. Other inclusions do not dissolve in it, either. Hence FeO is determined from Fe dissolved in the oxalic acid solution and other inclusions from the final residue.