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UNITED STATES BUREAU OF MINES
SCOTT TURNER, DIRECTOR

REPORT OF INVESTIGATIONS

THE DEVELOPMENT OF AN ELECTROLYTIC METHOD
FOR THE DETERMINATION OF INCLUSIONS
IN PLAIN-CARBON STEELS



BY

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NONMETALLIC INCLUSIONS: THE DEMAND FOR
"CLEAN" STEEL

Steel manufacturers have noticed a decided tendency on the part of many of their customers to become more exacting in their steel specifications. Under these conditions, the steel must not only meet the specifications of physical properties (tensile strength, reduction of area, elongation, impact strength, grain size, normality, etc.) and the chemical analyses, but must also pass the inspection test of "cleanliness."

By cleanliness is commonly meant the absence of oxide and sulphide inclusions. Other foreign particles such as furnace or ladle slag, ladle and runner brick, etc., must also be absent. The determination of cleanliness at present is usually made by microscopic inspection or macroetching.

The rejection of steel for lack of cleanliness is increasing, but cleanliness is one of the most difficult requirements for the manufacturer to fill. The reason for this is that every steel inspector has a different conception of a clean steel. A material which does not pass the examination of one inspector may be regarded as entirely satisfactory by the metallurgist of another company.

The cause of this confusion and disagreement concerning the definition of a clean or a dirty steel is simply that as yet no standardized procedure for the determination of impurities has been proposed and generally accepted, since many variables are encountered which interfere with the development of a satisfactory method. An idea of the complexity of this situation will be obtained from the following pages.

A Survey of Proposed Analytical Methods

Although no analytical method has been accepted, many procedures have been proposed, as may be seen in Table 1. Therein are listed 16 of the better-known processes, with references to the work of their originators, their mechanisms of determination, and their applicabilities. Among these is included the electrolytic method developed by one of the present authors, and some comparison between this and previously proposed procedures may be obtained by a study of the table. It appears that this new method has many advantages over the others, and this paper presents a critical study of its value.

It should be emphasized at this time that, as shown in Table 1, this procedure is recommended only for the determination of MnO, MnS, FeS, SiO₂, and Al₂O₃ in the plain and low carbon steels.

More recently another electrolytic method has been proposed by Scott (57).⁵ His procedure, which was recommended for the extraction of all types

⁵ Numbers in parentheses refer to the bibliography at the end of this paper.

of inclusions from all types of steels, called for the use of magnesium iodide solution to control the H-ion concentration by precipitation of magnesium hydroxide. This recommendation is interesting and important, but we feel that entirely too little work was done on the accuracy of this method to justify a broad statement of its usefulness.

The inclusion materials which usually exist in steel may be classified into two general types -- namely, oxides and sulphides. Many combinations of oxides such as the silicates have been recognized in steel, as well as combinations of such sulphides as FeS and MnS. Up to the present date the only method which has been proposed for the determination of FeS and MnS in plain-carbon steels is the electrolytic procedure (46). All of the other methods have been concerned with the determination of oxides and their combinations. In most cases the originators recommended their method for the determination of all types of oxide inclusions (including FeO) from all types of steel. Also, in most of these cases the results obtained have been questionable, even for some of the simple types of steels. In general some of the oxides, particularly MnO and the sulphides, are attacked and dissolved, thus giving low results, and at the same time other factors tend to contaminate the inclusion residue and to give high results. The balance between these two conditions constitutes the reported analysis.

It is improbable that a procedure which will determine all types of inclusions from all types of steels will ever be established. In order to obtain the oxide and sulphide contents of all types of steels, many and distinctly different methods will probably be needed.

The principal methods which are being used to-day are the Ledebur, the vacuum fusion, Kichline, Eggertz (or Willems), Dickenson, and the electrolytic procedures, as shown in Table 1. Of these, the methods which have withstood rather severe criticism are:

1. The vacuum fusion for the determination of total oxygen. (Its accuracy is still unknown (13).)
2. The modified Ledebur method for the determination of FeO. (Absolute accuracy still undetermined.)
3. The modified Kichline. (Accurate for Al_2O_3 in aluminum-killed steels.)
4. The electrolytic. (Accurate for MnO, MnS, FeS, SiO_2 , and Al_2O_3 in plain and low carbon steels only.)

The development of the fourth method will be described in the following pages and although the analysis of low and high alloy steels by this method is not recommended, information concerning the difficulties encountered in satisfactory procedure for alloy steels.

Table 1.- Proposed methods for determining oxides and sulphides in steel

Common name	Bibliography reference numbers	Mechanism	Recommended by originators for	Advantages	Disadvantages	Remarks
Snelus'	1	Mechanical separation of slag from metal by crushing metal	Wrought-iron slag	None	Many	No longer used
Tucker's	2	Fusion at atmospheric pressure in the presence of carbon	Total oxides	None	Many	Do.
Vacuum fusion	3-13 inclusive	$C + MeO \rightleftharpoons CO + Me$ CO collected by evacuation of system	Total oxides	Probably useful for FeO + MnO in plain-carbon steels	Complete reduction of SiO_2 and Al_2O_3 is questionable (13). Requires elaborate equipment. Slow	Being used in some research laboratories. Few if any plant laboratories use it for control or inspection
Ledebur's	14-22 inclusive; 60, 61, 62	$H_2 + MeO \rightleftharpoons H_2O + Me$ H_2O collected and weighed	FeO	Probably useful for FeO in plain-carbon steels	Many questions concerning accuracy. Requires elaborate equipment. Slow	Being used in some research laboratories. Used by few if any plant laboratories.
Fresenius', chlorine, or Pourcels'	23-26 inclusive; 50, 51, 52, 55	$2Fe + 3Cl_2 \rightleftharpoons 2FeCl_3$ $FeCl_3$ volatilized. Inclusions in residue	All types of oxide inclusions	Probably useful for SiO_2 in plain-carbon steels (51)	Considerable contamination. Inclusions attacked (26)	Only a few laboratories using method to-day.
Fresenius' galvanic	34	$CuCl_2 + Fe \rightleftharpoons FeCl_2 + Cu$ Inclusions in residue	Do.	None	Slow. Very small sample of steel dissolved. Analytical error great	No longer used
Troilius'	27	$2FeCl_3 + Fe \rightleftharpoons 3FeCl_2$ Inclusions in residue	Do.	None	Do.	Do.
Mercuric chloride	28, 29	$HgCl_2 + Fe \rightleftharpoons FeCl_2 + Hg$ Inclusions in residue	Do.	None	Many	Do.
Bischoff's	30	$CuNH_3Cl_2 + H_2O = CuCl + HCl + NH_4OH$ $2HCl + Fe = FeCl_2 + H_2$ $2CuCl + Fe = FeCl_2 + 2Cu$ Inclusions in residue	Do.	None	Do.	Do.

Table 1.- Proposed methods for determining oxides and sulphides in steel - Continued

Common name of method	Bibliography reference numbers	Mechanism	Recommended by originators for	Advantages	Disadvantages	Remarks
Kichline's	31, 32, 33	$2\text{HCl} + \text{Fe} \rightleftharpoons \text{FeCl}_2 + \text{H}_2$ Inclusions in residue	Al_2O_3	Accurate for Al_2O_3 in Al-"killed" steels (33)	Dissolves MnO-containing inclusions. Al_2O_3 analysis inaccurate when much MnO and SiO_2 are present	Being used in many plant laboratories for determination of FeO in liquid steels (33).
Bromine	32, 34, 35, 36, 56	$2\text{HBr} + \text{Fe} \rightleftharpoons \text{FeBr}_2 + \text{H}_2$ Inclusions in residue	All types of oxide inclusions	None	Contamination. Inclusions attacked	Practically extinct.
Eggertz'	37, 38, 39, 54	$2\text{HI} + \text{Fe} \rightleftharpoons \text{FeI}_2 + \text{H}_2$ Inclusions in residue	Oxides but not sulphides	May be fairly accurate for SiO_2	Sulphides attacked. Small sample. Analytical error large	Being used in some plant laboratories.
Willems'	40	$\text{I}_2 + \text{Fe} \rightleftharpoons \text{FeI}_2$ Inclusions in residue	Oxides but not sulphides	Do.	Do.	Do.
Dickenson's	41, 42, 43	$2\text{HNO}_3 + \text{Fe} \rightleftharpoons \text{Fe}(\text{NO}_3)_2 + \text{H}_2$ $3\text{HNO}_3 + \text{Fe} \rightleftharpoons \text{Fe}(\text{NO}_3)_3 + \frac{3}{2}\text{H}_2$ Inclusions in residue	SiO_2 and silicates	Fairly accurate for SiO_2 in Si-"killed" steel (43)	Dissolves Fe and Mn silicates, FeS and MnS	Do.
Phosphoric acid	44	$2\text{H}_3\text{PO}_4 + 3\text{Fe} \rightleftharpoons \text{Fe}_3(\text{PO}_4)_2 + 3\text{H}_2$ Inclusions in residue	Do.	None	Dissolves inclusions and precipitates iron phosphate	Never used practically.
Electrolytic	$\text{FeSO}_4 - \text{NaCl}$, 45-49 inclusive; miscellaneous, 57, 92, 93	$\text{Fe} - 2e \rightleftharpoons \text{Fe}^{++}$ Inclusions in residue	MnO, MnS, FeS, SiO_2 , and Al_2O_3 in plain-carbon steels (46)	Rapid solution, neutral electrolyte, recovers both oxides and sulphides (46)	Can not be used for alloy steels (46) in present state	Being used in plant and research laboratories.
Reviews	58, 59	-	-	-	-	-

ELECTROLYTIC PROCEDURE

Historical Review

The first experimental work on electrolytic extraction was done by Eckel (47) in 1927, who attempted to dissolve electrolytically the steel anode in a moving electrolyte containing FeSO_4 , FeCl_2 , and $(\text{NH}_4)_2\text{SO}_4$. An alumina dialyzing cup was used to separate the anode from the cathode. Difficulty was encountered due to the formation of certain basic iron salts. An attempt to overcome this was made by covering the electrolyte with oil to prevent oxidation, and increasing the acidity, but other conditions were encountered which were rather discouraging. It seemed necessary at that time to maintain reducing conditions so as to prevent oxidation of the iron salts. Hence Marshall (44) attempted electrolysis in ferrous sulphate electrolytes under several atmospheres pressure of hydrogen. In this case considerable hydroxide precipitation was encountered, although the basic salts did not form. Several other types of cells were devised by this investigator but with similar results. Hence it became apparent that a study of the hydrogen-ion concentration was essential for successful electrolysis and inclusion determination. In this connection Marshall studied the effect of certain buffer solutions on a 30 per cent ferrous sulphate electrolyte. He found that the H-ion concentration could be maintained at $10^{-6.75}$ by means of tartrate solutions, but simultaneously a basic iron tartrate precipitation contaminated the inclusion residue. A similar condition was encountered in connection with the citrate solution, but in this case the H-ion concentration was not easily controlled. Meneilly (48) was the next to work on this problem. Three main improvements resulted from his work from which was evolved the method now being used (46). These changes were:

1. The concentration of FeSO_4 was decreased to approximately 3 per cent to decrease hydrolysis.
2. NaCl was added to increase conductivity of a solution of such low H-ion concentration.
3. A collodion bag (dialyzer) was used to separate the anode from the cathode portions of the cell and to trap the falling inclusion residue.

Krockenberger (49) next studied the change of H-ion concentration of the electrolyte in the anode compartment both with and without electrolysis.

The data obtained from these experiments and work done by the other authors of this paper were all correlated in such a manner that the method recommended by Fitterer (46) was finally selected. The data on which this development was based are described herein.

Brief Description of the Electrolytic Procedure for Plain and Low Carbon Steels

The electrolytic procedure has been previously described in detail (46) so that any steel plant chemist should be able to follow the directions and obtain fair accuracy after some experience. Some precautions are necessary which were listed in the previous publication. The method will be briefly described herein for the purpose of clarity.

Preparation of Sample for Electrolysis

The steel specimen, weighing at least 50 grams, is soldered to a platinum wire and suspended from a copper bus bar. This is shown in Figure 1. A kink (marked C in the figure) is made in the platinum wire above which is suspended a rubber block, E, which serves as a support for the collodion (or cellophane) bag, F, which surrounds the sample. This dialyzing bag is first partially filled with electrolyte and then brought up and around the sample, after which the open end is tied above the rubber block.

The Electrolytic Cell

The collodion bags containing the samples and some electrolyte are immersed in the tank solution as shown in Figure 2. The walls of this tank are made of copper sheet and serve as cathodes during electrolysis. The bus bar upon which the samples and the bags are suspended is attached to the positive terminal and is insulated from the main part of the tank or cathode. About 10 liters of electrolyte, containing 3 per cent $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and 1 per cent NaCl in water, is used in each tank.

After approximately six samples have been placed in the tank, the current is turned on so that there are approximately 6 to 7 amperes per tank or one ampere per sample. The potential across the electrodes is approximately 3 to 4 volts. The source of power can be either a large battery charger or any d.c. current regulated by means of a lamp-bank series of resistances.

Theory of Electrolysis

The theory of the electrolytic procedure may be briefly described in the following manner. As soon as the power is turned on, the iron anode receives a positive charge. In doing this the iron becomes ionized with two positive charges, through the loss of two electrons, and passes into the solution at the rate of approximately 1 gram per hour for each sample. These iron ions then pass from the electrolyte inside the collodion bag through the walls of this membrane and finally into the external electrolyte. From this point they pass directly to the nearest wall of the tank, where they are deposited as metallic iron. Hence the iron anode gradually decreases in weight and after 24 hours approximately 24 grams of steel will be electrolytically dissolved. During this process most of the nonmetallic inclusions fall from the iron anode to the bottom of the collodion bag, where they are retained. It is believed that the pores of the collodion bag are small enough to retain these oxide particles and yet are sufficiently large for the passage of the iron ions.

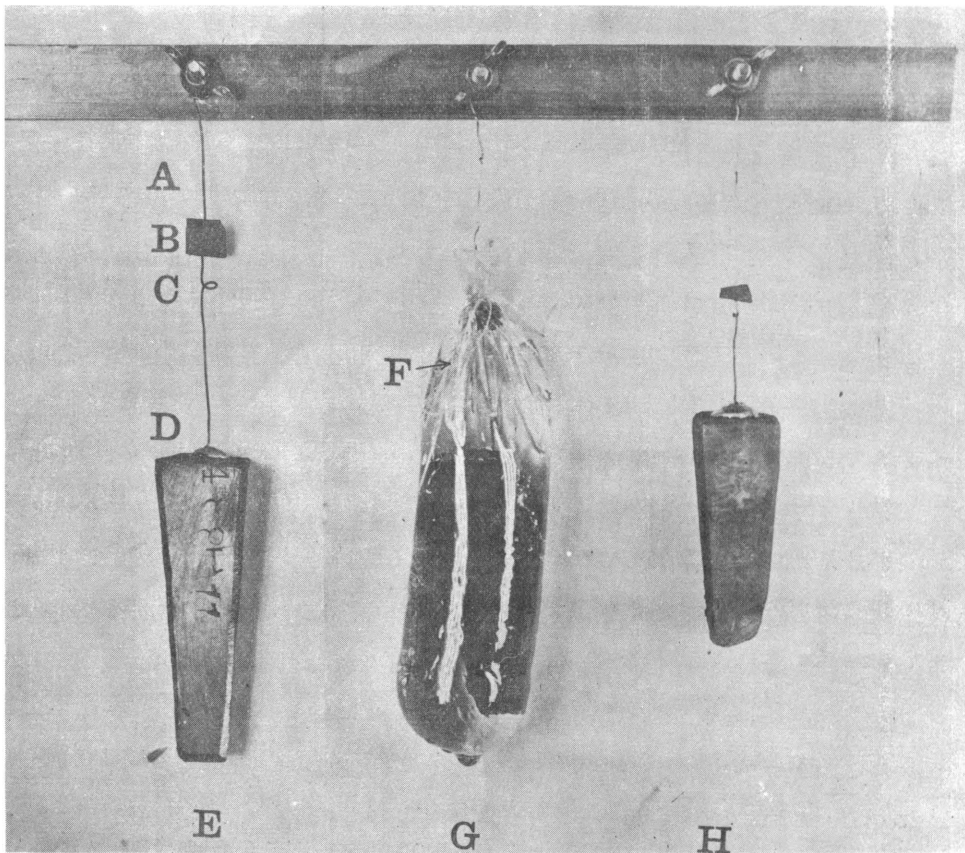


Figure 1.—Preparation of sample for electrolysis

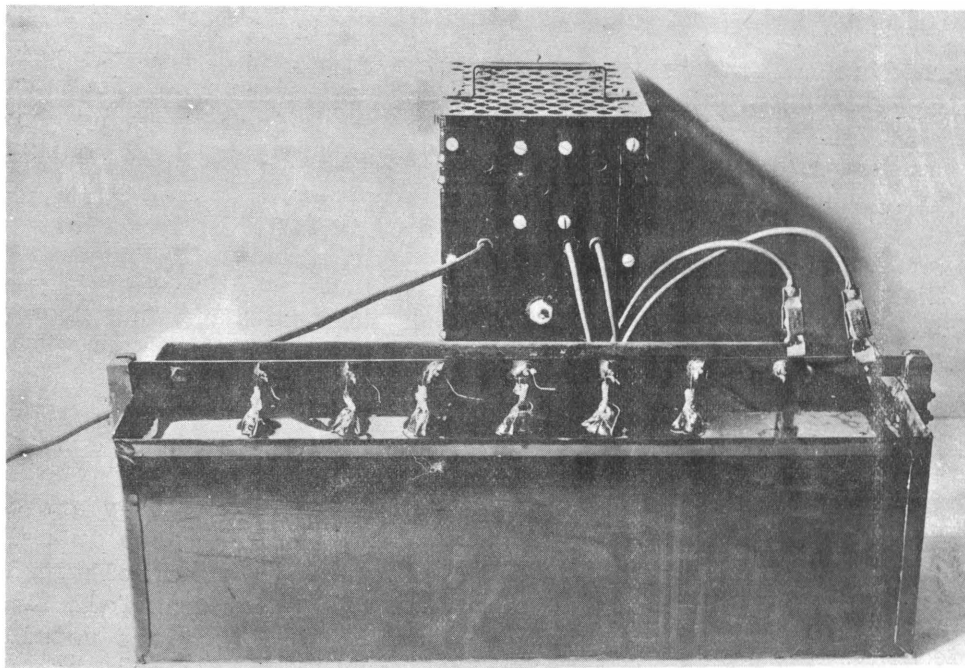


Figure 2.—Multiple electrolytic cell with six samples in position

After the 24-hour period, the inclusion residue at the bottom of the bag has become sufficiently large for an accurate analysis. The electrolyzed sample and collodion bag are then removed from the cell and the exterior of the bag is washed with water. The collodion bag is then opened and the contents collected in a beaker. Any nonmetallic material still adhering to the iron anode is scraped off and the sample washed free from such particles. This suspension is then filtered and washed about six times with warm water.

Analytical Procedure

The residue on the filter paper contains $\text{Fe}(\text{OH})_2$, $\text{Fe}(\text{OH})_3$, FeO (not determined by this procedure), graphite, FeS , MnO , MnS , SiO_2 , Al_2O_3 , and their many combinations. The paper is dried, folded, and placed in a clean platinum crucible and ignited for one hour at a low temperature (just sufficient to ignite the paper). The detailed analytical procedure is given in the previous paper (46).

Each analyst has a preference for analytical procedures. The methods used in these laboratories are briefly mentioned in the following discussion.

After fusion with sodium carbonate, the SiO_2 is determined in the usual manner with hydrofluoric acid. Al_2O_3 may be determined by sodium hydroxide, the phosphate method, or by the iron-aluminum hydroxide separation method. The procedure generally used at the Bureau of Mines is the sodium hydroxide separation. The total manganese present as $\text{MnO} + \text{MnS}$ is determined by the usual bismuthate method and a recommendation has been made for the separation of these two materials. It has been found, as will be shown in this paper, that MnO is entirely soluble in the sodium citrate solution, whereas manganese sulphide is entirely insoluble. This permits the separation of the two and also provides a means for determining the quantity of FeS present by difference.

STUDY OF THE FACTORS WHICH AFFECT THE ACCURACY OF THE ELECTROLYTIC DETERMINATION

In the development of a satisfactory method, it is necessary that an accurate study of many factors be made. Some of the variables encountered are described in the following pages.

The main problem which was encountered resolved itself into the selection of an electrolyte which would have such a low acidity that the inclusions (particularly MnO) would not be attacked or dissolved, but which at the same time would not be so low that the hydroxides, particularly $\text{Mn}(\text{OH})_2$, would precipitate. It is obvious that if MnO were soluble in the electrolyte the reported analysis would be low, whereas if the manganese hydroxide precipitated, the results would very likely be much higher. A solution was required which would have neither of these detrimental effects. However, it was realized that if a solution had a sufficiently high acidity so that the precipitation of $\text{Fe}(\text{OH})_2$ was prevented, the MnO would be highly soluble, whereas if an electrolyte was selected in which MnO would not dissolve,

considerable iron hydroxide contamination resulted. At the same time, the extent of manganese hydroxide precipitation was unknown. However, it seemed advisable to select an electrolyte which would be satisfactory for MnO and to postpone a study of the determination of FeO. Hence an electrolyte was required which would not dissolve MnO or precipitate manganese hydroxide but probably would precipitate iron hydroxide. It is now apparent that an electrolytic determination of FeO must be done under entirely different conditions than specified by the recommended procedure. The reasons for these conclusions will be given in the following pages.

Characteristics of the Recommended Electrolyte

It will be recalled from the historical part of this paper that Marshall (44) studied the electrolysis of steels in highly concentrated ferrous sulphate solutions (30 to 40 per cent). Also, it was obvious from Meneilly's work (48) that the H-ion concentration was a factor of hydrolysis of the ferrous sulphate, and for this reason he decreased the FeSO_4 concentration as low as possible without impairing the conductance of the electrolyte. He found this point to be at approximately 2 to 3 per cent $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. It also seemed apparent at that time that an addition of 1 to 2 per cent NaCl would greatly increase the conductance of the solution without increasing the acidity.

The solubilities of the oxides and the sulphides in the electrolyte are entirely dependent upon the H-ion concentration. In the more concentrated solutions such as those encountered in Marshall's work, very little nonmetallic matter was reported upon analysis of the residue. As the concentration was decreased, the inclusion contents increased and became fairly constant at the recommended concentrations. These indications were of course qualitative and were not sufficiently quantitative to be satisfactory for the accurate determination of the nonmetallic matter in steel. For this reason it seemed necessary to determine the H-ion concentration of the electrolyte and also the solubilities of the various nonmetallic materials in the electrolyte which has been selected. Finally, it was essential to quantitatively determine the extent of $\text{Mn}(\text{OH})_2$ precipitation before the accuracy of the MnO or MnO + MnS determination could be established.

Hydrogen-Ion Concentrations of FeSO_4 and FeSO_4 -NaCl Solutions

An apparatus was designed as shown in Figures 3 and 4 by means of which the change of acidity inside of a collodion bag could be determined during the electrolysis of a low-carbon steel sample. An electrolytic cell for the electrolysis of a single sample was constructed. The steel sample, \bar{h} (0.02 per cent carbon, 0.15 per cent manganese, 0.018 per cent phosphorous, 0.02 per cent sulphur, and 0.08 per cent Si), had 20 square centimeters of its surface exposed to the action of the electrolyte. This sample served as the anode and a copper cathode was employed as in the large cell. The electrolysis took place in a 1-liter solution containing in all cases 3 per cent $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ with amounts of sodium chloride varying from 0 to 2 per cent. As in the recommended procedure (46) the sample was separated from the main body of electrolyte by means of a collodion bag, \bar{i} .

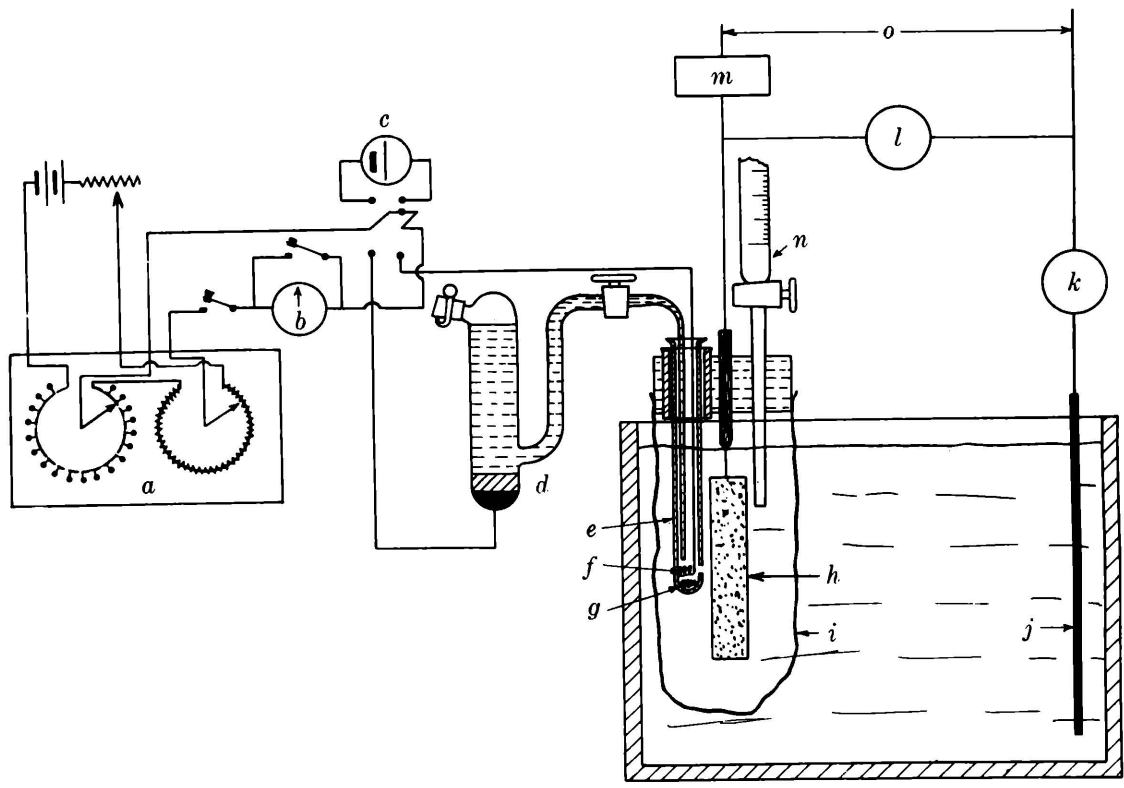


Figure 3.—Apparatus for determination of H^+ change during electrolysis

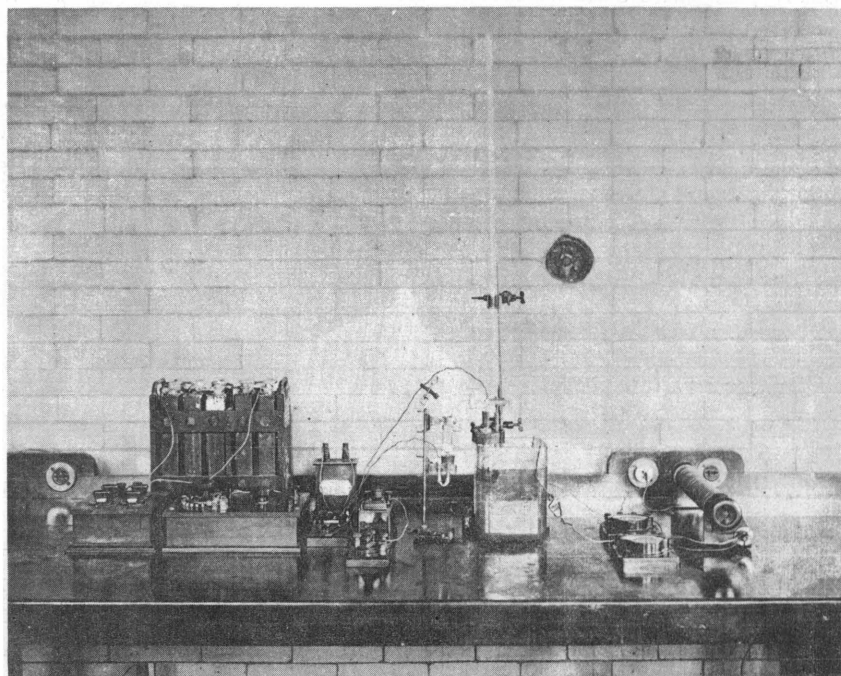


Figure 4.—Apparatus for determination of H^+ change during electrolysis

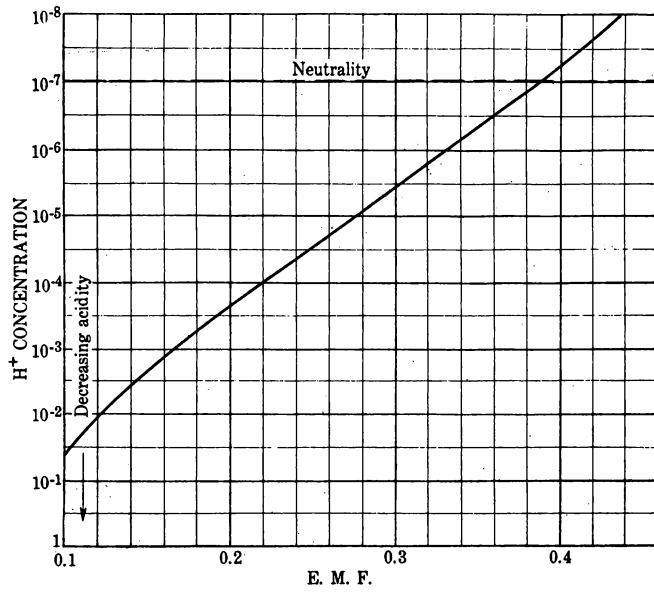


Figure 5.—Antimony-antimony trioxide electrode calibration curve

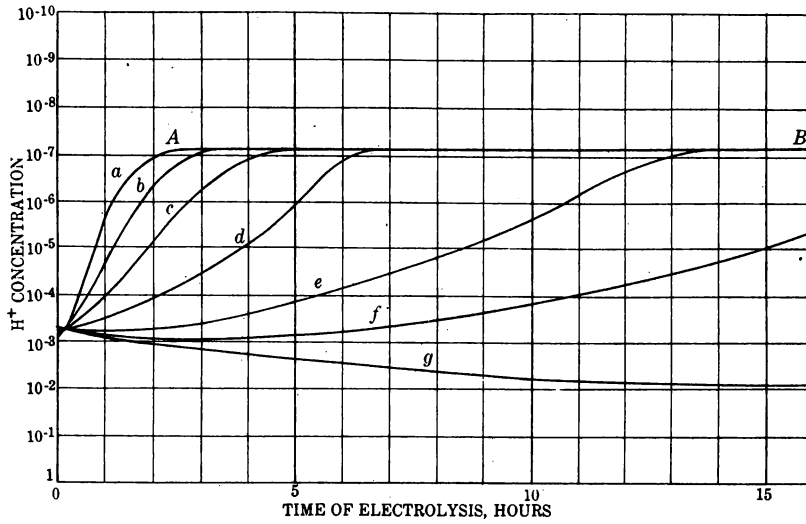


Figure 6.—Change of H^+ concentration of electrolyte during electrolysis

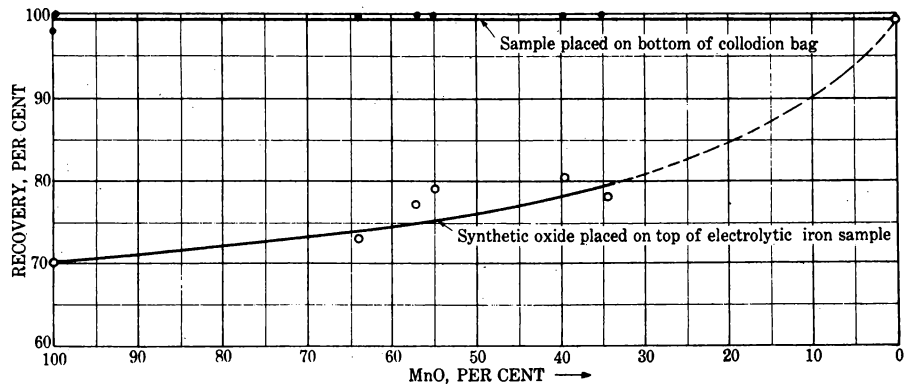


Figure 7.—Solubility of FeO-MnO synthetic slags in electrolyte. (24 hours)

The external circuit for supplying power to the electrodes was supplied with a variable resistance, m, a voltmeter, l, and an ammeter, k. The electrolyte was freshly prepared in every case and as soon as the sample was immersed in the solution, the external circuit was closed and the electrolysis started with a current of 1 ampere and a potential of 2.5 to 12 volts. This of course approximates the conditions in the previously mentioned large cell.

The H-ion concentration was determined for each freshly prepared solution containing the constant amount of ferrous sulphate and a variable amount of sodium chloride. The determination was made in the anode compartment or inside the collodion bag. After the current was turned on a determination was made approximately every half hour for a period of 20 hours. The H-ion concentration at any period was determined by cutting out the external circuit and inserting a special antimony-antimony trioxide electrode into the collodion bag as shown in the figure.

This type of electrode was suggested by Roberts and Fenwick, (53) and was recommended for the determination of H-ion concentrations varying from 10^{-1} to 10^{-10} . It is highly essential in the preparation of this type of standard electrode that cubic antimony trioxide be present and that at no time during the determination should any unstable solid phase such as the orthorhombic antimony trioxide be present. It is also extremely necessary that all dissolved oxygen be eliminated from the solution and that the equilibrium be approached from the alkaline side. Under these conditions it was found that the cubic antimony trioxide is stable in sulphuric acid solutions up to a concentration of 1 N. Care was taken in this work to observe these precautions at all times.

This electrode was prepared by plating antimony on a platinum wire, f, from an antimony trifluoride solution. This wire was then placed in a small test tube to which had been added some properly crystallized (cubic) antimony trioxide, g. The test tube, e, had a small hole in the side near the bottom so as to allow the electrolyte to enter and make contact with the plated electrode. The tip of the calomel electrode, d, was also placed inside of the test tube and the potentiometer, a, and galvanometer, b, were connected between these two electrodes for the determination of the hydrogen ion. The system was checked from time to time against the Weston standard cell, c, in order to determine if the electrode had changed in any way. The hydrogen-ion values were obtained from the millivolt readings by means of the calibration curve, Figure 5. The slope of this curve will give an idea of the sensitivity of these determinations. It was impossible to take readings unless the electrolytic circuit, o, had been opened, as this voltage set up an electric field. After completion of a reading the electrodes were removed so that no antimony was allowed to get into the electrolytic cell.

Results of Hydrogen-Ion Determinations

The results obtained from the study of the change of hydrogen-ion concentration inside the collodion bag during electrolysis are illustrated in Figure 6. It may be seen from this figure that all solutions had a hydrogen-ion concentration of $10^{-3.2}$ in the freshly prepared condition due to the

hydrolysis of FeSO_4 . Curve g represents the change of hydrogen-ion concentration in a solution containing only 3 per cent $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and no sodium chloride. It is obvious that under these conditions the solution became more acid by changing from hydrogen-ion concentration of $10^{-5.2}$ to 10^{-2} in 15 or 16 hours. After this time the concentration seemed to be holding fairly constant. However, with increasing amounts of sodium chloride in the solution, for example 0.1, 0.2, 0.5, 1.0, and 2.0 per cent respectively for curves f, e, d, c, b, and a, it was found that the hydrogen ion concentration decreased appreciably with the time of electrolysis, rather than increasing as in the case of curve g. With 1 per cent sodium chloride (the concentration which is being used for regular electrolytic analyses, curve b) it can be seen that the hydrogen-ion concentration decreases from 10^{-3} to approximately 10^{-7} within a period of three hours. From that time on the concentration remains fairly constant at 10^{-7} . In other words, the ferrous sulphate solutions containing appreciable quantities of sodium chloride have the tendency to become automatically neutralized. The hydrogen-ion concentration of 10^{-7} is considered as the value for pure water, although a concentration of $10^{-6.5}$ is ordinarily used as the standard and represents the hydrogen-ion concentration of pure water saturated with CO_2 .

The significance of these results is simply that a solution prepared similarly to the recommended electrolyte for electrolytic analysis, automatically neutralizes itself within a 3-hour period and from that time on the electrolysis takes place in a neutral solution. It has long been the belief of the authors that if nonmetallic materials, particularly MnO , could be extracted from steel in a neutral solution, little or no solubility would take place. It has also been conceived that a solution having this hydrogen-ion concentration would probably precipitate $\text{Fe}(\text{OH})_2$ but not $\text{Mn}(\text{OH})_2$. This was concluded from the available data concerning the solubility products of these hydroxides, although this type of information is qualitative in nature and can not be considered quantitative in connection with these two hydroxides. Hence at this point in the study of the electrolytic method it has been shown that electrolytic solution of the iron may be successfully obtained in a neutral solution--namely, the one specified above. It now remains to be proved that the ordinary nonmetallic materials do not dissolve in this type of electrolyte and that contamination of the inclusion residue does not occur through the precipitation of such materials as manganese hydroxide.

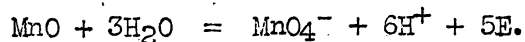
It might be advisable to point out at this time that it is not necessary to electrolyze the regular samples during the period when the hydrogen ion is changing from $10^{-3.2}$ to the constant value reached after a 3-hour period (H-ion concentration, 10^{-7}). Instead, any ordinary samples of steel may be electrolyzed without collodion bags during this 3-hour period. These samples may then be taken out of the solution and the regular samples in collodion bags may be placed in the electrolyte which has been neutralized in this manner.

Solubilities of Certain Oxides and Sulphides
in the Recommended Electrolyte

Although the previous discussion indicated that the electrolysis in the recommended electrolyte took place in a neutral solution and suggested that a neutral solution possibly would not dissolve inclusion materials, some direct determinations of these factors were made. It is of course impossible to study the solubilities of true inclusion materials because we have as yet no accepted means for their extraction from the steel. It is, however, possible to make solubility determinations on synthetic materials if they are in the same crystalline state of aggregation as are the inclusions. For example, SiO_2 , the iron-manganese silicates, and Al_2O_3 are all amorphous when present in steel as inclusions. Hence corresponding synthetic substances which are in the amorphous state should be used for solubility determination.

Two types of solubility determinations were made. In the first, a known quantity of the substance was placed in the bottom of the collodion bag in which a sample of electrolytic iron was electrolyzed for the usual period of 24 hours. The residue was then filtered and analyzed in the usual manner. The percentage recovery was determined by the ratio of the amount recovered to the amount originally placed in the bottom of the collodion bag. Any solubility exhibited under these conditions was due to the attack of the solution itself and was not a function of the electrolytic process.

In another series of experiments the solubility induced by anodic or galvanic reactions was determined. The synthetic material was finely distributed over the top of the electrolytic iron sample and care was taken not to have any at the bottom of the bag. This iron sample also was electrolyzed for 24 hours and the solubilities were determined. These values were not only dependent upon the ordinary solubility of the inclusion material in the electrolyte but also upon any anodic reactions which might occur. An example of this type of reaction is:



This type of reaction would be somewhat dependent upon the voltage across the electrodes, and the higher this voltage the greater the induced solubility. This type of determination was much more severe than the treatment which is received by any inclusion material in actual steels, because these oxide and sulphide particles remained in contact with both the iron anode and the electrolyte for the entire period of 24 hours. It has been determined that a given inclusion is actually in contact with these two materials for a few minutes. In the higher-carbon steels, however, the graphitic sludge formed from the decomposition of the carbides tends to retain the inclusions at the sample's surface.

Solubility of FeO in the Electrolyte

Although a direct determination of FeO content of different steels can not be made because of hydroxide precipitation, it is believed that FeO is insoluble in the electrolyte. This belief is based upon indirect evidence, but the following sources of information have been found:

1. During the electrolysis of a number of rimming steel samples, it was observed that the iron oxide in the blowholes was unattached during the usual 24-hour electrolysis period. The oxide remained as a shell which had conformed to the shape of the original blowhole and was retained as such on the filter paper after electrolysis. This oxide film is largely composed of FeO.

2. The solubility was determined by two methods: By placing a sample of synthetically prepared FeO (1) in the bottom of the collodion bag; and (2) on top of the electrolytic iron sample. The original sample of FeO was analyzed and found to be practically pure. An X-ray determination also indicated the same space lattice constant as determined by Wyckoff and Grittenden (63). This sample was quenched at 1600° C. FeO inclusions in steel are cooled at much slower rates from similar temperatures and it may be concluded that such particles are crystalline. In fact, an X-ray examination of electrolytically extracted FeO showed crystallinity and the size of the unit cube was checked within 1.5 per cent. It was necessary to wash the synthetic FeO samples with a small amount of very dilute hydrochloric acid after electrolysis so as to remove any of the iron hydroxide or ferric basic sulphate which may have been formed during the electrolysis. Recovery in both cases was nearly 100 per cent, although this acid treatment had been given. This treatment is not to be recommended as a standard procedure.

3. In an addendum to this thesis, Krockenberger determined the solubility of FeO in various concentrations of sulphuric acid. The FeO used for this work was the same as mentioned above. All of the solutions were of much higher acidity than the recommended electrolyte, but FeO was practically insoluble up to a concentration of 1.88 c.c. of 95 per cent H₂SO₄ per liter of H₂O, as shown by Table 2.

Table 2. - The solubility of FeO in H₂SO₄ and H₂SO₄-FeSO₄ solutions

Solution		Time exposed, hours	FeO recovered, per cent
Cubic centimeters of 95 per cent H ₂ SO ₄ per liter of water	Grams FeSO ₄ .7H ₂ O per liter of water		
0.47	0	24	97
.94	0	24	97
1.88	0	24	98
9.40	0	24	91
.47	50	30	Basic salt formed.
.94	50	24	98
.94	100	24	99
.94	150	48	98

A solution containing 50 grams of FeSO₄.7H₂O and 0.47 c.c. of sulphuric acid per liter of water became sufficiently oxidized during the 30-hour exposure period so that the basic ferric sulphate formed. This did not occur in any of the other solutions given in the table. The iron hydroxides were not observed in any of these solutions during exposure periods of from 24 to 48 hours. It was found that steel could be readily electrolyzed in these solutions and could be used without dissolving FeO or precipitating either basic sulphate or the hydroxides. It is also a fair certainty that little or no metallic iron will fall from the anode and become part of the electrolytic residue in these solutions, because the electrolysis is quite efficient. It is important, however, to keep in mind that the higher the acidity the greater the tendency to dissolve FeO, whereas the carbides will become more stable. The proper balance between these two factors should be thoroughly determined before any electrolyte can be recommended for the electrolytic analysis of FeO. The higher carbon steels offer some difficulties because of the contamination of the oxide residue with undecomposed iron carbide. In this connection it is questionable if an electrolytic method could be devised for the determination of FeO in any but the low-carbon steels. The accuracy of such a method, even in this type of material, must be determined before any recommendations can be made.

Krockenberger electrolyzed samples of electrolytic iron upon which were placed known quantities of nearly pure FeO in the following electrolyte: 3.68 c.c. of 95 per cent H₂SO₄, 2 grams of NaCl, 200 grams of FeSO₄.7H₂O, and 2 liters of H₂O. He found that this electrolyte did not attack the FeO particles during the period of 24 hours. However, as could be expected, hydrogen gas was liberated at the cathode and the acidity of the solution was decreased in proportion to the amperage so that basic ferric sulphate formed within three hours. Hence it was necessary to control the acidity to

practically the same value as that of the freshly prepared electrolyte. The acidity was roughly controlled by dropping 10 c.c. of sulphuric acid solution per hour (40 c.c. of concentrated H_2SO_4 per liter of solution) into the electrolyte. Under these conditions the electrolyte apparently functioned properly without precipitating the hydroxides or dissolving the FeO, although time was not available to establish a method for the exact control of the acidity. In order to do this, it would be necessary to utilize the hydrogen-ion apparatus which was previously described.

It may be seen from the above discussion that the electrolytic determination of FeO is possible if adequate means are provided for the control of the hydrogen-ion concentration.

Solubility of MnO in the Electrolyte

The solubilities of MnO-containing slags were determined by the two procedures just outlined. The ordinary solubility of MnO in the electrolyte, together with the solubility induced by the galvanic action occurring between the inclusions, steel, and solution, were determined.

Three types of synthetic materials were studied and their solubilities determined by these two procedures. Pure MnO was first studied, then combinations of FeO and MnO, and finally MnO-SiO₂ combinations. In every case the solubility of MnO in the bottom of the collodion bag was practically zero. Some solubility was found, however, when the pure MnO and FeO-MnO materials were placed on top of the electrolytic iron anode. This was only the case with pure MnO and FeO-MnO samples. In the latter case the solubility decreased with decreasing MnO content, as would be expected. All samples of manganous silicates were totally insoluble in both types of solubility determination. No samples of MnO-MnS combinations were available for this work, although such determinations on these materials would be valuable.

Solubility of Pure MnO

A sample of pure MnO was prepared by Daniloff (64) by passing hydrogen over finely powdered manganous carbonate for three hours at 850° to 1000° C. The material as prepared at 850° C. contained 99.3 per cent MnO. It is believed that a very small percentage of this material is present as Mn₂O₄. Before solubility determinations were made the sample was screened to approximately 300 mesh. It might be interesting to note at this time that MnO inclusions are usually small--approximately 300 mesh screen size, and are thoroughly crystalline. This has been shown by Fitterer (65). In each of the solubility tests 0.05 to 0.1 gram of synthetic material was used. This is the same as having 0.2 per cent MnO in a steel of which 25 grams are electrolyzed. It can be seen from Table 3 that the solubility of MnO in the electrolyte is negligible. In the two cases shown, the recovery was from 98 to 100 per cent. However, when the sample was placed on top of the electrolytic iron sample, where it was subjected not only to the ordinary solubility in the electrolyte but also to the anodic reactions, the solubility is approximately 30 per cent. These results are also shown in the table.

Table 3. - The solubility of MnO in the electrolyte at pH 7

Sample number	Analysis, per cent				Recovery of MnO, per cent		Recovery of SiO ₂ , per cent
	MnO	FeO	Fe ₂ O ₃	SiO ₂	When sample is placed on bottom of bag	When sample is placed on electrolytic iron sample	
1	98.5	-	-	-	98.0	-	-
1	98.5	-	-	-	100.0	-	-
1	98.5	-	-	-	100.0	70.8	-
1	98.5	-	-	-	100.0	70.2	-
1	98.5	-	-	-	100.0	73.8	-
3-A	64.8	34.18	0.26	-	100.0	73.0	-
3-F	34.45	61.86	3.78	-	100.0	78.5	-
15-H	55.51	38.74	3.78	-	100.0	79.0	-
10-F	57.59	41.54	1.50	-	100.0	77.0	-
9-D	39.64	55.54	4.02	-	100.0	80.3	-
9	58.8	-	-	41.2	100.0	1/ 96.0	92.9
12	48.9	-	-	51.1	100.0	101.5	100.0
13	44.2	-	-	55.8	100.0	1/ 102.0	100.0
14	39.4	-	-	60.6	100.0	101.0	104.4
73	84.3	-	-	15.7	100.0	1/ 96.0	98.0
93	71.0	-	-	29.0	100.0	100.5	102.5
95	66.0	-	-	34.0	100.0	98.8	98.9
98	52.0	-	-	48.0	100.0	101.0	100.5
101	23.5	-	-	76.5	100.0	98.6	102.0

1/ The analytical error seems to be ± 2 per cent in handling such small quantities of inclusion materials.

Solubility of MnO When Existing in FeO-MnO Slags

The solubilities of five FeO-MnO synthetic slags as prepared by Daniloff (64) were determined by the two previously mentioned methods. The analyses of the slags, together with their recoveries after 24 hours of electrolysis, both in the bottom of the collodion bag and on top of the electrolytic iron sample, are shown in Table 3. In the bottom of the collodion bag the manganese oxide recovery in every case is 100 per cent, whereas when the slag was in contact with both the electrolyte and the anode the recovery varied from 73 to 80 per cent. It is obvious from comparison of the analysis of the slag with the recoveries in the second condition that the MnO is more insoluble as the FeO content of the slag increases. The solubilities of these materials are shown graphically in Figure 7. A straight line at 100 per cent recovery represents the results of solubility determination in the bottom of the collodion bag, whereas the recoveries when the sample is placed on top of the electrolytic iron, represented by a line, gradually vary from 70 per cent recovery at pure MnO to 100 per cent recovery at 100 per cent FeO or 0 per cent MnO.

These results are somewhat discouraging in view of the fact that it was hoped that a neutral electrolyte such as was used in this method would not attack MnO. In fact, the electrolyte itself does not, but it requires the impetus given by the ionization reactions which occur on the surface of the sample during electrolysis. Although time was not available for the determination of such factors, it has been conceived that the true solubility of MnO-containing inclusions, either as pure MnO or as FeO-MnO complexes, lies somewhere between the two values obtained by these experiments. It was microscopically determined by Meneilly (48) that a given inclusion particle is not simultaneously in contact with the electrode and electrolyte for a period of more than 15 minutes. During this time the inclusion had been bared to the action of the electrolyte by electrolysis and sufficient iron had been dissolved so that the inclusion particle dropped from the anode into the bottom of the collodion bag. In other words, for a period of 15 minutes the inclusion was subjected to the anodic reactions and the ordinary solubility in the electrolyte, and then for the remaining period, the difference between 15 minutes and 24 hours, was subjected only to the solubility in the electrolyte. This it will be recalled is zero. Because of these experiments it is conceivable that the actual solubility of inclusions during the electrolytic process is much less than the 30 per cent value as indicated here. It is believed that the experiments in which the slag samples were in contact with both the electrolyte and the anode for the full period are more drastic than is actually the case with real inclusions. Future experiments should be made which will determine the rate of fall of inclusion particles from the anode to the bottom of the bag, and also which will determine the solubilities when the sample is subjected to anodic reactions for periods of 15, 30, 45, and 60 minutes, etc., so as to correct the values given here to the necessary extent as shown by these experiments.

Solubilities of MnO-SiO₂ Slags

With the increasing application of the manganese-silicon alloys as proposed by Herty and Fitterer (65, 66) for the deoxidation of steels and the removal of the deoxidation products by means of fluxing reactions, interest is growing in the oxide system MnO-SiO₂. Conley and Royer (67) and Smith (68) studied the apparent fusion points of MnO-SiO₂ slags. Nearly all of their samples, as prepared, were supercooled glasses. These materials were compared under polarized light with inclusions extracted from steels deoxidized with manganese-silicon alloys. Both types of silicates were supercooled liquids and only in a few cases were there any evidence of crystallinity. The structures of these two types of materials compared favorably.

The solubilities of the synthetic slags (Nos. 9, 12, 13, 14, 73, 93, 95, and 98) were determined in the usual manner. As shown in Table 3, these materials varied in analysis from 39.4 to 84.3 per cent MnO. The solubilities at both the bottom of the collodion bag and the top of the sample were found to be very small.

It is also interesting to note that the SiO₂ recoveries of these manganese silicates varied from 98 to 102 per cent. This can be taken as a ± 2 per cent error in either analyzing or handling such small quantities.

Solubilities of MnO-Containing Inclusions in Practical Steels (Summary)

The stress which has been placed in the foregoing pages upon the importance of MnO recovery is entirely justified when one considers that up to this time no method has been proposed which will recover either pure MnO or MnO which is combined with other oxides. The solubility of this material in the reagents of other methods is as high as the recovery in the electrolytic method. Hence in this manner great progress has been made.

Although it was thought from the first experiments made in these laboratories that MnO was totally insoluble in the electrolyte, the foregoing data are somewhat to the contrary and show some appreciable solubilities. However, it must be remembered that the tests wherein the sample was placed in contact with the anode were extremely drastic.

Other factors which will tend to make MnO more insoluble in the electrolyte under these most drastic conditions are:

- (1) (a) The combination of MnO with MnS.
- (b) The combination of MnO with FeO in high FeO complexes (as shown).
- (c) The combination of MnO with SiO₂ (as shown).
- (d) The combination of MnO with Al₂O₃, etc.

(2) It should be recalled that in these experiments electrolytic iron was used which contained no manganese. In actual electrolysis the steel sample contains the alloy manganese which ionizes and passes into the sulphate electrolyte. Hence as the Mn⁺⁺ concentration increases, the solution potential decreases and there is less tendency for the MnO to go into solution. In fact, the Mn⁺⁺ concentration could increase to a point where it would precipitate as it formed because of the solubility product of Mn⁺⁺ (OH⁻)₂.

Solubility of FeS and MnS in the Electrolyte

Solubility of synthetic materials. - Very pure MnS and FeS were prepared according to the method proposed by Anderson (69), who passed CO₂ and CS₂ over iron oxides (FeO + Fe₂O₃) and manganous sulphate at 850° and 750° C. respectively. The solubilities of these sulphides were determined by placing a known quantity of the material on top of an electrolytic iron sample. After electrolyzing for 24 hours, recoveries were determined. In the case of iron sulphide it was necessary to determine the recovery, which was 97 to 98 per cent, on the basis of the sulphur content rather than the iron content, due to contamination by the hydroxides, etc. The loss in this case might very likely have been mechanical. In the case of manganese sulphide, two 0.05-gram samples were each placed on top of an electrolytic iron anode for 24 hours and recoveries were 0.0496 and 0.0499 gram, or 99.2 and 99.8 per cent, respectively.

Recovery of total sulphides as compared with the ordinary sulphur determinations. - The discussion of a previous publication (46) raised a question as to whether all of the sulphides were recovered in the electrolytic

residue. Some experiments had been made in which a sample was electrolyzed and the sulphur content on the electrolytic residue was determined by placing the residue in an evolution flask with hydrochloric acid. According to their experiments, the percentage of sulphur recovered by the electrolytic method was much lower than the ordinary sulphur analysis of the same steel. There was some difference in opinion as to just what recoveries were obtained, but it was thought that the values were low.

Some experiments of a similar nature had previously been made in these laboratories but in a somewhat different manner. It was found that an addition of metallic zinc to the flask was necessary so as to form a considerable amount of hydrogen gas. This flushed out any H_2S which was formed from the sulphides in the electrolytic residue and carried it over into the cadmium chloride solution. It was also found that it was necessary to have sufficient acid and zinc together in the flask so as to evolve hydrogen for a period of from one-half to one hour. The evolution of H_2S in all cases was found to be slow at first and became very rapid after approximately one-half hour has elapsed. When these factors were taken into consideration, it was found in all cases that the sulphur content of plain-carbon steels as based on the electrolytic residue could be checked very closely with the ordinary sulphur determination on the same steel. Illustrations of this point are given in the following table.

Table 4. - Comparison of ordinary sulphur analysis with sulphide sulphur retained in electrolytic residue (plain-carbon steels)

Sample number	Analysis of steel, per cent		Steel electrolyzed, grams	S recovered by evolution of sulphide S in electrolytic residue, grams	S, per cent	Difference between steel and inclusion analysis, per cent S
	Mn	S				
49	0.46	0.090	26.6	0.0239	0.090	0.000
52	2.43	.077	21.4	.0163	.076	.001

These results were considered by the authors to be very conclusive with regard to the recoveries of the sulphides in the electrolytic method. It indicates in conjunction with this that iron and manganese sulphides are not attacked by the electrolyte during electrolysis in the recommended solution. If elemental sulphur were formed on decomposition of sulphides, or if the sulphides were oxidized to sulphates during electrolysis, they would not have been determined as sulphides by the evolution method.

Separation of MnO from MnSSolubility of MnO in Citrate Solutions

At one time during the development of this method, it was recommended (by McNeill (48)) that sodium citrate be used as a buffer solution in connection with the electrolyte. It was hoped that with the use of this material the iron hydroxides and the basic sulphate would not be formed because the OH-ion would enter into molecular combination with the citrate ion without appreciably changing the hydrogen ion concentration. However, it was found after some investigation of citrate-sulphate solutions that other types of contamination resulted and the treatment was therefore discontinued. It was also found during this work that MnO was quite soluble in citrate-sulphate solutions. An example of this solubility may be illustrated as follows:

Two 0.05-gram samples of pure MnO prepared as previously described were each placed in the bottom of a collodion bag in which, in sample 1, 30.8 grams of electrolytic iron, and in sample 2, 35.3 grams of electrolytic iron, were electrolytically dissolved. The MnO in both cases was in contact with the electrolyte for over 30 hours. The residue of sample 1, together with approximately 50 c.c. of electrolyte, was treated with 50 c.c. of a 25 per cent solution of sodium citrate and allowed to stand for 12 hours at room temperature. Sample 2 was filtered directly without this additional citrate treatment. Recovery of sample 1 was 0.027 gram or 54 per cent of the amount placed in the bottom of the collodion bag, whereas recovery of sample 2 was 0.051 gram or 102 per cent. Hence it was conceived that a citrate separation of MnO from MnS might be possible, and determinations of the solubilities of MnO and MnS in citrate sulphate solutions were made. It was found that such a separation could be made because MnO is entirely soluble under certain conditions, whereas MnS is entirely insoluble. These findings therefore gave the basis for the separation which was recommended in the analytical procedure given by Fitterer (46). The solubilities of these materials, together with the solubility of FeS, are shown in the following table.

Table 5. - The solubilities of FeS, MnS, and MnO in citrate-sulphate solutions

Material	Grams tested	Solution, c.c.		Time, hours	Temperature, °C.	Grams recovered	Per cent recovery
		Electrolyte	20 per cent citrate				
MnO	0.02	50	50	1	80	1/ 0.001	5.0
MnO	.02	50	50	1	80	1/ .0006	3.0
MnS	.05	50	50	1	80	.0497	99.4
MnS	.05	100	50	1	80	.0499	99.8
MnS	.05	50	25	1-1/2	80	.0492	98.4
MnS	.05	50	25	1-1/2	80	.0492	98.4
FeS	.05	100	50	1	80	.0445	89.0
FeS	.05	50	50	12	60	.0440	88.0

1/ Analytical blanks.

The recoveries listed--namely, 0.001 and 0.0006 gram--are considered as analytical blanks. MnS treated under the same conditions is 99.4 per cent insoluble, as shown by the table, whereas FeS is 88 per cent insoluble. This latter value need not be considered as important, however, because in the separation of MnO from MnS just these two materials need be considered.

The procedure for determining these two materials is to make one electrolytic extraction upon which the combined value of per cent MnO + per cent MnS is determined and calculated to per cent MnO. The citrate separation is then made on a second electrolysis of the same sample and the insoluble material--MnS, is determined and calculated to MnO. The difference between the manganese values obtained in these two electrolyses then represents the percentage of MnO present in the steel. Inasmuch as the determination of MnS has been made by this method, the amount of FeS may be determined by difference between the total sulphur (as determined by ordinary steel analysis) and the sulphur as MnS. This separation is highly important and should prove to be very useful to many metallurgists who are working on low-carbon and plain-carbon steels.

It is particularly important to point out at this time that this separation would be inaccurate for steels containing appreciable amounts of manganese silicates. This is true because the MnO forms both compounds and solid solution with silica which will protect the MnO from citrate attack. This action would tend to make the MnS content of the steel higher than the actual amount and the MnO value lower. This consideration must be included in any sample where the determination of these two quantities is desired.

Separation of MnS from FeS

Solubility of MnO, MnS, and FeS in H_2SO_3 Solutions

According to Henderson and Wyszor (70), when SO_2 is passed through an ice-cold water suspension of FeS ferrous sulphite is precipitated. If the current of gas is continued, it is found that the precipitate dissolves and a solution of $Fe(HSO_3)_2$ is formed. However, if this solution is heated the sulphite reprecipitates. Rammelsberg (71) stated that if MnS is treated in the above manner the soluble thiosulphate and sulphur are formed, and the sulphite of manganese is not precipitated even on heating to boiling. In this connection, then, it was conceived that a mixture of these two sulphides could be separated by passing an excess of SO_2 through the water suspension. The soluble $Fe(HSO_3)_2$ and MnS_2O_3 will be formed and on heating to approximate- $80^\circ C$. the $FeSO_3$ reprecipitates and the manganese and iron salts could be separated by filtering. Also, Koene (72) found that the thiosulphates may be extracted from a water solution by means of ethyl alcohol in which they are soluble. The sulphides are insoluble in this liquid.

These data were correlated with the hope of development a method for the separation of MnO and MnS from FeS. It was considered that if the sum of MnS + MnO could be determined on one electrolytic residue and the separation

of MnS from FeS made on the second, then a complete separate analysis of all these materials would have been made. This separation could be made if the MnO were also changed to the thiosulphate by the SO₂ treatment. The MnO and MnS would then be in the filtrate as thiosulphates whereas the FeS could be determined from the precipitated ferrous sulphite. Hence, knowing the sulphur content of the steel, the MnS could be calculated by difference and the MnO also could be determined according to the relation

$$\text{Per cent MnO} + \text{per cent MnS (by first extraction)} - \text{per cent MnS (calculated from total sulphur - sulphur as FeS)} = \text{per cent MnO.}$$

The action of these materials in the SO₂ treatment was determined with this procedure in mind and the data obtained are shown in Table 6.

Table 6. - Solubility of MnO, MnS, and FeS in H₂SO₃

Material	Weight tested, grams	Time in SO ₂ treatment, minutes	Subsequent treatment	Grams recovered	Per cent recovery
MnO	0.02	20	10 min. at 80° C,	--	0.0
MnO	.02	2-3	do.	--	.0
MnS	.05	150	Filtered cold	0.001	2.0
MnS	.05	2-3	10 min. at 80° C.	--	0.0
FeS	.05	30	Filtered cold	.0476	95.2
FeS	.05	30	Filtered hot	.0424	84.8
FeS	.05	2-3	do.	.0499	99.8
Mixture	.1 FeS + .1 MnS	10	do.	.0923 FeS, .0001 MnS	92.3 FeS, 1.0 MnS
Mixture	.01 FeS + .01 MnS	10	do.	.0091 FeS, .0015 MnS	91.2 FeS, 1.5 MnS

The solubilities shown in the foregoing table indicate that this separation could probably be made in the manner suggested, but the experience of the authors in this connection indicates that the separation of these materials is more easily and accurately accomplished by the citrate method than by this secondary procedure. It is apparent, however, that both MnO and MnS entirely dissolve (probably as the thiosulphate) after from two to three minutes in the saturated solution of SO₂. These materials were also heated for 10 minutes at 80° C. FeS under the same conditions was found to be 99.8 per cent insoluble.

Many other means for separating these oxides and sulphides were considered and investigated, but these two procedures, and particularly the citrate method, seemed to be the most applicable.

CONTAMINATION OF THE ELECTROLYTIC RESIDUE WITH
MATERIALS WHICH WOULD AFFECT THE ANALYTICAL
RESULTS

It has been shown in the previous discussion that many of the interesting inclusion materials are insoluble in the electrolyte. If this were not the case, the reported analysis on each oxide would be considerably lower than the actual content of the steel.

There are other factors, however, which would tend to give higher results than actually exist as oxide and sulphide inclusions in the metal. For example, the iron hydroxides and basic ferric sulphate, precipitate during electrolysis together with FeO. Hence any analysis for FeO will be much higher than the true value.

Similarly, if the manganese (as alloy) in steel goes into solution as Mn^{++} and exceeds the $Mn^{++}(OH^-)_2$ solubility product, $Mn(OH)_2$ will precipitate, giving high results when an MnO determination is made. The MnS result would not be affected inasmuch as both MnO and $Mn(OH)_2$ are soluble in the citrate solution.

In a similar manner it is possible that H_2SiO_3 might form during electrolysis of steels containing the alloy silicon. The formation of this gel would greatly contaminate the SiO_2 residue and give high results.

Hence investigations along these lines were made so as to determine the reliability of the electrolytic extraction method. The data which follow indicate the results of these investigations and for the most part it was found that the method could be relied upon inasmuch as these contaminating factors were insignificant. Only contaminations which might result from the electrolysis of plain-carbon steels are given in the following sections. The alloy steels will be discussed in a separate section.

Contamination of FeO in the Residue
with $Fe(OH)_2$, $Fe(OH)SO_4$, and Fe_3C

The impossibility of determining FeO in the residue of a steel electrolyzed in the usual electrolyte (3 per cent $FeSO_4 \cdot 7H_2O$ + 1 per cent NaCl) has been indicated in the foregoing section. The reason for this is that the iron hydroxides and basic sulphate form. These would give abnormally high results, as would the presence of any undecomposed Fe_3C . For these reasons acid electrolytes of controlled H-ion concentration have been suggested for the determination of this oxide.

However, the characteristic reactions of ferrous sulphate solutions are interesting with regard to the reasons for such contamination and will be discussed in the following pages.

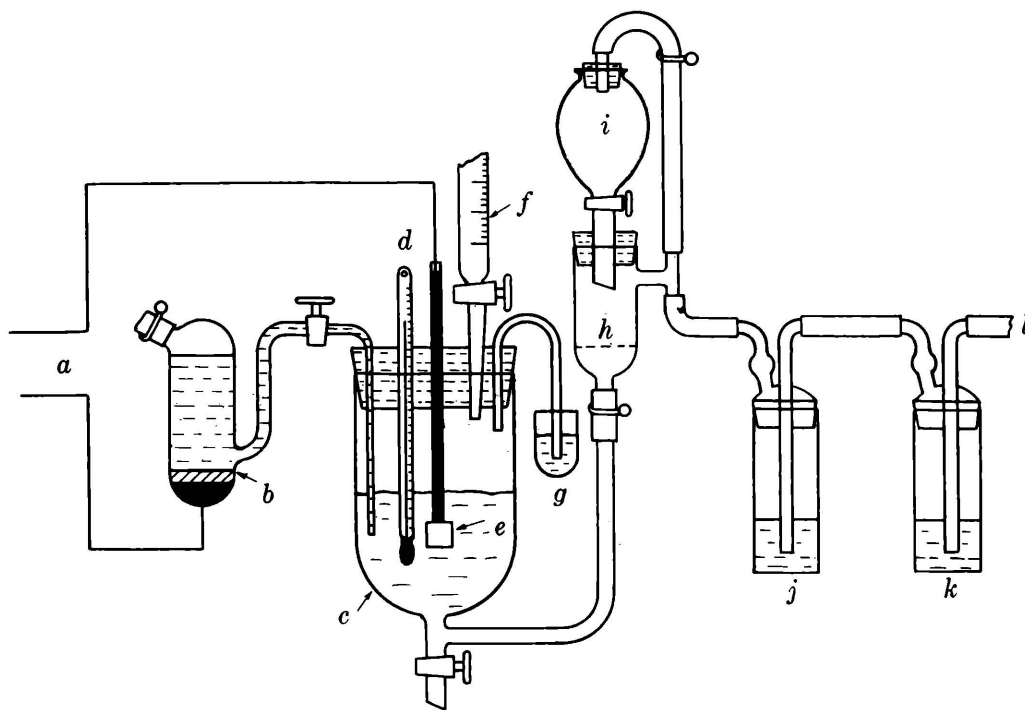


Figure 8.—Apparatus for determination of H^+ concentration in the absence of oxygen

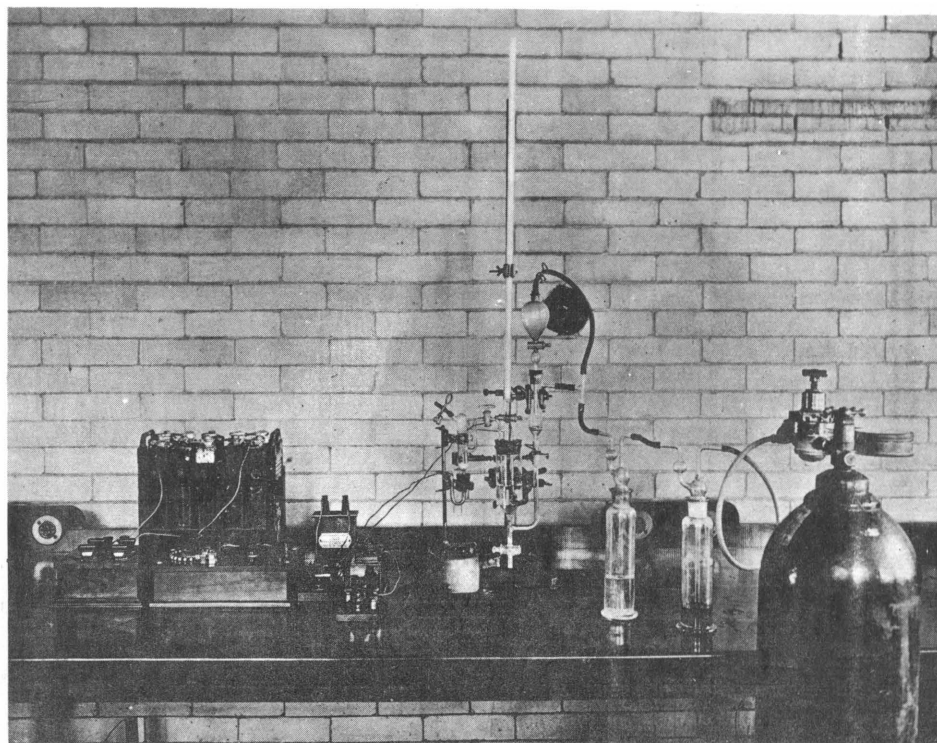


Figure 9.—Apparatus for determination of H^+ concentration in the absence of oxygen

Characteristic Reactions of Ferrous Sulphate Solutions

Ferrous sulphate solutions are very unstable in the presence of air, due to several reactions. Some knowledge of the exact conditions under which these reactions occur is required before the extraction of inclusions by the electrolytic process can be understood. One of the authors (49) studied the hydrolysis, oxidation, precipitation, and the H-ion concentration change with each phenomenon, both in the presence and absence of oxygen. Studies under the latter conditions were necessary for a basis of comparison.

Experimental Procedure

The apparatus used for the determination of the H-ion concentration during various reactions is represented by Figures 8 and 9. The complete equipment as shown therein was required for determination when oxygen was excluded from the system. It was not necessary, of course, to use all of these parts when the effects of oxygen were investigated. The experimental procedure also was much more simple in this case.

When investigations in the absence of oxygen were made, nitrogen was introduced at l and allowed to bubble through a solution of pyrogallol and sodium hydroxide (in tube, k of Figure 8), to remove the oxygen. This then moved through concentrated sulphuric acid (in tube, i) so as to remove any entrained sodium hydroxide. The stream then passes down through the empty calibrated dropping funnel, i, and into the mixing chamber, h. The mixing chamber at this time contains a weighed amount of dry ferrous sulphate. A little quinhydrone was mixed with the sulphate but not in a sufficient amount to change the H-ion concentration of the sulphate solution being studied. The nitrogen next circulates through the reaction chamber or cell (c of this figure). The cell is empty at this time and the gas displaces the air which escapes through the bubbling tube, g. This prevents any air from passing back into the system. Although several tubes are inserted through the rubber stopper, which closes the upper end of the cell, it is sealed gas-tight so as to exclude air. A bright platinum electrode, c, and a normal calomel electrode, b, were connected to the potentiometer circuit at a. A thermometer, d, was inserted so as to allow for any necessary temperature corrections. Also a burette, f, was inserted through the stopper so as to facilitate any acid additions which were made in some of the experiments.

The nitrogen was circulated through the system for about 15 minutes. The calibrated dropping funnel, i, was next filled with boiling distilled water which would contain a negligible amount of dissolved oxygen. During this process nitrogen was bubbled up through the funnel so as to displace any incoming air. The instant that the funnel was filled it was closed and sealed by the connecting nitrogen tube.

The water was slowly passed down over the dry ferrous sulphate and quinhydrone in the mixing chamber. As soon as the sulphate dissolved, the solution was led into the cell, c, where its H^+ concentration was determined

potentiometrically. The quinhydrone present in the solution dissociates into quinone and hydroquinone, but since its solubility in aqueous solutions is low, solid quinhydrone is always present. Hence in solutions more acid than those having hydrogen-ion concentrations of 10^{-7} quinhydrone maintains a practically constant value. The ratio (73) of $\frac{C \text{ hydroquinone}}{C \text{ quinone}} = 1$. Hence in the equation

$$E_h = E_k + \frac{RT}{F} \ln (H^+) - \frac{RT}{2F} \ln \frac{C \text{ hydroquinone}}{C \text{ quinone}}$$

the last factor is eliminated from the expression because it is practically equal to $\ln 1$. Then

$$E_h = E_k - 0.000198 T \text{ pH}$$

where the E_h is the observed electrode potential difference and E_k is a constant which is established by calibration. In this case calibration was made with reference to the normal calomel electrode, b , and e.m.f. values for different H-ion concentrations are shown in Figure 10. The calibration of this electrode was standardized according to several of Sorensen's standard mixtures (74).

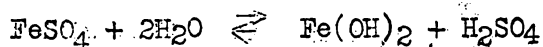
The solutions entering the cell were hot and temperature corrections were made according to the readings of the thermometer, d , and the above equation.

Three types of determinations were made with this equipment:

1. The hydrogen-ion concentration of freshly prepared solutions--hydrolysis (in the absence of oxygen).
2. The change of H-ion concentration with time (in the absence of oxygen).
3. A study of the oxidation of the electrolyte and the formation of $Fe(OH)SO_4$.

Hydrolysis of Ferrous Sulphate in Aqueous Solutions

Ferrous sulphate was known to hydrolyze according to the following reaction



but the extent to which this took place was not known. This reaction would of course affect the H-ion concentration of the sulphate solutions and for this reason the extent of hydrolysis of solutions containing from 0 to 12 per cent $FeSO_4 \cdot 7H_2O$ was determined. This was reflected in the H-ion concentrations of freshly prepared solutions in the absence of oxygen as determined with the apparatus just described. Figure 11 graphically represents the extent to which hydrolysis takes place at the different concentrations. This effect is very interesting in that hydrolysis appreciably increases the H-ion

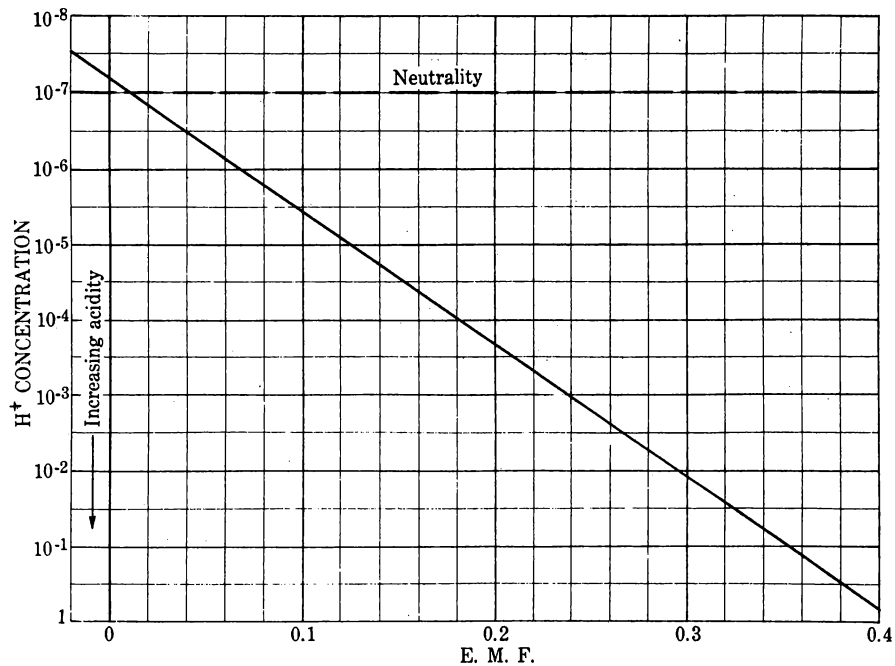


Figure 10.—Quinhydrone-electrode calibration curve

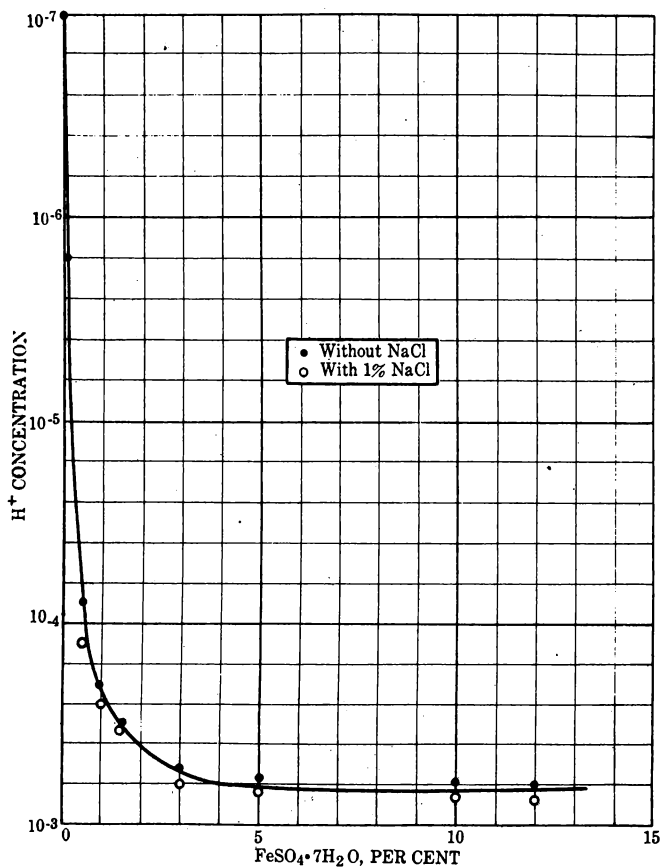


Figure 11.— H^+ concentration of freshly prepared ferrous sulphate electrolytes (hydrolysis)

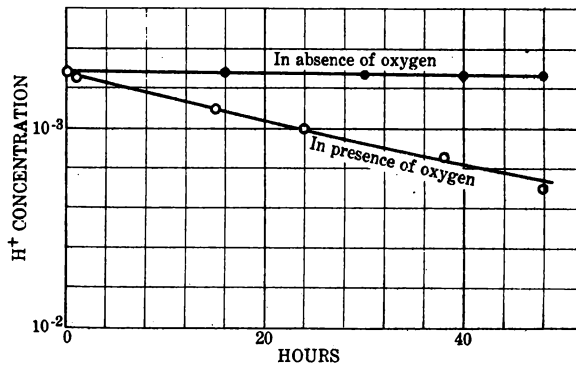


Figure 12.— H^+ change of 3 per cent $FeSO_4 \cdot 7H_2O$ solution with time in absence and presence of air

concentration from 10^{-7} to $10^{-3.3}$ when the $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ concentration is increased from 0 to 2 per cent. When the concentration of this salt is increased beyond 3 per cent, the H-ion concentration increases only slightly.

The effect of 1 per cent NaCl on the hydrolysis of all of these freshly prepared solutions was determined. This was found to be slight, as indicated by the open circles of Figure 11. From this curve it may be seen that a freshly prepared solution containing 3 per cent $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and 1 per cent NaCl would have a H-ion concentration of $10^{-3.2}$. This was previously shown to be the case when the change of H-ion concentration with time of electrolysis was discussed as shown in Figure 6.

Although the sodium chloride addition does not appreciably affect the H-ion concentration, it is advantageous to use it because it increases the conductance of the sulphate solution. This may be seen from a study of the following table:

Table 7. - Ionic conductances (91) of the various ions in the recommended electrolyte, 18° C.

Cation	l_c	Anion	l_a
H^+	313.0	OH^-	174.0
$1/2 \text{Fe}^{++}$	45.3	$1/2 \text{SO}_4^{--}$	67.9
Na^+	43.3	Cl^-	65.3

wherein $l_c = cF =$ ionic conductance per gram equivalent;
 $c =$ the absolute velocity of the cation in cm./sec.
 $F =$ Faraday's equivalent, 96,500 coulombs.

It will be recalled from Figure 6 that the H-ion concentration during electrolysis in the recommended electrolyte is 10^{-7} . (This is also true of the OH-ion concentration.) This value is small and little conductance in this electrolyte could be attributed to these ions, although their ionic conductances are large (313 and 174 amperes per second per equivalent, respectively). This would represent 3.13×10^{-5} amperes per second for H^+ and 1.74×10^{-5} amperes per second for OH^- .

On the basis of concentration the Fe^{++} and SO_4^{--} ions can carry 0.244 and 0.366 ampere per second, respectively. However, the sodium and chlorine ions can carry 0.742 and 1.12 amperes per second, respectively. Hence the conductance of the sulphate solution is greatly increased by the chloride addition.

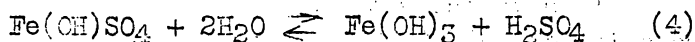
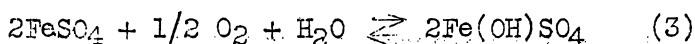
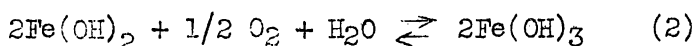
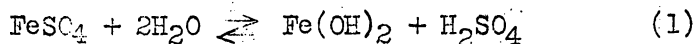
Change of the H⁺ Concentration of a 3 Per Cent
FeSO₄·7H₂O Solution with Time (N₂ Atmosphere)

When air is excluded from a 3 per cent FeSO₄·7H₂O solution (containing no NaCl), its hydrogen-ion concentration does not change with time. The freshly prepared solution has a hydrogen-ion concentration of 10^{-3.2} moles per liter and retains this value as long as 48 hours. Also, the solution remains perfectly clear during this time, since no precipitate occurred. The reason for this is that oxidation effects have been inhibited in these experiments and no electrolysis has taken place. The only reaction which has been permitted is the original hydrolysis of the salt upon the preparation of the solution. This is shown graphically as the upper curve of Figure 12.

Other reactions occur when the solution is allowed to stand in the presence of air without electrolysis. These reactions appreciably affect the pH of the solution, as will be shown in the next section.

Change of the H⁺ of a 3 Per Cent FeSO₄·7H₂O
Solution with Time (in the Presence of Air)

When ferrous sulphate solutions are allowed to stand in contact with air, certain detrimental oxidation reactions occur. Some of these are illustrated by the following equations:



The first occurs just as it did when air was excluded and is the reason for the H-ion concentration of 10^{-3.2} in the freshly prepared solution. The other reactions occur chiefly at the surface of the solution. This causes two effects, namely:

1. Precipitates occur as soon as the solubilities of Fe(OH)SO₄ and Fe(OH)₃ have been exceeded. These precipitates are yellow and reddish yellow, respectively, in color and noticeably cloud up the solution. These are the precipitates which have been so much discussed by various investigators who tried to use the proposed electrolytic method for the first time.

2. The H⁺ concentration is appreciably increased, as shown by the lower curve in Figure 12. After standing in the presence of air for 48 hours a 3 per cent solution changes its H-ion concentration from 10^{-3.2} to 10^{-2.8} or becomes quite acid. This is probably due principally to reaction (4), which involves the formation of H₂SO₄.

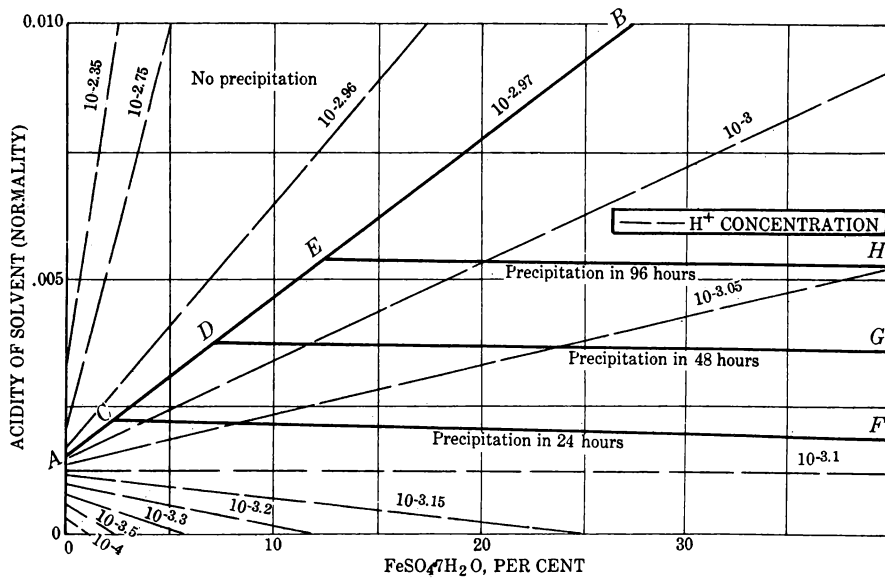


Figure 13.—Precipitation of basic salt in varying acid concentrations

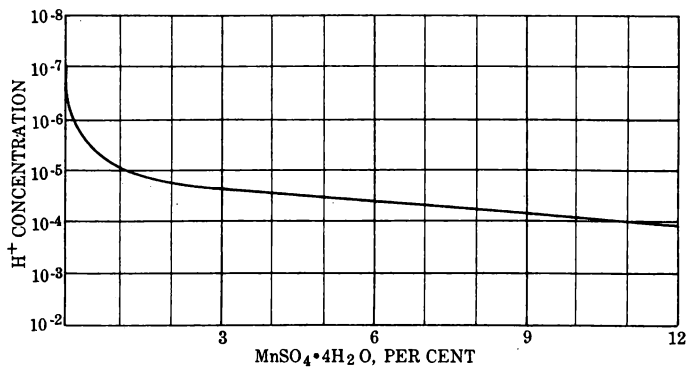


Figure 14.—Electrolysis of manganese sulphate solutions

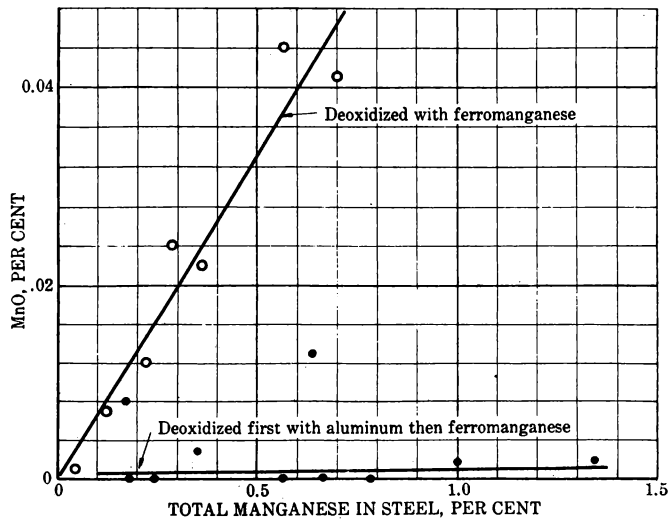


Figure 15.—The contamination of electrolytic residue with $Mn(OH)_2$ metallic particles resulting from the presence of the alloy manganese

Effects of Oxidation on an FeSO_4 Solution After
the H-ion Concentration Has Been Lowered to 10^{-7}

The ferric basic sulphate ($\text{Fe}(\text{OH})\text{SO}_4$) has been noticed by nearly every one who has operated the electrolytic extraction process. Because it is an intermediate product for the formation of sulphuric acid according to reaction (4) it is objectionable. Also, as stated before, it contaminates the electrolytic residue and prevents an accurate determination of FeO . The latter effect can not be overcome but the former can be minimized.

For example, it has been shown on page 12, that the automatic buffer action of ferrous hydroxide keeps the H-ion concentration at 10^{-7} as long as iron is being electrolyzed. However, if the solution at pH of 7 were allowed to stand with the external circuit open, its acidity would approach 10^{-3} according to reaction (4). Then if electrolysis is started again, the acidity will approach 10^{-7} by virtue of the automatic action of $\text{Fe}(\text{OH})_2$.

However, if inclusions are subjected to the electrolyte between the time that current is stopped and started again, there will be some loss due to the increased acidity during this period.

It was for these reasons that it was recommended that the electrolyte should not remain idle after preparation. Otherwise the acidity would increase. Samples of steel without collodion bags should be electrolyzed for at least three hours in order to decrease the acidity from $10^{-3.2}$ to 10^{-7} before regular samples are electrolyzed. Also, it was recommended that when the regular samples were removed others should be placed in the cell and electrolysis started immediately. Otherwise the acidity would increase to such an extent as to be detrimental to the next determinations.

Possibilities of Control of $\text{Fe}(\text{OH})\text{SO}_4$
Precipitation

The control of the formation of this basic salt is desirable but not necessary if the preceding precautions are followed (items 6, 7, and 8, page 206, reference 46). The only method which proved satisfactory at all was the addition of H_2SO_4 .

Although such an addition would increase the solubility of other types of inclusions, it can be seen from the previous discussion, page 15, that knowledge of the amount of acid required to prevent its precipitation would aid in the determination of FeO . For this reason these limits were determined.

The results of the H-ion determination on the ferrous sulphate-sodium chloride-sulphuric acid solutions are shown graphically in Figure 13. It can be seen from this figure that an acidity of $10^{-2.97}$ is necessary to prevent $\text{Fe}(\text{OH})\text{SO}_4$ precipitation.

All solutions represented in the figure above line AB remained clear after standing in air many days. Those represented below line AB were clouded to various degrees by the precipitation of the basic salt. Precipitation occurred after 24 hours in all solutions below line ACT, 48 hours in region FCDG, and 96 hours in region GDEH. It can be seen from Table 2 that FeO would be entirely insoluble in all solutions above line AB.

Errors in the FeO Analysis Due to Contamination of
Falling Iron and Iron Carbide

Investigation was made of the possibility that contamination by falling iron particles may cause errors in FeO determination. A number of steels were thoroughly deoxidized with manganese-silicon alloys (66) and electrolytic extraction was made on these samples. The weight of the dissolved iron, the weight of the residue, and the analysis of the residue were determined in each case. These are all shown in Table 8.

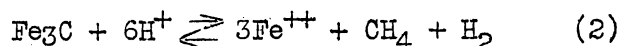
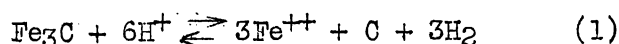
Table 8. - Iron content of extracted residues

Sample number	Weight of steel dissolved, grams	Weight of residue, grams	Percentage in residue			FeO in metal, per cent
			MnO	SiO ₂	Fe ₂ O ₃	
1535-21	32.9	0.1620	5.45	7.61	55.68	0.377
1515-11	34.0	.2305	8.23	12.63	56.52	.524
1537-11	36.2	.1379	5.91	44.07	15.81	.0824
1520-11	34.1	.2351	8.18	3.79	68.63	.650
1524-11	33.7	.1840	11.13	11.63	48.92	.378
1525-11	37.8	.2042	23.59	27.53	21.15	.157

From this table it may be seen that the total electrolytic residue weighed from 0.138 to 0.351 gram. Also, a large proportion of this residue was composed of iron compounds. These are reported in the Fe₂O₃ values listed in the table and vary from 16 to 68 per cent of the residues. These values are based on percentage of FeO in the metal as shown in the last column of the table. The values vary from 0.08 to 0.65 per cent. These latter values may be contrasted with Ledebur analyses of the same steels, which averaged approximately 0.01 per cent FeO. It was thought that this difference between the Ledebur analysis and the analysis for iron compounds in the electrolytic residue was due chiefly to falling metallic iron particles. However, electro-magnetic separation revealed the presence of only 0.01 to 0.02 per cent of metallic iron in every case. Hence the difference between metallic iron and the FeO values listed in the table must be due either to the basic sulphate, the hydroxide precipitates, or to FeO not determined by the Ledebur method. The formulas for these precipitates were given in the previous sections. However, there is another type of precipitation which should be discussed at this time. Iron hydroxides may be formed by the action of water upon iron carbide. Some discussion of these principles will be given in the next section.

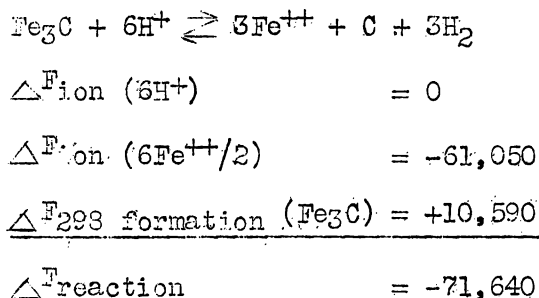
As described previously, the success of the electrolytic method, or of any other method for that matter, depends largely upon the complete solution of all constituents in the steel sample with the exception of the nonmetallic material. As a rule, compounds formed between electronegative and electropositive elements are more stable than those which are composed of two electropositive elements such as the metals. Various salts are of the former type, whereas the intermetallic compounds and such materials as the carbides of manganese and iron are of the latter. Hence in order to make this method quantitative, the carbides must be totally decomposed and the decomposition products must be of such a nature that they are readily taken into solution in the electrolyte and do not contaminate the electrolytic residue. At the same time the inclusion materials must remain unaffected by the process and be retained in the electrolytic residue in exactly the same state in which they existed previously in the steel.

Some information has been obtained concerning the decomposition of iron carbides which is particularly pertinent to the subject of extraction of non-metallic inclusions from steel. It has been found by previous workers that Fe_3C is not stable and tends to decompose into iron and graphitic carbon. Ralston (75) has shown this to be the case by calculating the free energy of formation of Fe_3C from its elements at 25°C . (298°K). This he found to be +10,590 calories. In other words, the compound has more of a tendency to decompose than it does to form at this temperature. It is also known from previous work that when Fe_3C is in the presence of water it tends to decompose rapidly to form graphitic carbon, methane, and many other hydrocarbons. In other words the reactions

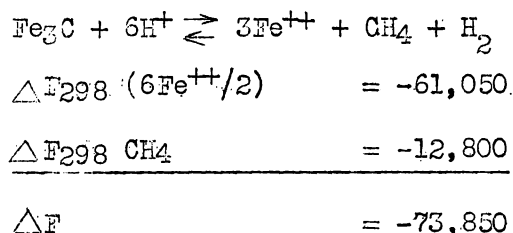


occur to an appreciable extent in aqueous solutions. White (76) found that the stability of iron carbide in aqueous solutions increased with increasing hydrogen-ion concentration. However, high concentrations of the ferrous ion also are necessary to keep the carbide stable. He also found that in electrolytic processes low current densities tend to increase the stability of iron carbide. However, it has been shown previously in this paper that the hydrogen-ion concentration of the recommended electrolyte is quite low and that a fairly high current density is being used. Hence the tendency for the iron carbide to decompose during the electrolytic extraction by the recommended process should be appreciable. Schenck (77) listed the above two equations and discussed them from the physical-chemical standpoint. However, further data are available at this time and this information has been recalculated.

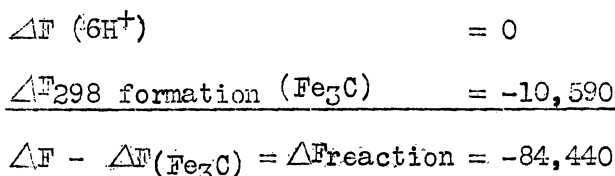
In the equation



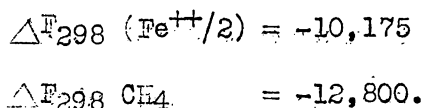
The formation of CH_4 by decomposition of Fe_3C



Again



Note: The foregoing calculations have been made using Lewis' (78) data for



These thermodynamic calculations indicate that both reactions between the iron carbide and the hydrogen ion take place to an appreciable extent, inasmuch as there is a large negative free-energy change in both reactions. Also, the tendency to form methane is greater by 12,800 calories. Practically, however, it is known that the decomposition of iron carbide results in the formation of both graphitic carbon and the saturated and unsaturated hydrocarbons. Graphitic carbon has been observed in all of the electrolytic residues which have been obtained in these laboratories to date. Also an odor of acetylene is noticed by the operator when taking the sample from the bag and washing it in water. From the amount of graphite present it has been the authors' contention that in spite of the thermodynamic data given, the first reaction which results in the formation of graphitic carbon is by far the more important. It is highly possible that although the free energies as calculated from the equilibrium data roughly indicate that methane should have

a greater tendency to form than graphite, yet it is possible that the rate of reaction which involves the formation of graphite might be much larger than the one for the second reaction. This would involve a greater deposit of graphitic carbon than an evolution of methane.

In any case these data all indicate that the iron carbide was very largely decomposed in the recommended electrolyte. However, there is a possibility that in the higher-carbon steels large globules of carbide may be present. When these particles are exposed to the solution by electrolysis, it is highly probable that a surface coating of graphite forms which clings to the particles and prevents further decomposition of the carbide in its central portion. These protected particles drop to the bottom of the collodion bag without being thoroughly decomposed. Schenck and others (77) have shown that Fe_3C is completely decomposed in 1/30, 1/3, and 5N solutions of sulphuric acid at 60° C. Also, it is thoroughly decomposed with a 1N acetic acid solution; and if 0.4 mole of Fe^{++} per liter is present in the solution, the iron carbides completely decompose into graphite without the formation of either methane or the higher hydrocarbons. The effects of these solutions on iron carbide may prove useful to investigators who are working on high-carbon steels and who suspect that a certain amount of undecomposed carbide as previously described is present in their electrolytic residue. Schenck and his associates also indicated that many other and higher hydrocarbons form under various conditions through the action of aqueous solutions on the iron carbide. However, it was believed that the two reactions given above which involve the formation of either graphite or methane were by far the most important. Further data (94) have been obtained concerning the decomposition of Fe_3C during the electrolysis of high-carbon steels. This work will probably be published in the near future.

CONTAMINATION OF MnO IN THE ELECTROLYTIC RESIDUE WITH $MN(OH)_2$, Mn_3C , AND FALLING METALLIC PARTICLES

The discussion of the solubility of various types of manganese-containing inclusions has shown that in most of the ordinary combinations of manganese oxide in steel, high recoveries are obtained. However, it is also the purpose of this investigation to determine the extent to which various contamination factors affect the electrolytic analyses for manganese oxide. The following section is devoted to a study of these factors and for most part indicates that contaminations of this type are negligible.

Contamination from Falling Metallic Particles

According to Heyn and Grossmann (79) an electrolytic current does not have a selective action upon either metal when the two metals form a solid solution. It has been shown by Krivobok (80) that manganese forms a solid solution in plain-carbon steel at room temperature up to 1.4 per cent. Hence in all practical steels the manganese should be in solid solution, with the exception possibly of any manganese which is present as carbide, and according to Heyn's theory it should dissolve as metallic ions. In other words, the reaction



takes place without interference or selective action insofar as the electrolytic current is concerned. From the practical standpoint a survey of approximately 100 electrolytic residues has shown that in no case has the weight of the electrolytic residue been larger than 0.3 gram. This has been previously illustrated by the values given in Table 8 in which the electrolytic residues varied from 0.138 to 0.23 gram. If, for an extreme example, 0.3 gram residue is obtained through the electrolysis of a 30-gram sample of steel, the residue will represent of course 1 per cent of the total weight of steel electrolyzed. Now, if we assume that all of this residue is composed entirely of metallic particles and that the steel contains 0.60 per cent manganese, a maximum contamination of 0.006 per cent of manganese in the electrolytic residue will result. This would represent 0.0077 per cent MnO as analyzed in the electrolytic residue composed as described in this extreme case. However, it was shown previously that magnetic separation of metallic particles from the electrolytic residue gave approximately only 0.01 to 0.02 gram of metallic iron. Actually then the contamination due to metallic particles as determined magnetically would be one-tenth of the value given above or 0.00077 per cent MnO. This amount of contamination is well within the analytical error and may be conscientiously neglected.

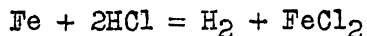
In this connection, certain steels containing more than 1.4 per cent manganese were electrolyzed and the manganese oxide (MnO) contents were found to be rather high--from 0.13 to 0.194 per cent. The SiO₂ concentrations in these samples are also high. Unfortunately, the MnO-MnS separation was not made on these samples, but even if it had been the results probably would have been inaccurate inasmuch as so much SiO₂ is present. The inclusions probably exist as manganese silicates and the leaching action of citrate would have little effect on the MnO combined in this manner. However, the results of this investigation are shown in Table 9.

Table 9. - The extraction of inclusions from manganese steels

Sample number	Metal analysis, per cent			Inclusions, per cent		Contamination magnetic portion of electrolytic residue, per cent	
	C	Mn	Si	MnO+	SiO ₂	MnO + MnS	SiO ₂
				MnS			
41060-P5	0.51	1.49	0.119	0.194	0.114	0.001	0.002
41060-P6	.52	1.55	.121	.133	.120	.001	.002
41060-P7	.52	1.53	.124	.130	.111	.001	.001

Because the manganese contents were higher than the solubility of manganese in iron at room temperature (1.4 per cent), it was thought that high MnO concentrations were probably due to the selective action of electrolytic current on the iron and that high-manganese metal probably dropped into the anode sludge. A magnetic separation was made on electrolytic residues when from 35 to 53 grams of these steels were electrolyzed. As can be seen from the table, the contamination resulting from these metallic particles is low with regard to both MnO and SiO₂. In no case has the contamination exceeded 0.002 per cent.

Another method was tried in order to determine the quantity of metallic iron in the residue. A billet sample of steel weighing 30.6 grams was electrolyzed and the residue treated with hydrochloric acid in such a way that the hydrogen evolved from the action of the acid upon any metallic iron which might have been present was accurately collected and measured and the volume corrected to 0° C. and 760 mm. pressure. This was calculated back on the basis of the equation



and the equivalent amount of iron determined. It was found that this represented 0.35 gram of metallic iron. This amount is higher than the value shown above, but the hydrogen gas was probably contaminated with H₂S resulting from the reaction of the acid with iron and manganese sulphides.

Possibility of Formation of Mn(OH)₂ Through
the Electrolysis of Manganese Alloyed with Iron

Theoretical Calculation from Hydrogen-
Ion Determination

To ascertain whether manganese sulphate solutions reacted in a manner similar to ferrous sulphate solutions with respect to the formation of hydroxides and basic sulphates, certain experiments were conducted similar to those studied in the determination of ferrous sulphate contaminations, in which the manganese sulphate concentration varied from 0 to 12 per cent. The hydrogen-ion concentrations of these solutions were determined immediately on preparation by means of the previously discussed quinhydrone electrode. The acidities were also studied at different periods so as to determine the effect of oxidation from the atmosphere for as long as three days. The results of the investigation are shown in Figure 14, which indicates that on preparation the hydrogen-ion concentrations varied rapidly from 10⁻⁷ to 10⁻⁵ with 1 per cent MnSO₄·4H₂O present in the solution. Greater concentrations, however, did not appreciably increase the hydrogen-ion concentration. A small increase from 10⁻⁵ to 10⁻⁴ was indicated when the concentration was raised from 1 per cent to 12 per cent. After this solution stood in the presence of air for a period as long as three days, no evidence of the formation of basic manganous salt nor any appreciable change in hydrogen-ion concentration could be detected. It was therefore believed that no contamination of this type (due to Mn(OH)SO₄) existed in any electrolysis of manganese-containing steels.

Manganese Hydroxide Precipitation

Since it was determined previously that ferrous hydroxide precipitated continually throughout electrolysis, it was also believed that the precipitation of manganese hydroxide was entirely possible inasmuch as manganese ions from the alloyed manganese are continually forced into solution by the electrolytic solution pressure. However, it must be realized that precipitation of manganese hydroxide would depend entirely upon the relative values of the solubility products of manganous hydroxide and of ferrous hydroxide and upon the relative concentrations of ferrous and manganous ions present

together in the electrolyte. An exact theoretical calculation is impossible because the exact solubility product of ferrous hydroxide is unknown and the extent to which the concentration of manganese ions will build up in solution without precipitation is also unknown. Various investigators have attempted to determine the solubility product of ferrous hydroxide and have obtained values varying from 10^{-14} to 10^{-22} . The reason for this discrepancy is probably that the basic ferric sulphate forms during the determination and appears during the early stages of the experiments as a colloid. However, experiments were made with the object of determining the occurrence and extent of precipitation of manganese hydroxide under various conditions. The first studied involved an investigation of the concentration of manganese in the electrolyte which would cause sufficient precipitation of the hydroxide to be detected by the eye.

In these experiments, electrolytes were prepared which contained various known amounts of manganese ions and ferrous ions. The total metallic-ion content was kept constant at a value equivalent to that of 3 per cent ferrous sulphate.

The electrolytes were exposed to the electrolysis of manganese-free electrolytic iron in collodion bags in the usual manner. Upon the completion of the electrolysis the residue inside the bag was filtered, washed, and analyzed for manganese. The results shown in Table 10 indicate that up to a ratio of 1 part of manganese to 1 part of ferrous ions there is no precipitation of manganese hydroxide. Actual determination at this point showed the presence of 0.0005 gram of manganese which may be considered as an analytical blank. With higher ratios there is some slight evidence of precipitation. In no practical case ever encountered by the authors have they electrolyzed in a solution which contained even as high a ratio as 1/3 unless it was in the case of the electrolysis of ferromanganese described on page 48. Hence no precipitation would be expected in ordinary steel samples.

Table 10. - Precipitation of $Mn(OH)_2$ during electrolysis
in iron-manganese sulphate electrolytes

Ratio of Mn^{++}/Fe^{++} in electrolyte	Grams of Mn^{++} in 1 liter of electrolyte	Time of electrolysis, hours	Grams of MnO in residue in bag
1/3	1.50	12	0.0002
1/3	1.50	8	.0002
2/3	2.40	16	.0002
1/1	3.00	16	.0005
5/4	3.33	12	.0009
3/2	3.60	10	.0013

In the second series of tests, the 3 per cent $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and 1 per cent sodium chloride electrolyte contained no manganese ions at the beginning of the experiment, but manganese sulphate was added in amounts equivalent to those which would go into solution through the electrolysis of practical manganese steels, according to the usual solution rate of 1 gram of steel dissolved per hour. This solution was added inside the collodion bag by means of a burette. Electrolytic iron was again used in these experiments as the anode. The solution inside the collodion bag was treated as in previous experiments. The results of these experiments indicate that the manganese content of the electrolyte may be as large as the equivalent amount which would be present after the electrolysis of a 5 per cent manganese steel. At and above this concentration the manganese ions become sufficiently concentrated in the solution to cause precipitation. The results of these experiments are shown in Table 11.

Table 11. - Precipitation of $\text{Mn}(\text{OH})_2$ resulting from the addition of MnSO_4 to the ferrous sulphate electrolyte, during electrolysis

Manganese steel equivalent, per cent	Time of electrolysis, hours	Grams of MnO in residue in bag
0.5	4	0.0002
.5	8	.0002
.5	16	.0003
1.0	8	.0002
5.0	12	.0005
10.0	10	.0014

In connection with these experiments similar tests were made with electrolytes varying in sodium chloride content. The manganese-ion equivalent of a 0.5 per cent manganese steel was added to the solution. These results show that the sodium chloride content did not affect the precipitation, for in no case did the MnO analysis become appreciable. The results of these experiments are shown in Table 12.

Table 12. - The effect of NaCl upon $\text{Mn}(\text{OH})_2$ precipitation during electrolysis

NaCl content of electrolyte	Time of electrolysis, hours	Grams of MnO in residue in bag
0.0	6	1/ 0.0003
.1	8	.0004
1.0	16	.0003
2.0	10	.0003

1/ No precipitation of ferrous hydroxide occurred.

Hence it may be concluded from these experiments that in no case will manganese hydroxide precipitate through the electrolysis of the ordinary manganese steels in the recommended electrolyte. However, it is important to point out at this time that a given electrolytic solution should not be used for more than three successive electrolyses because the manganese-ion concentration will increase in the fourth run to an extent sufficient to give some precipitation. If this precaution is observed, no precipitation of manganese hydroxides should occur.

Precipitation of $Mn(OH)_2$ According
to the Solubility-Product Principle

According to Sackur and Fritzmam (81) the solubility product of $Mn^{++}(OH^-)^2 = 4 \times 10^{-14}$. Hence if we assume that the recommended electrolyte has the constant hydrogen ion concentration of 10^{-7} it will also have an (OH^-) concentration of 10^{-7} because the ionic product for water is 10^{-14} . Thus the manganese concentration must exceed 4 moles per liter before precipitation of $Mn(OH)_2$ can occur.

$$(H^+) (OH^-) = 10^{-14} \text{ and } H^+ = 10^{-7}$$

$$Mn^{++}(OH^-)^2 = 4 \times 10^{-14}$$

$$Mn^{++} = \frac{4 \times 10^{-14}}{(10^{-7})^2} = 4$$

Four moles per liter of manganese = $4 \times 54.93 = 219.72$ grams per liter.

For the purpose of comparison let us assume that low-carbon ferromanganese containing 80 per cent Mn is electrolyzed for a period of 24 hours at the rate of 1 gram per hour. One liter of solution would contain 0.80×24 or 19.2 grams of Mn^{++} . Hence no precipitation should occur from this source.

It can be seen that $\frac{219}{19.2}$ or 11 and a fraction of such samples could be electrolyzed in the same solution before the manganese hydroxide would precipitate as based upon these calculations, which, it must be admitted, may be subject to considerable error.

In pure manganese sulphate solutions 700 grams of $MnSO_4 \cdot 4H_2O$ per liter of water must be added before this precipitation would occur.

PRACTICAL DETERMINATION OF MANGANESE HYDROXIDE PRECIPITATION
BY THE ELECTROLYSIS OF OXYGEN-FREE STEELS

A sample of oxygen-free vacuum-fused iron was made available through previous experiments at the Bureau of Mines on the problem of case carburizing (82). This pure iron-manganese sample contained 0.522 per cent manganese. One of the authors electrolyzed 32.6 grams of this material, and analysis of the residue indicated that 0.0005 per cent of MnO was present in the steel.

This was considered as an analytical blank and because the sample contained little or no sulphur it was not believed to have been manganese sulphide. Hence it can be concluded from this single experiment that no contamination of electrolytic residue was encountered through the electrolytic solution of 0.522 per cent manganese steel or 0.17 gram of manganese. This amount of manganese is very similar to the amounts found in ordinary or practical steels. Unfortunately, adequate vacuum equipment was not available in these laboratories for further experiments of this nature. However, another method of making the same type of determination was devised, and this problem will be described in the following pages.

Electrolytic Iron Heat

One hundred pounds of relatively pure electrolytic iron was melted in the newly lined (with pure magnesite) Lectromelt furnace. The slag under which this was carried out was composed chiefly of lime and iron oxides. The actual analysis at tap was 17.5 per cent FeO, 22.4 per cent Fe₂O₃, 6.3 per cent SiO₂, 3.4 per cent Al₂O₃, 0.24 per cent MnO, 45.4 per cent CaO, and 5.9 per cent MgO. It can be seen that electrolytic iron melted under these conditions would contain considerable dissolved iron oxide and very little carbon. Also, because the manganese oxide content of the slag is very small, it could be expected that the residual manganese in the iron at tap would be very low. In fact, the first sample poured from this heat contained 0.06 per cent carbon, 0.005 per cent manganese, 0.0113 per cent sulphur, and 0.005 per cent silicon. Some of these values are extremely low and probably represent analytical blanks.

Steels to Which Aluminum Was Added Prior to the Manganese Addition

Small amounts of the melted electrolytic iron were taken from the furnace with large test spoons. In the first series of samples the liquid metal was deoxidized thoroughly with approximately 1 per cent of pure aluminum. While the metal was still molten in the large test spoon, various amounts of low-carbon ferromanganese were added and the metal was held in a liquid condition as long as possible so as to ensure homogeneity. Under these circumstances the iron should contain little if any manganese oxide because of the aluminum deoxidation prior to the manganese addition. A similar heat was also prepared in which boiler punchings or low-carbon steel scrap was used as a base. The original metal in this case contained approximately 0.1 per cent manganese before deoxidation, and for this reason the results were not expected to be as convincing as in the electrolytic iron heat. However, this was not the case, as the results in the second heat were just as important as in the first. The results of these tests are shown in Table 13 and indicate that no contamination due to the electrolytic solution of manganese is obtained in steels containing as high as 1.34 per cent alloyed manganese as in sample 45 of this table. The electrolytic iron samples varied from 0.005 per cent manganese in sample 1 to 0.662 per cent manganese in sample 3. The first electrolytic analysis of these samples indicated as high as 0.031 per cent MnO.

However, as shown in the table, this is present as either MnO or MnS. It was believed that this was entirely MnS, inasmuch as appreciable amounts of sulphur were present in every case. For this reason citrate separations were made as described in the previous publication on this method (46). MnO and $Mn(OH)_2$ are both entirely soluble in the citrate sulphate solution, whereas manganese sulphide is entirely insoluble. A second electrolysis was made on each of the samples, and the electrolytic residue was subjected to the separation of sulphide from oxide. It was found in practically every case that accurate checks were obtained on previous determinations without the citrate separation. In other words, no MnO or $Mn(OH)_2$ is present, and all of the manganese in the inclusion residue is present as MnS.

Similar tests were just as conclusive in the low-carbon steel samples, as illustrated by samples 41, 43, 45, and 47. The manganese contents of these samples varied from 0.35 to 1.34 per cent, and the manganese in the inclusion residue was found again to be present entirely as MnS. The authors consider the values listed in the last column of Table 13 as highly conclusive that manganese as alloyed in steel does not contaminate the inclusion residue in any way. As shown in this table, the Al_2O_3 contents of these steels are quite high--approximately 0.225 per cent. This is taken as an indication that practically all of the oxygen which was present in the samples before deoxidation was transformed into Al_2O_3 and that no MnO was present in spite of the subsequent addition of ferromanganese. If this deoxidation with aluminum had been incomplete or heterogeneous in any way, high manganese values would have been obtained due to the formation of MnO. On the other hand, in case this deoxidation was complete and no MnO had formed, and manganese hydroxide had formed, the values in this column would also have been high. The MnO values given in this table are plotted against the manganese content and are represented by the lower curve in Figure 15.

Steels to Which Only Ferromanganese Was Added

For the basis of comparison several other types of tests were made on these two heats. For example, in one series of tests both in the electrolytic iron heat and in the low-carbon steel heat, the aluminum addition was eliminated. Test spoons containing the liquid iron were partially deoxidized with various amounts of low-carbon ferromanganese. In the electrolytic iron heat the samples varied in manganese content from 0.045 to 0.563, whereas the low-carbon steel samples varied from 0.120 to 0.700 per cent manganese. The results of these tests are shown in Table 14 and the upper curve of Figure 15. As would be expected, the manganese content (as per cent MnO + per cent MnS) was appreciable in all of these samples. The citrate extraction was also made on these samples and it was found by means of contrast with the previous series that considerable MnO was present in every case as shown by the last column in this table. It may be concluded from the preceding series that no $Mn(OH)_2$ was present in the electrolytic residues of this second series inasmuch as the manganese contents of the steels were even lower than in the first series. By virtue of this reasoning it may also be concluded that the values listed in the last column of this table really represent MnO inclusions rather than any type of contamination.

Table 13. - Electrolytic analyses of samples to which aluminum was added previous to the manganese addition, per cent

METAL ANALYSIS - ELECTROLYTIC IRON HEAT

Sample number	Mn	S	C	Si	SiO ₂ ^{1/}	Al ₂ O ₃ ^{1/}	MnO + MnS	MnS ^{2/}	MnO ^{3/}
1	0.005	0.0113	0.060	0.005	0.005	0.226	0.002	Not determined	--
9	.170	.0214	.010	.005	.002	.225	.031	0.023	^{4/} 0.008
7	.242	.0176	.026	.005	.002	.216	.022	.023	- .001
5	.560	.0164	.036	.005	.007	Not determined	.019	.019	.000
3	.662	.0176	.040	.005	.008	.296	.022	.023	- .001

METAL ANALYSIS - LOW-CARBON STEEL SCRAP HEAT

43	0.350	.034	.10	.005	--	--	.029	.026	0.003
41	.640	.030	.08	.005	--	--	.041	.028	^{4/} .013
47	.780	.032	.09	.005	--	--	.034	.035	- .001
45	1.340	.034	.09	.005	--	--	.048	.046	.002

^{1/} Determined on electrolytic residue.

^{2/} Determined as insoluble matter in sodium citrate separation.

^{3/} Determined by subtracting MnS from MnO + MnS.

^{4/} Large values unexplained. May be due to segregation in steel specimen.

Table 14. - Steels deoxidized with low-carbon ferromanganese (no aluminum addition), metal analysis, per cent

ELECTROLYTIC IRON HEAT

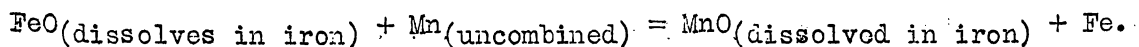
Sample number	Mn	S	C	Si	SiO ₂	Al ₂ O ₃	MnO + MnS	MnS	MnO
6	0.045	0.0176	0.010	0.004	0.002	0.007	0.011	0.010	0.001
2	.222	.0113	.050	.004	.004	0.006	.045	.033	.012
4	.284	.0176	.032	.004	.003	.010	.066	.042	.024
8	.563	.0176	.020	.004	.002	.011	.084	.040	.044

LOW-CARBON STEEL SCRAP HEAT

46	.120	.034	.040	.004	--	--	.040	.033	.007
42	.360	.029	.065	.004	--	--	.066	.044	.022
44	.700	.031	.085	.004	--	--	.108	.067	.041

It interesting to note that both the MnO and the MnS contents of these steels increase gradually with the total manganese contents, as would be expected. The values for the two heats also compare favorably on the basis of equivalent amounts of total manganese. The MnO contents of these samples have also been plotted against the total manganese contents of the steels in Figure 15. A comparison of these two curves is interesting inasmuch as little or no MnO is present in the first series and as much as 0.044 per cent is present in the second series.

A very rough conception of what the deoxidation constant of manganese might possibly be at 1600° C. may be gotten from the values in the last table. Sample 6 would have to be discarded for this purpose, inasmuch as only 0.001 per cent MnO is present, which is of the order of an analytical blank. However, the other samples may be used for this rough calculation. The reaction involved is:



It may be seen from this equation alone that the calculation involves many assumptions and should not be taken as final. For example, it must be assumed that the temperature of deoxidation in each case was exactly 1600° C. and that no appreciable variation was present even in the two heats. Also, it must be assumed that the reaction is entirely homogeneous although it is not known whether all of the MnO present was dissolved in the steel at 1600° C. There is quite a possibility that the reaction was somewhat heterogeneous and that some of the MnO existed as an insoluble phase, probably as inclusions containing both MnO and some FeO. Contrary to many systems of this type, the slag

phase which is present does not necessarily form an immiscible layer but is represented by colloidal particles which are distributed throughout the liquid iron. It must also be assumed that 0.470 per cent FeO (as shown by 0.225 per cent Al_2O_3 in the aluminum-killed steels) was present in all samples before deoxidation with manganese. The last assumption which must be made is that the reaction reached equilibrium before the sample was poured from the test spoon into the mold and did not change in temperature from the time of the addition to the time that it reached equilibrium. Although many assumptions are involved in making these calculations, the equilibrium constants as calculated in each case are surprisingly uniform as compared with previous work on the subject. The free or uncombined manganese was calculated by subtracting the manganese present as MnO and MnS from the total manganese. The "free" FeO was calculated by subtracting the oxygen combined as MnO from the total oxygen as determined by aluminum deoxidation--namely, 0.47 per cent FeO. The calculated values are listed in Table 15. The maximum variation in values of the equilibrium constant,

$$K = \frac{\text{per cent MnO}}{(\text{per cent FeO}) (\text{per cent Mn})}$$

is from 0.14 to 0.30, and may be due to differences in temperature alone. The average value for this constant is 0.177.

Table 15. - Calculation of manganese-FeO equilibrium

Sample number	Percent				K
	FeO at start	MnO	Free FeO	Free Mn	
2	0.470	0.012	0.458	0.222 - 0.035 = 0.187	0.140
4	.470	.024	.446	.284 - .051 = .233	.230
8	.470	.044	.426	.563 - .065 = .498	.207
46	.470	.007	.463	.120 - .031 = .089	.170
42	.470	.022	.448	.360 - .051 = .309	.159
44	.470	.041	.429	.700 - .084 = .616	.155

The calculation of this constant has been particularly difficult previous to this time and it is to be regretted that time was not available for its accurate determination by eliminating some of the variables. Up to this time it has been highly questionable as to whether any of the values previously determined on this constant were at all useful. The reason for this is that no determination of MnO in the metallic phase was possible. However, a determination of this type is possible with a fair degree of accuracy through the use of the electrolytic method as described in this paper. It is somewhat questionable from the standpoint of electrolytic extraction and the solubility of MnO inclusions in the electrolyte (discussed previously) as to whether the MnO values are as large as they should be.

Further experiments on this point and investigations involving more thorough study of this solubility under the conditions specified and studies concerning the solubility under different conditions of electrolytic potential should be made. A thorough study of all these considerations should enable future investigators to determine such important physical-chemical relations as the distribution ratio of MnO under various types of slags and consequently the solubility of MnO in steel at various temperatures and also the accurate equilibrium constant for the reaction of manganese with FeO in liquid steel at various temperatures. In spite of the large bulk of information given on this subject by previous investigators, the entire system needs a thorough investigation before these values can be satisfactorily established.

High-Sulphur Steels

Some interesting information was obtained concerning the effect of sulphur on the determinations previously made, where aluminum was both present and absent. The results are given in Table 16.

In the first series of samples the molten electrolytic iron of the 'Lectromelt heat was taken from the furnace by means of a test spoon and various amounts of FeS₂ were added. This was followed immediately by an addition of low-carbon ferromanganese while the iron was still molten. No aluminum addition was made. The manganese varied from 0.234 per cent in sample 10 to 1.275 per cent in sample 12 and the sulphur content in the same samples varied from 0.049 to 0.145 per cent respectively. All other constituents, with the exception of manganese inclusions, were practically the same. The MnO + MnS content of sample 10 was 0.044 per cent, whereas that for sample 12 was 0.372. Of these amounts 0.036 and 0.300 per cent, respectively, was present as MnS. This is entirely as would be expected inasmuch as sample 10 was a low-manganese low-sulphur steel, whereas sample 12 was a high-manganese high-sulphur steel. The MnO contents as given by the last column were both proportional to the total manganese.

The second series of samples as shown in Table 16 was divided into two groups, the first being made in an electrolytic iron heat and the second in a low-carbon steel heat. In both of these series the sample was first deoxidized thoroughly with aluminum and then additions of FeS₂ and low-carbon ferromanganese were made as soon as possible. It is to be expected that the MnO contents of these steels are all low regardless of the manganese addition, inasmuch as the aluminum was added previous to the manganese addition. That this was the case is illustrated by the last column of the table inasmuch as the sample containing 0.168 per cent manganese showed a negative amount of MnO as -0.004 and the highest manganese-containing steel (2.43) contained 0.036 per cent MnO. This value is higher than would be expected, but it is highly possible that some MnO was added as a constituent part of the low-carbon ferromanganese, particularly since this sample contained a very large amount of manganese as compared to the ordinary steels. It is also possible that selective electrolytic action was encountered in this sample inasmuch as according to Krivobok's (80) determinations two immiscible solid solutions occurred in steels containing more than 1.4 per cent manganese. Hence the electrolytic residue might have contained sufficient falling metallic particles to raise the manganese content to 0.036 per cent.

Table 16. - Analyses of high-sulphur steels, per centELECTROLYTIC IRON HEAT (FeS₂ addition followed
by Mn; no aluminum)

Sample number	Mn	S	C	Si	SiO ₂	Al ₂ O ₃	MnO + MnS	MnS	MnO
10	0.234	0.049	0.034	0.005	0.007	0.006	0.044	0.036	0.008
12	1.275	.145	.040	.005	.011	.018	.372	.300	.072

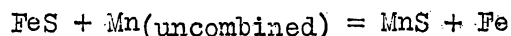
ELECTROLYTIC IRON HEAT (aluminum addition
followed by FeS₂ then by manganese)

11	0.168	0.071	0.020	0.004	0.004	0.272	0.100	0.104	0.004
13	.474	.080	.040	.004	.004	Not determined	.140	.124	.016

LOW-CARBON STEEL SCRAP HEAT (Al addition followed
by FeS₂ then by manganese)

49	0.460	0.090	0.065	--	--	--	0.107	0.081	0.026
50	.790	.068	.080	--	--	--	.116	.106	.010
51	1.000	.046	.090	--	--	--	.058	.056	.002
52	2.430	.077	.120	--	--	--	.132	.096	.036

It is interesting to note the effect of the high sulphur additions on the MnS contents of the steels as given in the next to the last column in this table. The values seem to increase in proportion to the amounts of manganese and sulphur added. In fact, an attempt was made to determine the iron sulphide-manganese equilibrium constant under somewhat the same assumptions as made previously for the manganese oxide equation and in this case also the calculated equilibrium constant remained in approximately the same order of magnitude with the exception of one sample. The values used to calculate this constant for the reaction



are given in Table 17. It was of course impossible to use any samples which were not deoxidized with aluminum because of difficulties encountered with the MnO. The manganese inclusions in these samples should be nearly all MnS as shown by the previous table. The average constant as given by these calculations is approximately 1.9 and probably represents the first calculation

of this type in which a determination of the reaction products was made. The fact that these values are of a similar order of magnitude is encouraging. Some of the experimental conditions can be controlled so that eventually the constant will be determined accurately.

Table 17. - A calculation of the equilibrium in the reaction
 $\text{FeS} + \text{Mn} \rightleftharpoons \text{MnS} + \text{Fe}$ from available data

Sample number	Per cent					Apparent K = MnS FeS x Mn	Ratio Per cent MnS Per cent FeS
	Total Mn	S	MnS	FeS	Free Mn		
9	0.170	0.0214	0.023	0.0356	0.155	4.16	0.65
7	.242	.0176	.023	.0252	.227	4.00	.91
5	.560	.0164	.019	.0258	.548	1.35	.74
3	.662	.0176	.023	.0252	.647	1.42	.91
43	.350	.0340	.026	.067	.334	1.16	.39
41	.640	.0300	.028	.054	.622	.84	.52
47	.780	.0320	.035	.0522	.758	.89	.67
45	1.340	.0340	.046	.0588	1.311	.60	.52
13	.474	.0800	.124	.094	.395	3.34	1.32
49	.460	.0900	.081	.1065	.409	1.85	.76
50	.790	.0680	.106	.0795	.723	1.85	1.33
51	1.000	.0460	.056	.0695	.965	.84	.80
52	2.430	.0770	.096	.114	2.369	.36	.84

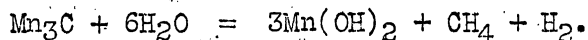
Samples which have "constants" which are approximately the same as the average (1.9), are samples 3, 5, 43, 49, and 50. The sulphur contents of these steels are 0.0176, 0.0164, 0.0340, 0.090, and 0.068 per cent, respectively, and the manganese contents are 0.662, 0.560, 0.350, 0.460, and 0.790 per cent, respectively. These values show a variation which approximates the amounts of manganese and sulphur in practical steels.

These calculations are made with no finality, inasmuch as the errors involved are thoroughly realized. They are merely given with the idea of stimulating interest in the calculation of such a constant through the use of electrolytic extraction. The future experiments on this type of determination would of course be made under conditions which are less variable than those which were present in the preparation of these samples. Although the variation in this constant from 0.623 in sample 52 to 10.3 in sample 11 is quite large, these results are looked upon with greater favor than the constant calculated for the manganese oxide reaction, inasmuch as no value for the total sulphur content was assumed. In the case of the manganese oxide reaction an assumption had to be made which involved the total oxygen content of the samples. The same value was assumed in all cases. This probably is the reason that the manganese deoxidation constant varies so little from sample to sample. On the other hand, the total sulphur as used in the

desulphurizing constant varied from 0.0164 in sample 3 to 0.09 in sample 49. This represents quite a wide range in total sulphur contents and ranges from the sulphur content of the lowest sulphur steels to that of screw-stock material.

Contamination of the Inclusion Residue
with Manganese Carbide

It has been generally understood for years that manganese forms manganese carbide in steels and that it exists together with iron carbide in practically all steels which contain even small percentages of manganese. In fact manganese is usually added to steel in the form of ferromanganese which should be considered as a mixture of iron and manganese carbides rather than as an iron-manganese alloy. However, the exact proportion of manganese which combines with carbon in a given type of steel is an important factor in connection with the contamination of the electrolytic residue. Although the heat and free energy of formation of manganese carbide are not available it is believed that manganese carbide is unstable under the condition of the recommended electrolytic process. It would be expected that if these values were known the free energy of reaction with water or with the hydrogen ion would be quite appreciable--in fact a much larger value than for iron carbide. Arnold and Read (83) and White (76) have extracted Mn_3C from steels by employing an electrolytic method. In each case the electrolyte was a concentrated solution of HCl. When dilute solutions were used, this carbide decomposed to a considerable extent. Arnold and Read extracted Mn_3C and washed it with ether. When the sample was nearly dried it oxidized very quickly and took fire. Also, White stated that manganese carbide decomposes immediately when placed in water. A more detailed study of the stability of this carbide was made by Moissan (84). This investigator's experiments indicated that Mn_3C is completely decomposed in the presence of water with the formation of manganous hydroxide, methane, and hydrogen. The reaction is expressed by the equation



This investigator stated that the conditions largely determined whether graphitic carbon or methane is formed, but he showed by experiment that the total carbon as Mn_3C is equivalent to the graphite and the carbon in the methane. Moissan also agreed with other investigators in this field that manganese carbide becomes more stable with increased acidity. Hence, it is quite possible that Mn_3C remains undecomposed in the electrolytic residue during the electrolysis of steels in the dilute ferrous sulphate electrolyte which is practically neutral and has a low hydrogen ion concentration (10^{-7}). Besides this, all residues are washed six times with hot water on the filter paper before they are analyzed.

In spite of the fact that Mn_3C very likely does not exist in the electrolytic residue, its decomposition product, manganese hydroxide, might be present and determinations of this factor were made. Unfortunately, vacuum melted samples which were high in manganese and carbon contents were not available. These represent the most satisfactory type of sample for this type of experiment.

However, several tests were made which proved to be fairly conclusive with regard to manganese hydroxide contamination. The first series of tests involved the electrolysis of ferromanganese inasmuch as ferromanganese contains a high percentage of both carbon and manganese. Two types of material were available. One contained 78 per cent manganese and approximately 8 per cent carbon, whereas the other contained 80 per cent manganese and 1.3 per cent carbon. In the first sample sufficient carbon was present so that all the manganese and iron are probably combined as manganese iron carbides. In the second sample, which contains lower carbon, there is sufficient carbon for 61 per cent of the 80 per cent manganese present to exist as manganese carbide. These samples were electrolyzed and sample No. 1 contained 1.02 per cent MnO, whereas sample No. 2 contained 3.5 per cent MnO. In other words, in these two cases 100 per cent manganese carbide was electrolyzed and between 1 and 3.5 per cent contamination resulted from this type of solution. These values were much lower than was expected when the tests were made for several reasons. In the first place, ferromanganese is quite brittle and it was thought before these tests were made that sufficient spalling of the electrode would take place to give a very large reported analysis of the electrolytic residue. Also, it was believed that the electrolysis of material containing as high a concentration as 80 per cent manganese would increase the manganese-ion concentration of the electrolyte inside of the collodion bag so as to exceed the $Mn(OH)_2$ solubility product within a few minutes after starting the run and that manganese hydroxide would precipitate for the remainder of the 24-hour period. Material containing as high a concentration of both carbon and manganese as described in the foregoing tests is of course a severe test for the electrolytic method with respect to contamination resulting from carbide decomposition. According to Arnold and Read (83) the actual percentages of manganese in the carbide in practical steel are very small. The results of their work are shown graphically in Figure 16. It may be seen that a steel containing 1 per cent manganese (which is higher than the ordinary material) contains only 6 per cent manganese in the carbide. In other words, in ordinary carbide steels containing from 0.1 to 1.0 per cent of manganese only a very small percentage of this total manganese is combined with carbon as Mn_3C . For an extreme example, 6 per cent of manganese would be present in the form of manganese carbide in a steel containing 1 per cent manganese. If 30 grams of steel were electrolyzed and none of the Mn_3C decomposed, the total manganese in the residue due to this contamination would be 0.018 gram. This would be equivalent to 0.0232 gram of MnO. However, we have just shown from the above experiments with the electrolysis of ferromanganese samples that the carbide does decompose and that only from 1 to 3.5 per cent remains in the inclusion residue as contamination. Hence the contamination as based upon these ferromanganese experiments would amount to only 0.000232 gram of MnO. This is equivalent to 0.000773 per cent MnO when a 30 gram sample is used for electrolysis. The maximum contamination of 0.0027 per cent MnO could be present if all but 3.5 per cent of the manganese carbide decomposed.

Another type of test was made with the hope of determining the extent to which manganese carbide contaminates the inclusion analysis. In this series of tests, samples 1, 2, 4, 5, 6, 7, 8, and 11 were case carburized until the outside surface of the sample contained from 1 to 1.3 per cent carbon. It will

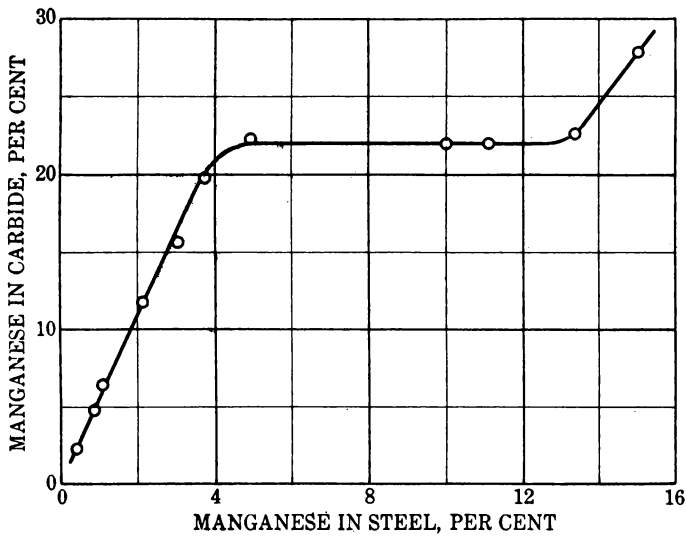


Figure 16.—The relation of per cent manganese in steel with per cent manganese in carbide (Arnold and Reed)

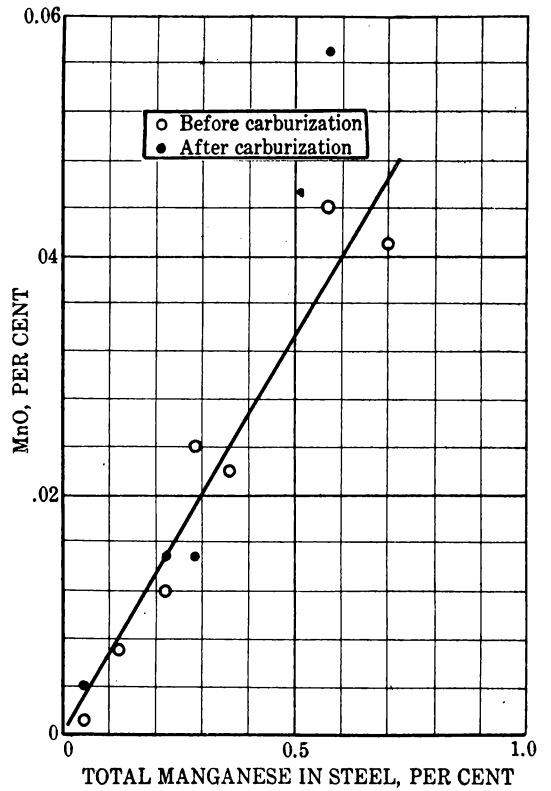


Figure 17.—Effect of case carburization on the electrolytic analysis of steels deoxidized only with ferromanganese

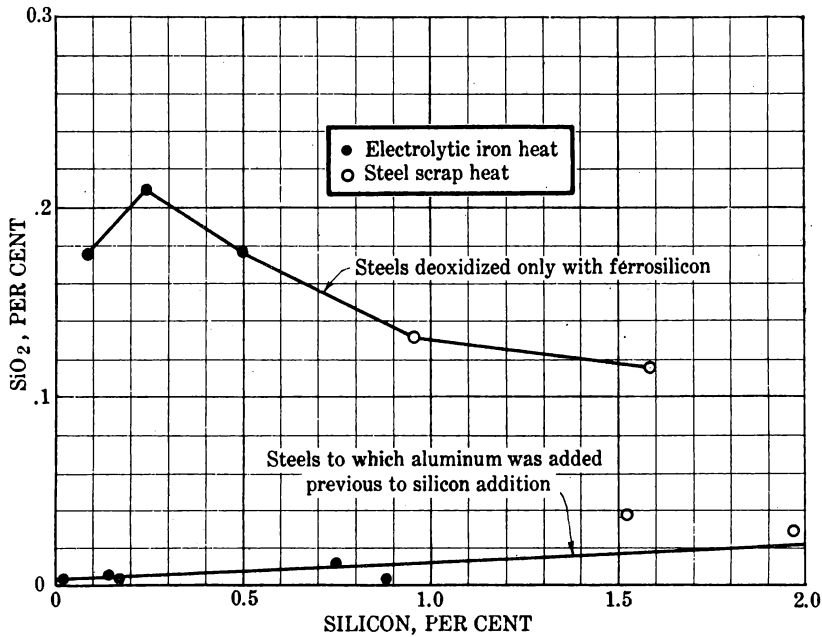


Figure 18.—The contamination of the electrolytic residue with silicic acid gel

be recalled from Tables 13 and 14 that these samples contained from 0.045 to 0.563 per cent manganese and before carburization all of their carbon contents were quite low, ranging from 0.01 to 0.05 per cent. It was believed that the electrolysis of these samples after carburization should show the effect of manganese carbide when present. Also, the difference between the MnO analysis before and after carburization is a very important factor in determining this effect. The results of these tests are shown in Table 18. The analyses before and after carburization are both shown in this table. It may be seen that the MnS values both before and after carburization check fairly well. In some cases the analyses before and after this treatment are perfect checks, as in samples 4 and 7. However, the MnO contents as determined by difference from the citrate separation do not check as well as the MnS values before and after carburization. These values, however, are fair checks with the exception of samples 4 and 5. Sample 5 particularly is off in this regard. The analytical accuracy seems to be approximately ± 0.004 , as illustrated in the MnO results both before and after carburization in sample 11. At any rate, the contamination resulting from manganese carbide has been shown by these experiments to be small and not of sufficient order of magnitude to make any appreciable change in the electrolytic determination of MnO and MnS. However, it will be recalled that the highest manganese content of any of these steels was 0.563. It is entirely possible that the contamination will become appreciable as the manganese concentration is increased above this value. Particularly one would expect contamination due to selective anodic reactions when the manganese content is greater than 1.4, which represents the solid solubility of manganese in iron at room temperature. The effect of manganese carbide on the electrolytic analysis of steel for MnO is shown graphically in Figure 17.

Table 18. - The effect of carbon on the electrolytic determination of manganese oxide and sulphide - The case-carburized manganese steels

(Surface of samples all contained approximately 1 per cent carbon after carburization)

Sample number	Case-carburized samples, per cent			Analyses of samples before carburizing, per cent 1/		
	MnO + MnS	MnS	MnO	MnO + MnS	MnS	MnO
1	0.001	0.001	--	0.002	--	--
2	.039	.024	0.015	.045	0.033	0.012
4	.060	.045	.015	.066	.042	.024
5	.047	.032	.015	.019	.019	.000
6	.021	.017	.004	.011	.010	.001
7	.031	.023	.008	.022	.023	- .001
8	.105	.048	.057	.084	.040	.044
11	.118	.121	- .003	.100	.104	- .004

The phenomena accompanying the decomposition of Mn_3C during the electrolysis of high-carbon steel have been studied in detail by H. Freeman (94).

DETERMINATION OF SiO_2

Many types of analyses were made in connection with the accuracy of the electrolytic determination of SiO_2 in steel. The most important factors which were determined were (1) the solubility of SiO_2 , particularly when that oxide existed in a manganese silicate; and (2) the determination of factors such as precipitation which would tend to make the SiO_2 content by analysis higher than the amount actually present.

Solubility of SiO_2 in the Electrolyte

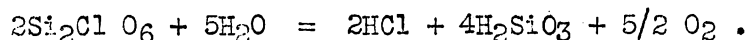
Previous experiments (43) of the solubility of SiO_2 in dilute acids led the authors to the conclusion that SiO_2 in ferrous and manganous silicates was more soluble than in any other form, such as the aluminum silicates or pure SiO_2 . The solubility of SiO_2 as manganous silicates was determined in this investigation. When the samples listed in Table 3, page 17, were placed at the bottom of collodion bags in which approximately 24 grams of electrolytic iron was electrolyzed, the solubilities were nil in every case.

A similar situation was encountered when the silicate was subjected to anodic reactions on top of the iron sample. Greater variations were found in these experiments, probably because of mechanical losses in placing and removing the silicate at the top of the specimen to be electrolyzed. The recovery values in this case varied from 92.9 in sample 9, containing 41.2 per cent SiO_2 , to 104.4 in sample 14 containing 60.0 per cent SiO_2 . The average of all the recoveries is 99.9 per cent.

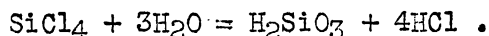
Contamination of SiO_2 Inclusions with Silicic Acid Gel

Theoretically the function of silicon as dissolved or alloyed in the metal is very interesting. It is rather hard to picture the process which takes place during the electrolysis of this material. In fact, the exact mechanism of the electrolysis of silicon is not known in this regard. It has been known for some time that the SiO_2 reported from analysis of the electrolytic residue was a very small value in most steels when compared with the total silicon content of the same steel. In other words, it was definitely known that Si (metal) passes from solid solution in the iron to the aqueous solution of the electrolyte, although the exact mechanism is not obvious. Several samples were studied in trying to ascertain this solution effect, with the hope of determining if possible the mechanism and the extent to which it takes place. One point which was of particular interest was the determination of the extent to which the silicon diffuses through the collodion bag. Thirty-five grams of a steel containing 0.747 per cent silicon was electrolyzed in a cell containing a total of 1 liter of electrolyte and after the electrolysis the solution was analyzed both inside and outside of the collodion bag and it was found that the concentration was practically the same in both cases. In other words, the silicon

is combined in such a manner that the molecular agglomerate is of sufficiently small dimensions so that it may easily pass through the collodion bag. This is a particularly important discovery in view of the fact that if it did not diffuse through the pores of the dialyzing medium the concentration would build up within the anode chamber and early precipitation would result. It was thought for some time that one of the many silicon oxychlorides might possibly form in view of the fact that both oxygen and chlorine are being liberated at the anode. However, previous workers have shown that this material can not exist in the presence of water inasmuch as violent reactions occur. For example, Friedel (85) and Ladenburg (86) state that all of the silicon oxychlorides decompose in the presence of water. An example of this type of decomposition is given by the equation.



In other words, it is their contention that silicic acid forms in preference to the silicon oxychloride. It was then thought that silicon tetrachloride might form under these conditions, but according to Berzelius (87) this is not the case. He states that silicon tetrachloride also forms silicic acid in the presence of water according to the following equation:



This was also found to be the case by Berthelot (88). Under these circumstances it appears that silicic acid is the most probable compound which the silicon forms in the electrolysis of a silicon-containing steel. It must also be conceded for the explanation of the difference between the SiO_2 residue analysis and the total silicon content of steel that this silicic acid has an appreciable solubility in the electrolyte under consideration.

Tests were made with the idea of determining the solubility of this material in the electrolyte under different conditions. A 29-gram vacuum-fused sample, which contained 0.88 per cent silicon, was electrolyzed and the inclusion residue analyzed. It was found that 0.003 per cent of SiO_2 was recovered by this test. According to the analysis of the steel and the weight of steel dissolved, over 2.5 grams of silicon was electrolytically dissolved in this test but less than 0.0005 gram of silicon was reported as SiO_2 . Because the sample was vacuum fused, no SiO_2 would be expected in the residue and the amount reported was so small that it can be considered as an analytical blank.

It should be pointed out at this time that practical steels contain only about 0.1 per cent Si or one-eighth the amount used in this test, so that little or no contamination should occur during the electrolysis of ordinary steel samples.

However, further tests were made in order to determine the extent of this type of contamination. A series of samples was prepared in a similar manner as were those described in the manganese series. Some of the molten electrolytic iron was taken from the furnace in the heat which was previously described. In one series of samples the steels were deoxidized only with

silicon (as 50 per cent FeSi). Large amounts of SiO₂ would be expected in these samples, inasmuch as the original metal contained appreciable quantities of iron oxide. In the second series of samples the steels were deoxidized thoroughly with aluminum (approximately 1 per cent) and while the metal was still molten varying amounts of silicon were added. Under these circumstances little or no SiO₂ should form, inasmuch as the steel had been previously deoxidized with aluminum. The results of these tests are given in Table 19. The most interesting samples from the standpoint of silicic acid contamination are samples 14, 16, and 18. It may be seen that the SiO₂ contents reported in these analyses were 0.004, 0.006, and 0.012 per cent, respectively. The two lower values may be considered as analytical blanks and were obtained on steels which contained practical amounts of silicon--namely, 0.16 and 0.138 per cent respectively. The higher contamination--0.012 per cent--was obtained through the electrolysis of a steel containing 0.747 per cent Si, which is higher than the silicon content of ordinary steels. The electrolytic analyses of samples 15, 17, and 19 may be contrasted with the above results. This is done graphically in Figure 18. Inasmuch as they represent steels which were deoxidized only with silicon, the SiO₂ values were all high and of a similar order of magnitude, varying from 0.176 to 0.220 per cent.

Table 19. - Contamination of electrolytic residue with silicic acid gel, per cent

ELECTROLYTIC IRON HEAT

Sample number	Si	SiO ₂	Al ₂ O ₃	MnO + MnS	Mn	S	C	SiO ₂ content after carburizing to 1.3 per cent carbon on surface and normalizing
Samples to which Al was added previous to Si addition								
40	0.003	0.003	--	--	0.003	0.039	--	--
14	.160	.004	0.218	0.005	.031	--	0.01	0.023
16	.138	.006	.519	.003	.031	--	.01	.005
18	.747	.012	.190	.002	.031	--	.01	.118
Vacuum distilled sample								
X	.880	.003	--	--	--	--	--	--
Samples deoxidized only with FeSi								
15	.084	.176	.017	.003	.031	--	.01	.218
17	.235	.212	.006	.002	.031	--	.01	.213
19	.498	.177	.014	.005	.031	--	.01	.201

STEEL SCRAP HEAT

Samples to which Al was added previous to Si addition								
54	1.51	1/0.039	0.131	--	--	--	--	--
56	1.97	1/.030	.171	--	--	--	--	--
Samples deoxidized only with FeSi								
53	.94	.131	.005	--	--	--	--	--
55	1.58	.117	.006	--	--	--	--	--

1/ May be due either to SiO₂ existing in steel scrap before deoxidation with Al or to precipitation of silicic acid gel during electrolysis.

Effect of Carbon on Silicic Acid
Contamination

The steels listed in the above table were case carburized at the same time as were the carburized manganese samples, with the hope of determining the effect of carbon upon silicic acid contamination. It was found that in nearly every case where no aluminum had been added reasonable checks were obtained. However, when aluminum was present in the steel, high silica contents were reported as shown by the last column of Table 19. The exact reason for this phenomenon is not known but it is unquestionably appreciable. In recent work which has been done at one steel company, it has been found that titanium has this same effect. In other words, when a steel has been deoxidized with both silicon and titanium abnormally high results will be obtained, whereas if the titanium addition is eliminated on the same steel the electrolytic analysis will show low results. This effect should be kept in mind by any investigator who is studying high-carbon steels. Caution should be exercised before accepting any results on steels containing high carbon and which were deoxidized with either a combination of silicon and aluminum or silicon and titanium. It is not known how many other elements might affect this factor but it is almost a certainty that manganese and chromium do not.

Contamination of the SiO₂ Determination
with Silicon in Falling Iron Particles

It was shown previously in Table 9 that the manganese contamination resulting from falling metallic-iron particles was low. In this same table the SiO₂ analyses in these samples were also reported. Although the SiO₂ contents of the residues as determined by regular electrolysis indicated over 0.1 per cent in all cases, the magnetic material contained only 0.001 to 0.002 per cent of SiO₂. This is quite indicative that contamination from this source is negligible.

Use of Cellophane as Compared with
Collodion Bags

Greene (89) recommended that cellophane bags of the type used for covering acid-bottle stoppers may be successfully used in place of collodion bags which were recommended by the authors in the previous paper (46).

Because it was not known whether the pores of cellophane were just as permeable to the manganese and silicon ion or molecular complexes as was the collodion, some tests were made for the determination of this factor. No difference was observed between the electrolysis in cellophane as compared with collodion bags. In samples 3 and 5, Table 13, 0.022 and 0.019 per cent MnO + MnS, respectively, was present when collodion bags were used. Analyses of the same steels after electrolysis in cellophane bags gave values of 0.021 and 0.018 per cent, respectively. These are exceptionally good checks and no difficulty should be encountered in the manganese determination when cellophane bags are used in place of collodion bags in the recommended electrolyte. The same results were shown in comparing the SiO₂ analyses of samples 14 and 16

when the sample was electrolyzed in cellophane and collodion bags. The results and electrolytic residue analyses in collodion bags (see Table 19) were 0.004 and 0.006 per cent SiO_2 , respectively, in these samples as compared with 0.003 and 0.004 per cent SiO_2 , respectively, when the samples were electrolyzed in cellophane.

MISCELLANEOUS DATA CONCERNING THE EXTRACTION OF ALLOY OXIDES AND SULPHIDES FROM ALLOY STEELS

The recommended electrolytic extraction process has been in use in various steel laboratories for the past few years. When this procedure was first recommended the exact applications to specific types of steel were not known. Recently sufficient information has been obtained to indicate that the recommended electrolytic method can be used only for plain-carbon steels. Also, as has been shown by previous discussion of contamination factors, certain precautions must be taken in electrolyzing plain-carbon steels in order to avoid erratic results. In spite of this the procedure is surprisingly simple and the checks obtained are particularly satisfactory.

At the beginning of the investigation on electrolytic processes it was hoped that sufficient time and equipment would be available for development of a method which would be applicable for alloy steels. However, such was not the case because it was soon found that entirely too many variables were encountered for the solution of all these problems in the time available. Every type of steel presented new problems for solution and many of them were almost insurmountable. The authors believe that special methods must be devised for each classification of alloy steels. Unquestionably if such methods can be devised many interesting and valuable data will be obtained which will solve many problems in the alloy-steel industry. The authors regret that the data concerning the electrolysis of alloy steels are very sketchy, but believe that sufficient work was done for the determination of the limitations of the method. Some of the variables encountered, together with the possibilities of solution, will be given in the following pages.

Chromium

Contamination of Cr_2O_3 Analysis with the Alloy Chromium

A series of chromium steels was prepared in the electrolytic heat in the same manner as were the manganese and silicon samples. Two samples were prepared in which the highly oxidized molten electrolytic iron was deoxidized with chromium. The results of electrolytic extraction, together with other analyses of these samples, are listed in Table 20.

Table 20. - Determination of chromium-containing inclusions

Sample number	Addition	Per cent				Cr ₂ O ₃ after carburization
		C	S	Total Cr	Cr ₂ O ₃	
20	Chromium	0.05	0.020	0.056	0.092	0.077
21	Aluminum, then chromium	.04	.020	.666	.032	.438
57	Chromium	.07	.045	.62	.300	---
23	Aluminum, then chromium	.08	.020	1.55	.029	.490

Sample 20 was prepared in the electrolytic heat, whereas sample 57 was prepared in a low-carbon steel heat. Samples 21 and 23 were prepared by deoxidizing liquid electrolytic iron first with aluminum (1 per cent) and then by adding different amounts of chromium. It was found that the inclusion residues from the electrolysis of samples 20 and 57 were quite high, as would be expected, because no aluminum was added. Sample 20 contained 0.092 per cent Cr₂O₃, whereas sample 57 contained 0.300 per cent. In contrast to this, samples 21 and 23 contained similar amounts of Cr₂O₃--namely, 0.023 and 0.029 per cent, respectively. These samples all contained small amounts of carbon so that these latter values in the samples deoxidized with aluminum could not be expected to contain very much chromium carbide. However, the small values listed herein may be due to chromium carbide in the electrolytic residue. On the other hand, it is highly possible that samples contained some chromium sulphide which is given here as Cr₂O₃. However, there is a third possibility that chromium hydroxide Cr(OH)₃ formed to such an extent as to give this amount of contamination. It is believed by the authors that this latter type of contamination is the more probable.

Contamination from Chromium Carbide

The effect of carbon upon the results of these analyses was determined with three of the samples case carburized so that their surfaces contained as much as 1.3 per cent carbon. It is interesting to note that the value on the case-carburized sample--No. 20--is a fair check on the electrolytic analysis before carburization; that is, 0.077 per cent was obtained on the carburized sample as compared with 0.092 per cent previous to carburization. However, it is also very important that the aluminum-killed samples were far from adequate checks and some 10 to 15 times as much Cr₂O₃ was reported in the carburized aluminum-killed samples as in the values obtained before carburization. The aluminum has apparently caused a change in the stability of the carbide but no attempt will be made herein to analyze this effect. This is certainly important enough for future study and it is hoped that such investigations will be made either in these laboratories or by some other interested parties. Most of the chromium steels contain appreciable amounts of carbon,

and for this reason no further mention of electrolytic extraction will be made herein on chromium-containing steels. However, other work has been done which leads directly to a recommendation for future work on a different type of method of extraction of Cr_2O_3 from alloy steels.

Solubility of Cr_2O_3 in Sulphuric
Acid

The solubility of Cr_2O_3 in sulphuric acid solutions was determined and it was found in the three solutions studied that Cr_2O_3 was quite insoluble. The results of these tests are given in Table 21.

Table 21. - The Solubility of Cr_2O_3 in sulphuric
acid solutions

H_2SO_4 concentration, (volume, per cent)	Quantities used		Time in Solution, hours	Tempera- ture, °C.	Recovery, per cent
	Solvent, Cubic centimeters	Cr_2O_3 , grams			
10	25	0.1	48	28	99.63
33-1/3	25	.1	24	28	99.25
25	100	.1	1/2	100	97.50

The crystalline structure of the oxide studied was hexagonal. It has been observed in samples studied in these laboratories that pure Cr_2O_3 inclusions in steel are also hexagonal. Hence these tests are fairly indicative of the solubilities of Cr_2O_3 inclusions when subjected to the treatments given in Table 21.

According to these results it should be possible to subject drillings from a Cr_2O_3 -containing sample to a solution composed of one part of H_2SO_4 and two parts of H_2O . At room temperature a fairly large sample of steel could be dissolved in 24 hours. Under these conditions Cr_2O_3 would be insoluble, the recovery under these conditions being 99.25 per cent.

However, since the acidity of this solution is quite appreciable and because it was shown previously that the stability of carbides increased with increasing hydrogen-ion concentration, it is entirely probable that the residue obtained from this sulphuric acid solution would contain not only chromium oxide but also its carbide.

Separation of Chromium Carbide from
Chromium Oxide

A survey of previous methods and investigations of extraction phenomena indicated that chromium oxide could be separated from the chromium carbides by the chlorine method as described by Wasmuht (52). The results as obtained

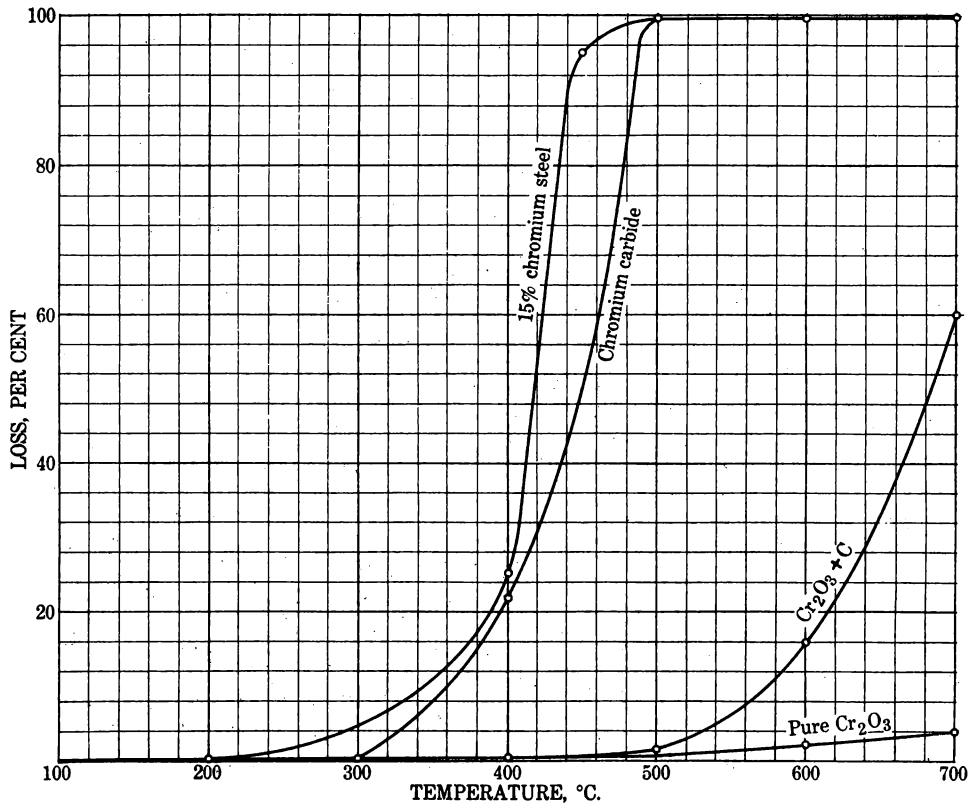


Figure 19.—Behavior of chromium oxide and carbide in the presence of chlorine (Wasmuht)

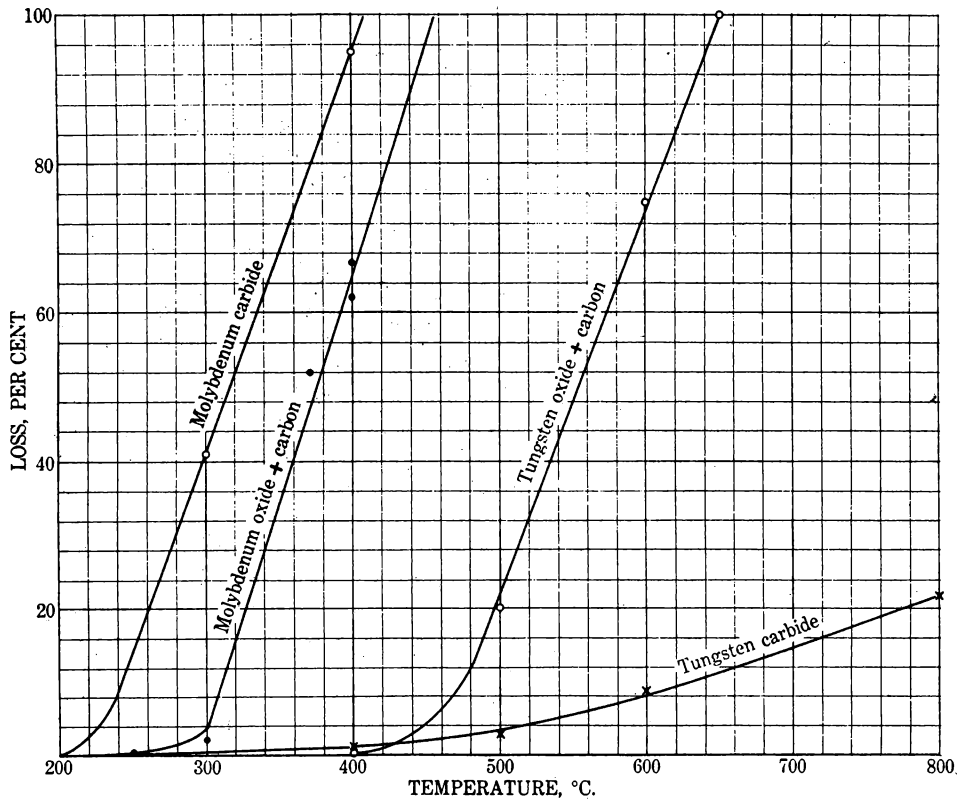


Figure 20.—Behavior of tungsten and molybdenum compounds in the presence of chlorine (Wasmuht)

by this investigator are indicated in Figure 19. The curves shown therein indicate definitely that if a chlorine stream is passed over a mixture of chromium carbide and chromium oxide at 500°, the chromium carbide will completely decompose and will be removed by volatilization as the chromium chloride. The decomposition would leave some graphite with the chromium oxide and the effect of the chlorine stream on a combination of graphite and chromium oxide is shown by one of the curves in this figure. It can be seen that at this temperature and under these conditions chromium oxide is only slightly affected. In fact, only 1.5 per cent Cr₂O₃ would be lost by the process.

Recommended Method for the Determination of Cr₂O₃ Inclusions in Alloy Steels

This then forms the basis for a recommendation of a new method for the extraction and determination of chromium oxide from steels. It is to be recommended that future investigators study in detail the effects of extraction in sulphuric acid solution as shown above, followed by a treatment of the inclusion residue (containing both the carbide and the oxide) with chlorine at 500°. It is believed that this type of investigation will prove fruitful in this respect. The curves as shown by Wasmuht should be investigated more thoroughly between the temperature ranges of 400° and 600°, in order to determine if these curves are absolutely correct. If they are satisfactory the authors have no doubt that this recommended procedure will be entirely satisfactory for the extraction of chromium oxide from alloy steels. However, future investigators will unquestionably encounter many difficulties when other alloys such as nickel, vanadium, etc., are present and future investigations will be complicated by these factors.

Nickel

Samples containing variable amounts of nickel were prepared in the low-carbon steel heat. Samples 59 and 61 were prepared by adding variable amounts of electrolytic nickel to the molten electrolytic iron in the test spoon. As a result the samples contained 1.82 and 3.46 per cent nickel respectively, as shown by Table 22. Samples 60 and 62 were thoroughly deoxidized with aluminum (1 per cent) and electrolytic nickel additions were made immediately thereafter. The nickel contents were 1.96 and 4.23 per cent, respectively. Samples 63 and 64 were high-sulphur materials; the former had no aluminum addition, whereas the latter was deoxidized with aluminum previous to the nickel addition.

Table 22. - Nickel oxide and sulphide inclusions in steel

Sample number	Additions, grams	Per cent						Ks = $\frac{\% \text{NiS}}{\% \text{FeS} \times \% \text{free Ni}}$	
		C	Ni	S	Nickel inclusions calculated to NiS	S as by dif- ference	Free nickel		
59	20 Ni	0.031	1.82	0.038	0.043	0.015	0.063	1.79	0.38
60	7.5 Al, then 20 Ni	.041	1.96	.040	.067	.024	.044	1.92	.79
61	40 Ni	.023	4.46	.035	.046	.016	.052	3.43	.258
62	7.5 Al, then 40 Ni	.034	2.23	.043	.107	.038	.014	4.16	1.82
63	20 Ni, 1 FeS ₂	.041	1.90	.076	.052	.018	.159	1.87	.175
64	7.5 Al, then 40 Ni, 1 FeS ₂	.042	3.31	.083	.067	.024	.162	2.27	.182

In this series of samples, as in some of the others which were described previously, the aluminum-killed samples were higher in the nickel recovered in the electrolytic residue than those which were not killed with aluminum. However, in this case it might be pointed out that these aluminum-killed samples were higher in both sulphur and nickel contents. Also, large quantities of nickel were found in the electrolytic residue in the high-sulphur samples 63 and 64. Time was not available for the determination of the solubility of nickel oxide or nickel sulphide in the electrolytic residue. Houdremont (90) has recently shown that nickel sulphide occurs in stainless steels, and it is believed by the authors that the values for nickel inclusions in Table 22 are largely due to the formation of nickel sulphide. These values are not sufficient to establish the amounts of nickel-containing inclusions in steel, but can be used as an indication that such materials may exist in nickel-containing steels. The calculated values for the nickel desulphurizing constant, given in Table 22, are erratic and vary tenfold. Under these conditions further work should be done in this direction before all of the variables can be determined.

Molybdenum

Certain results were obtained which may be used to indicate that inclusions resulting from reactions of molybdenum with iron oxide and iron sulphide exist in steel. Three samples were prepared in which molybdenum was added to liquid iron prepared in the electrolytic heat. Sample 29 was prepared by adding only ferromolybdenum to the liquid iron in the test spoon. Sample 30 was deoxidized first with aluminum which was followed by an addition of ferromolybdenum. Sample 36 was deoxidized with aluminum and additions of FeS₂ and ferromolybdenum were made. Unfortunately, the molybdenum content of sample 29 was not determined. However, it is believed that this is approximately the same as in sample 30,

Inasmuch as the same weight of ferromolybdenum was added. Approximately the same amount of molybdenum inclusions was found in samples 29 and 30. No attempt was made to determine the exact compound in which molybdenum exists in the electrolytic residue. The analyses of these samples are given in Table 23. However, as may be seen by a comparison of the molybdenum in the residue and the total molybdenum, practically all of this element was recovered in the electrolytic residue. The same is the case in sample 36 which contained more sulphur than the other two samples--0.024 per cent. No attempt was made to determine the form in which the molybdenum exists in the residue, but these results indicate that it is possible to form molybdenum-containing inclusions. It is believed by the authors that the possibility of sulphide formation is appreciable.

Table 23. - Molybdenum-containing inclusions

Sample number	Per cent				Molybdenum inclusions in steel, per cent
	C	S	Mn	Mo	
29	0.014	0.010	0.003	--	0.195
30	.02	.010	.003	0.18	.145
36	.02	.010	.003	.68	.415

It is possible that molybdenum formed the carbide as well as the oxide and sulphide in these samples. If this is true it would be very difficult to determine the amount of such inclusions because of the carbide contamination. According to Wasmuht (52), Figure 20, the oxide and carbide can not be separated by means of chloride volatilization as was suggested for chromium. When the carbide is completely decomposed at 410° C., 60 per cent of the oxide has been lost. This is unfortunate because many major difficulties will be encountered in trying to solve the question of molybdenum inclusions.

Tungsten

Only one sample of tungsten-containing steel was prepared which was satisfactory for inclusion analysis. This sample was prepared by adding only tungsten to the highly oxidized electrolytic iron to such an extent that 0.467 per cent tungsten was obtained in the final material. Electrolytic extraction of this sample indicated 0.167 per cent WO_3 in the electrolytic residue. This could of course be present as tungsten oxide, sulphide, or some type of contamination such as the carbide. The steel sample contained 0.025 per cent sulphur, which is equivalent to 0.073 per cent WS_2 . This of course would not account for all of the tungsten in the electrolytic residue. It is believed by the authors that the carbide contamination is the more probable explanation of this quantity of tungsten in the electrolytic residue, although it may possibly be due to the formation of either the oxides or the sulphides of tungsten. Wasmuht's (52) work indicated that tungsten carbide and oxide are difficult to separate by chlorination (Figure 20). When the carbide has been completely removed at 650° C., 11 per cent of the oxide has been lost.

Vanadium

Two samples containing vanadium were prepared the electrolytic heat, both of which were deoxidized with aluminum previous to the ferrovandium addition. The second was also treated with an addition of FeS_2 . Sample 32 contained 0.297 per cent vanadium, whereas sample 33 contained 0.627 per cent. Appreciable quantities of vanadium were found in the electrolytic residue, since 0.055, 0.152, and 0.004 per cent V_2O_5 was found in samples 32 and 38, respectively. Sample 32 contained 0.045 per cent sulphur, whereas sample 38 contained 0.101 per cent. Hence the increase in vanadium concentration in the electrolytic residue of sample 38 might possibly be due to the increased sulphur content. It is very unlikely that any V_2O_5 existed in these two samples, inasmuch as the samples were previously deoxidized with aluminum. However, the vanadium in the electrolytic residue also is proportional to the vanadium contents of the two steels. With this in mind it is possible that the high residue analysis was due to some form of contamination from the vanadium alloy, rather than from any particular inclusion material.

Copper

Two samples of steel were made which contained practically no material other than copper. Sample 33 was prepared with only an addition of pure copper. Sample 34 was prepared by an addition of aluminum preceding the copper. Both of these samples contained the same amount of total copper--namely, 0.34 per cent. It is also interesting to note that both samples contained approximately the same amount of sulphur--0.042 and 0.047 per cent, respectively. These samples were practically the same in all respects, with the exception that one was highly oxidized whereas the other was completely deoxidized with aluminum prior to the addition of copper. Contrary to the expectations in this regard, the one to which the aluminum had been added was very much higher in the copper analysis of the electrolytic residue than the other. Sample 33 contained 0.04 per cent copper as inclusions in the electrolytic residue, whereas sample 34 contained 0.227 per cent. No explanation of this phenomenon can be made without introducing the hypothesis that aluminum changes the molecular state of copper in steel. The only suggestion which will be made by the authors in this regard is that it is possible that the compound CuAl_2 might form under these conditions. If this material were present it would probably be insoluble in the iron and would be recovered in the electrolytic residue as such. Time was not available for the determination of the truth of this statement. However, the samples are still on hand and if the opportunity presents itself in the future this point will be determined.

SUMMARY AND CONCLUSIONS

The work done and described in this paper has led to a number of specific conclusions, which are as follows:

The Electrolyte

1. An electrolyte containing 3 per cent $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and 1 per cent sodium chloride has been found to be the most satisfactory.

2. This electrolyte as prepared has a hydrogen-ion concentration of $10^{-3.2}$ but after three hours of electrolysis changes to 10^{-7} or neutrality.

3. During electrolysis the steel sample is in contact at all times with a neutral electrolyte. This is particularly advantageous because a neutral solution does not dissolve the various nonmetallic inclusions.

Determination of FeO

1. Crystalline ferrous oxide is not soluble in the recommended electrolyte.

2. Basic ferric sulphate and ferrous hydroxide precipitate during electrolysis and contaminate the residue so that no FeO determination can be made.

3. Falling particles of metallic iron do not appreciably contaminate the electrolytic residue.

4. FeO can be determined in more acid solutions having automatically controlled hydrogen-ion concentrations.

Determination of MnO

1. Pure MnO is insoluble in the electrolyte.

2. MnO is partially soluble when the MnO inclusion is in contact with both the anode and the electrolyte. Galvanic action seems to induce solubility which varies from 0 to 30 per cent.

3. When MnO is combined with other oxide materials such as FeO, SiO₂, Al₂O₃, etc., this induced solubility of MnO is reduced and in most cases is zero.

4. No basic manganous sulphate, Mn(OH)SO₄, is formed during electrolysis in this solution.

5. Mn(OH)₂ probably forms but does not exceed its solubility product and therefore does not precipitate.

6. The alloy manganese which goes into solution together with the metallic iron does not contaminate the residue.

7. Either cellophane or collodion bags may be used for MnO determination.

Determination of SiO₂

1. SiO₂ is entirely insoluble in the electrolyte even when combined with other oxides such as MnO (Table 3).

2. No contamination results in steels containing up to 0.9 per cent Si. The residual silicon apparently goes into solution as silicic acid but does not precipitate as the gel, due to the low H^+ ion concentration of the solution.

3. The silicic acid molecular complex is sufficiently small to migrate through the pores of either collodion or cellophane bags.

4. Cellophane is just as satisfactory as collodion for the determination of SiO_2 .

Determination of Al_2O_3

1. Al_2O_3 is entirely insoluble in the electrolyte.

2. The electrolytic method is probably much more satisfactory for the determination of Al_2O_3 in steels partially deoxidized with aluminum than is the modified Kichline method. Iron and manganese aluminates and aluminum silicates are present in steels of this type. These materials are soluble in the concentrated HCl used in the latter method, whereas they are entirely insoluble in the recommended electrolyte.

Determination of MnS

1. MnS is insoluble in the electrolyte and is recovered in the electrolytic residue.

2. This compound may be separated from MnO by means of sodium citrate solution. MnO is soluble in this solution, whereas MnS is not.

Determination of FeS

1. FeS is entirely insoluble in the electrolyte and is recovered without loss in the electrolytic residue.

2. The best method of determination of FeS is by difference between the value of total sulphur in the steel and the sulphur as MnS, which gives the remainder as FeS.

Determination of Oxides and Sulphides in Alloy Steels

1. Too many variables are presented for the determination of alloy oxides and sulphides by means of this electrolytic method. The method is recommended only for low-carbon and plain-carbon steels.

2. Cr_2O_3 may be determined by dissolving the steel in a weak sulphuric acid solution and separating the carbides from the oxides in the residue by means of the selective action of chlorine upon the carbide. At $500^\circ C$. the carbide is entirely removed, whereas the oxide is not attacked.

3. The results of this investigation show that nickel sulphide probably exists as an inclusion in steel.

4. Molybdenum sulphide also is a possible inclusion.

5. Copper sulphide may also exist as an inclusion in steel. New methods must be devised for the determination of oxides and sulphides in each class of alloy steels. Entirely different problems are presented by each type of steel and the solution of these problems for any one class will not necessarily apply to any other. The electrolytic method presents some very marked possibilities in certain cases but apparently will be useless for the determination of nonmetallic inclusions in some of the alloy steels.

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