P-III

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UNIT-II

2 Analysis of Finished Products

2.1 Analysis of Steel

2.1.1 Introduction:

The analysis of steel is one of the most important types of applied analysis. The physical and chemical properties of ferrous material are determined by the kind of subsidiary elements that are present and detecting of these constituents.

The elements found in steel may be derived into three groups from analytical standard point

1. The first group induces certain elements that are always present such as carbon, manganese, Phosphorous, Sulphur and silica are determined because it effects on the properties of ferrous materials.
2. The second group compresses allying elements whose determined is often required such as copper, chromium, nickel, molybdenum, tungsten and aluminum.
3. The third group elements compresses whose personal their usual amount is not much important and which is frequently determined such as tin, zinc and Arsenic.

2.1.2 Dissolution:

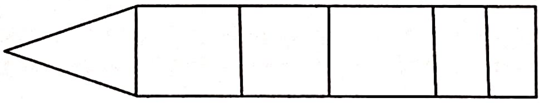
The sample is dissolved in Con HNO_3 the solution is boiled until reddish brown fumes are completely evolved the solution is cooled and filtered the insoluble residue is used for the estimation of Si, Mn, P_2O_5, sulphur, Chromium, Molybdenum, during dissolution phosphorus is oxidized to phosphate and sulphur is oxidized to sulphate.

2.1.3 Determination of Carbon:

Generally carbon exists in combined and uncombined state i.e. free state. The carbon which is present in combined state is called "Carbide". The carbon which is present in Free State is called "Graphite". The sum of the carbon in Free State and combined state is known as "Total Carbon".

Combustion Tube

The typical arrangement for determination of carbon by the combustion method is shown in figure.



Apparatus

A = Oxygen Supply

B = Oxygen Reservoir

C = Mercury Manometer

D = Tower containing soda lime placed at the top which can be used to purify the oxygen coming from oxygen cylinder. A layer of about ½ thickness anhydrous $Mg(ClO_4)_2$ is placed on top to remove any trace of gas.

E = Containing Mercury is introduced in the line to limit the pressure to the working value.

F = Combustion Tube

G = Electric Furnace

L = Nanometer connection of Gauge

M = Glass tube lightly packed with absorbent cotton to remove solid particles coming from combustion tube along with glass

N = Bottle containing 25ml of sulphuric acid saturated with chromic acid to remove gasses of sulphur

I = Bottle contains 50ml of sulphuric acid for removing the bulk of the moisture

O = U tube containing anhydrous $Mg(ClO_4)_2$ which can be used to absorbed moisture but not Co_2

J = Absorbing bulb containing 20-30 mesh inert base impregnated with NaOH for absorbing Co_2

K = H_2SO_4 bath

Combustion Apparatus:

Generally electrical heater is required for the combustion. The sample is heated at 1000-1100°C used for analysis of carbon in steels and low alloy steels. Combustion tube is made up of porcelain clay, quartz and platinum etc., and must be gas tight. The length of the combustion tube is 30˙ and internal diameter is $1\frac{1}{4}$ For the determination of carbon small boat like crucible is introduced into the combustion tube.

Catalyzes:

Ionized asbestos, CuO, Platinised Quartz, platinum gauge are often put at the end of the combustion tube to ensure that the total carbon burned out CO_2 or not it serve as buffers for holding back, finely divided solid metallic oxides and SO_3

Boat and Covers:

The boats and covers made up of alundum clay zirconium oxide or Ni, Pt preferably receive a lining with granule alundum. Ni boats made up of sheet of Ni containing minimum 0.1% Carbon.

Absorbing Bulbs:

Fleming, miller, turner and Midvale bulbs have proved satisfactory Midvale bulbs are cheaper and open bulbs in this bulbs oxygen will be lost by diffusion.

Oxygen Purifiers:

The purity of oxygen should not be less than 99.5% organic matter of any kind is an undesirable impurity oxygen gas passed through an absorbent such as 20-30Mesh inert base impregnated with NaOH followed by anhydrous $Mg(ClO_4)_2$

CO_2 Purifier:

The purifiers following the combustion tube must remove finely divided solid metallic oxides and oxides of Se and S and dried finely divided solid oxides are removed from the gases by passing them through the coloums of solids when small amount of SO_2 given off from low S Content materials absorbed by sulphuric acid bath saturated with chromic acid

CO_2 Absorbent:

The most desirable absorbent for CO_2 is 20-30 Mesh base impregnated with NaOH followed by anhydrous $Mg(ClO_4)_2$

[Or]

The cylinder “A” contains 99.5% pure oxygen and free from carbonaceous matter. Constant pressure is maintained with the help of the reservoir “B” a safety valve “C” containing mercury is introduced in the lime to limit the pressure to the working value. The vessel “E” contains alternately layers of soda asbestos and anhydrone as CO_2 absorbent desiccant respectively. The furnace “G” is electrically heated and can heat the samples up to 1100-1200°C.

1-5g of sample is spread on the bed in the boat it is introduced into the hot combustion tube, close the tube, sample is heated for 1-2min then oxygen is allowed to admit at a rate of 500-1000ml per minute during the combustion. When combustion is complete the rate of flow of oxygen is reduced to 300-400ml per minute. The flow of oxygen is continued for 6-8min to sleep out the CO_2. Then exist gases are passed through an absorption train. Chromic acid is used as an absorbent for SO_2. A small bulb “N” is provided to prevent suck back of liquid into the combustion tube. Then exist gases are passed through a tube “I” it contains anhydrous magnesium perclorate $Mg(ClO_4)_2$ and J Contains anhydrone at the bottom and it is covered with soda asbestos. Anhydrone is used as a desiccant the absorption may be completely isolated and weighed at each time the tube J is weighed before and after the combustion the increase in weight represents the CO_2Produced.

Principle:

The principle involved in the estimation of carbon that when a regulated steam of oxygen is passed over the heated steam sample. Carbon and sulphur are oxidized to CO_2 and SO_2 respectively. After removing SO_2 gas. CO_2 is absorbed in a suitable absorbent. The increase in weight gives the amount of CO_2 form this percentage of Carbon can be calculated.

Procedure:

1-5g of the sample is heated for 1-2min depending upon the particle size. The oxygen is then allowed to admit at a rate of 500-1000ml/min at 1100-1400°C when combustion is complete flow of oxygen continued for 6-8min to sweep out the CO_2 after absorbing CO_2 we have to weigh the absorption tube. The increase in weight represents the weight of CO_2.

$$\% \, of \, carbon = \frac{Wt \, of \, CO_2 \, X \, 0.2729 \, X \, 100}{Wt \, of \, the \, sample}$$

$$G \, F = \frac{C}{CO_2} = 0.2729$$

2.1.4 Determination of Manganese:

Periodate Method:

Principle: Small quantities of manganese are usually estimated by colorimetric method i.e. steel sample having less than 0.5% of Mn. Here manganese in the sample is oxidized to permanganic acid and color of the solution is matched with that of standard solution prepared under identical conditions.

Ammonium persulphate is widely used as an oxidizing agent. However it is generally unsatisfactory because in a number of cases, the reaction is not complete. Potassium per iodate has been found very satisfactory as an oxidizing agent and when added in the hot acid solution of the manganese salt, it oxidizes manganese quantitatively to form permanganic acid.

$$2Mn + 5KIO_4 + 3H_2O \rightarrow 2MnO_4 + 5KIO_3 + 3H_2$$

Concentration Range: Range from 0.2 - 0.8 mg of Mn per 50ml of the solution

Stability of Color: The color formed is stable for more than 24Hours

Interfering Elements: The elements present in steel don't interfere per chloric acid treatment.

Spectral Transmittance: 526mμ - 545mμ

Reagents:

Standard Mn Solution: Dissolve 0.4g of manganese in 20ml HNO_3 by heating cool and diluted to 500ml in a volumetric flask transfer 20ml of this solution into 500ml VF and diluted.

KIO_4 Solution: Dissolve 7.5g of KIO_4 in 200ml hot HNO_3 [1:1] to this add 400ml H_3PO_4 and then cool and diluted to 1liter.

HNO_3 – H_3PO_4 Mixture: Take 400ml H_2O, then add 100ml HNO_3 and 400ml H_3PO_4 mixed thoroughly and diluted to 1liter.

Procedure: Take 5 flasks of different concentrations of Mn solution a 50ml VF to this add 10ml KIO_4 solution and shake the solution then add 10ml HNO_3 – H_3PO_4 mixture and make up to the mark with distilled water. Take this solution into cells and measure the transmittance at 545nm. Measure the transmittance for the steel sample in the same manner. By Knowing the transmittance we can calculate the concentration of Mn Present in the steel sample from calibration curve.

Note: H_3PO_4 is added to prevent the precipitation of ferric iodate.

Sodium Bismuthate Method:

Principle: This method is based on the fact that when the Manganese salts is treated with excess of Sodium Bismuthate in the presence of Nitric acid, it oxidized to permanganic acid. The excess sodium Bismuthate is removed by filtration. Then add known excess of Ferrous Ammonium Sulphate to reduce the permanganic acid to the manganous state. The unreacted ferrous ammonium sulphate is determined by titrating with standard potassium permanganate solution. The Mn content can be calculated by knowing the volume of ferrous ammonium sulphate consumed by the sample.The reaction involved in the titration is

$$2M(NO_3)_2 + 5NaBiO_3 + 16HNO_3 \rightarrow 2NaMnO_4 + 5Bi(NO_3)_3 + 3NaNO_3 + 7H_2O$$

$$2HMnO_4 + 10FeSO_4 + 7H_2SO_4 \rightarrow 5F(SO_4)_3 + 2MnSO_4 + 8H_2O$$

$$2KMnO_4 + 10FeSO_4 + 8H_2SO_4 \rightarrow 5Fe(SO_4)_3 + 2MnSO_4 + K_2SO_4 + 8H_2O$$

Solutions Required:

Standard Ferrous Ammonium Sulphate: Dissolve 39.5g of Ferrous Ammonium Sulphate in 1liter of 5% H_2SO_4 standardize against a standard $KMnO_4$ solution immediately before use

Standard Potassium Permanganate: Dissolve 3.2g of potassium permanganate in 1liter of water standardize against a standard sodium oxalate solution in the usual way

3% Nitric Acid [HNO_3]: Dilute 3ml of ConHNO_3 in 100ml of water.

Procedure: 1g of sample dissolved in 50ml of dil HNO_3 it boiled until brown fumes are evolved then the solution is cooled and adds 0.5g of sodium Bismuthate again boiled for 2-3min. Appearance of pink color is due to the due to permanganic acid. If any residue is formed it is washed with dil HNO_3 until the washings are color less. Combine the filtrate and washing to this add standard ferrous ammonium sulphate from burette until pink color disappear a slight excess of ferrous ammonium sulphate is added. The unreacted ferrous ammonium sulphate is determined by titrated with standard potassium permanganate solution until a pink color is obtained. By knowing the volume of Ammonium Ferrous sulphate reacts with the sample we can calculate the amount of Mn present in the sample

1ml of 0.1N $FeSO_4$ = 0.00110g of Mn

2.1.5 Determination of Phosphorous:

Phosphorous exists in steel as iron Phosphide Fe_3P this is oxidized by adding HNO_3 to phosphoric acid which is partly in the Meta and partly in the ortho condition. The Meta phosphoric acid is converted into ortho phosphoric Acid by addition of $KMnO_4$. Then phosphate is precipitated as ammonium Phospho Molybdate by adding ammonium Molybdate solution. Form the precipitate, we can determine the phosphate either by the volumetric or by the gravimetric method.

Volumetric Method:

Reagents:

$KMnO_4$ Solution: 25g of $KMnO_4$ dissolved in 1liter

Ammonium Molybdate solution: 65g of Ammonium Hepta Molybdate + 25g of Ammonium Nitrate + 15ml of Ammonium Hydroxide and 600ml water in 800ml beaker shake thoroughly after dissolution it can filter if necessary and dilute to 1liter.

Standard HNO_3: 10ml of the commercial HNO_3 is diluted to 1liter shake thoroughly until uniform solution obtained standardized HNO_3 with standard NaOH using Phenapthalen indicator.

Standard NaOH

Procedure:

Take 2g of sample and transfer into a 300ml conical flask. Add slowly about 30ml of HNO_3. Dissolve the steel by gentle boiling. Boil off all brown fumes then add 5ml of $KMnO_4$ and digest for 5min to convert Meta phosphoric acid to ortho phosphoric acid and destroy any organic matter present, which is necessary to precipitate phosphorus by ammonium Molybdate as ammonium Phospho Molybdate.

Destroy the precipitated MnO_2 by adding 5% KNO_2 drop by drop. Phosphorous Free Na_2SO_3 or $FeSO_4$ solution can also be utilized in the place of the KNO_2 solution. Boil the solution until the MnO_2 has been dissolved. Add 15ml of Con HNO_3 and 50ml Ammonium Molybdate solution and shake vigorously and stand for 5 – 10min. Then Phosphorus present in the sample is precipitated as ammonium Phospho Molybdate. Filter the precipitate and washed with HNO_3 and then with 1% Con KNO_3 solution until the precipitate is free from acid.

Transfer the washed precipitate along with the filer paper into the flask and add Known excess of Standard NaOH solution in the flask and shake until the filter paper doesn't contain any yellow tinges on it. Then titrate excess of the NaOH solution with Standard HNO_3 using Phenolphthalein as indicator. By knowing the amount of NaOH consumed with Phosphate precipitate then we can determine the amount of phosphorous present the sample.

$$\%\,Of\ Phosphorous = \frac{[(A - BC) - (D - EC)]F\ X\ 100}{G}$$

Where A: ml of NaOH required by the sample

B: ml of HNO_3 required by the sample

C: ml of NaOH equivalent to 1ml of HNO_3

D: ml of NaOH required by the blank

E: ml of HNO_3 required by the blank

F: P equivalent of the NaOH solution in g/ml

G: Sample taken

$$Fe_3P + 11HNO_3 \rightarrow 3F(NO_3)_2 + PH_3 + 4H_2O + 2NO$$

$$3PH_3 + 8HNO_3 \rightarrow 3H_3PO_4[Ortho] + 4H_2O + 8NO$$

$$3PH_3 + 8HNO_3 \rightarrow 3HPO_3[Meta] + 7H_2O + 8NO$$

$$PO_4^{-3} + HNO_3 + 12(N\ )\,{}_{4\,2}MoO\quad{}_4 \rightarrow (NH_4)_3PO_4 + 2NH_4NO_3 + 12H_2O$$

$$PO_4^{-3} + HNO_3 + 12(N\ )_{4\,2}MoO\quad{}_4 \rightarrow (N)_{4\,3}PO\,12MoO_4\quad{}_3 + 2NH_4NO_3 + 12H_2O$$

$$2[(NH_4)_3PO_412MoO_3] + 46NaOH \rightarrow (NH_4)_2MoO_4 + 2(NH_4)_2HPO_4 + 23Na_2MoO_4 + 22H_2O$$

2.1.6 Determination of Sulphur:

Sulphur is present mainly as sulphides of iron and Manganese.

It is usually occur as impurity in steel sample.

Principle: In this process HCl is added to the steel sample, the sulphides of iron and manganese are decomposed and an equivalent amount of H_2S gas is evolved. The gas is absorbed in a solution of ammonium cadmium chloride which forms a precipitate of yellow cadmium sulphate. This is titrated with a known excess of Iodine in presence of HCl. The excess of Iodine is determined by titrating with standard sodium thio sulphate by knowing the amount of the iodine solution consumed with sample we can measure the sulphur present in the sample.

$$FeS + HCl \rightarrow FeCl_2 + H_2S$$

$$MnS + 2HCl \rightarrow MnCl_2 + H_2S$$

$$H_2S + CdCl_2 \rightarrow CdS + 2HCl$$

$$CdS + 2HCl + I_2 \rightarrow CdCl_2 + 2HI + S$$

$$2Na_2S_2O_3 + I_2 \rightarrow 2NaI + Na_2S_4O_6$$

Solutions Required:

Stock Ammonical Cadmium Chloride: Dissolved 6.25g of Cadmium chloride in 100ml water and add 500ml ammonia

Sodium Thio Sulphate Solution: Dissolved 7.7422go of sodium thio sulphate in water and add 0.5g of sodium bicarbonate make up to 1liter.

Iodine Solution: Dissolve exactly 1.5296g of pure potassium dichromate add 15ml of 1:2 H_2SO_4 cool and add 15g of potassium iodide and make up to 1liter

Procedure:

Take 5g of sample in a dry 300ml Florence flask to this add HCl solution and diluted with water. Then immerse the end of the delivery tube in 200ml of dilute Ammonical Cadmium chloride which is made by a mixture of 40ml of the stock solution with 160ml water. Then cadmium chloride reacts with H_2S which is liberated in reaction. Then CdS precipitate is formed. Then cool the solution in the absorption vessel and add 30ml of HCl. Run from a burette the standard Iodine solution until yellow color appears it shows the presence of excess iodine. Then excess iodine is determined by titrating with hypo using starch as indicator until blue color of the solution becomes color less it is the end point.

1ml of Iodine solution = 0.0054g of S

$$\text{\% of Sulphur} = \frac{\text{wt of sulphur X 100}}{\text{Wt of sample}}$$

Wt of sulphur = 0.0054 X ml's of iodine react with sample

Gravimetric method: same as Iron ore analysis.

Silica: Same as Iron Ore analysis

2.1.7 Determination of Nickel:

Dimethyl Glyoxime Method: [D.M.G]

Principle:

This method of nickel estimation is important because of the fact that removal of iron is unnecessary. Iron must however be prevented from precipitation while making nickel solution ammonical. This is done by adding tartaric or citric acid which keeps the iron in solution in the form of non ionized tartrate or citrate.

In gravimetric method nickel is precipitate as Nickel Dimethyl Glyoxime [Bright Red] in faintly alkali medium by the addition of 1% D.M.G. Precipitate is filtered, dried at 120⁰C and weighed as Nickel Dimethyl Glyoxime. The amount of nickel present in the sample is calculate by ignited the precipitate then it converts to NiO from the weight of NiO we can calculate the amount of nickel present in the sample

$$Ni^{+2} + 2C_4H_8O_2N_2 \rightarrow N(C_4H_7N_2O_2)_2 + 2H^+$$

Solutions Required:

1% DMG: It is prepared by dissolving 1g of DMG in 100ml of absolute ethyl alcohol.

Dil CH_3COOH: 35ml of acetic acid is diluted to 100ml with distilled water.

Procedure:

1g of the sample is taken in 150ml beaker and dissolves it in 30ml of 1: 1 HCl. Ferrous iron is oxidized to Ferric Iron by adding 20ml of 1:2 HNO_3. Heat the solution and add 30ml of 10% H_2SO_4 solution. It is transferred into beaker and diluted with water. The add 5-6g of tartaric acid and stir until dissolved. Add ammonia until solution becomes alkaline and the make the solution acidic with acetic acid. This is done because the Nickel complex precipitate is soluble in mineral acids as well as in strongly ammonical solution. Heat the solution to about 70ºc and add 25ml of 1% DMG now add ammonia so that the solution becomes alkali. This addition of ammonium hydroxide is made to take care of the acid which is produced when Ni – DMG is precipitated as shown by the following equation

$$Ni^{+2} + 2C_4H_8O_2N_2 \rightarrow N(C_4H_7N_2O_2)_2 + 2H^+$$

Cool the solution and filter the precipitate. The nickel complex tends to volatilize above 250 ºC. it may, therefore be wrapped in a moist filter paper, heated at as low a temperature as possible to burn off most of the organic matter and finally ignited at 800ºC to convert it to NiO, from the weight of NiO we can calculate the amount of nickel present in the sample

$$\%\ of\ Nickel = \frac{wt\ of\ Precipitate\ X\ 0.2031\ X\ 100}{wt\ of\ the\ sample}$$

$$Gf = 0.2031 = \frac{Ni}{Ni\ DMG}$$

The precipitate is ignited at 800ºC for 1hour it is cooled and weighed as NiO

$$\%\ of\ Nickel = \frac{wt\ of\ Precipitate\ X\ 0.7858\ X\ 100}{wt\ of\ the\ sample}$$

$$Gf = 0.7858 = \frac{Ni}{NiO}$$

2.1.8 Determination of Chromium:

Persulphate Oxidation Method:

Reagent:

H_2SO_4 – H_3PO_4 mixture: Add 320ml of H_2SO_4 (1:1) to 600ml water cool and add 80ml of H_3PO_4

Silver Nitrate Solution: 10g of $AgNO_3$ dissolved in 1liter water

Ammonium persulphate solution: [$(NH_4)_2S_2O_8$]: 150g of ammonium persulphate solution dissolved in 1liter it is prepared freshly for use.

Standard Ferrous Ammonium Sulphate Solution: [0.08N] Take 25ml of ferrous salt solution and dilute to 300ml with dil H_2SO_4 [to this add 2ml H_3PO_4 mixed and titrated with $KMnO_4$ solution pink color is persisted]

Volume of $KMnO_4$ = 1ml of ferrous salt solution

Standard $KMnO_4$ solution [0.06N]

Procedure: Take 2g of the sample in a 600ml beaker. Add 70ml of the phosphoric – Sulphuric acid solution cover the beaker with a watch glass and digest for 20 -30min. oxidize with 2ml of con HNO_3 and gradually evaporate to fumes. Add 100ml of water. Boil and diluted to 250ml with boiled water.

Add few pieces of glass beads, 25ml silver nitrate solution and 2g of ammonium persulphate or 40ml ammonium pre sulphate are added and shake thoroughly cover the beaker with a watch glass and boil for 10min after the pink color develops. Cr and any Mn oxidized to dichromate and Permanganate with per sulphate in the presence of $AgNO_3$ as catalyst. The appearance of pink color indicates that both Mn and Cr have been oxidized to the high valency. However the permanganate must be removed before the addition of the excess ferrous ammonium sulphate solution.

To discharge the pink color, add 15ml of HCL boil for 5min and cool to room temperature. If the pink color is not discharged, make a further addition of HCL and boil until the permanganic acid color disappears. Then add a known excess of Ferrous ammonium sulphate solution. The unreacted ferrous ammonium sulphate is determined by titrating with $KMnO_4$ unit pink color appears. By knowing the amount of ferrous ammonium sulphate reacts with sample we can calculate the % of Chromium present in the sample

$$\%\, of\ Chromium = \frac{[AB - (C - D)] X\ E\ X\ 0.0173}{F}$$

A = ml of AFS used

B = ml of $KMnO_4$ equivalent to 1ml of ferrous salt

C = ml of $KMnO_4$ solution required for titration

D = ml of $KMno_4$ solution required for the end point correction

E = Normality of $KMnO_4$

F = Wt of the Sample

$$2Cr_2(SO_4)_3 + 3(NH_4)_3S_2O_8 + 4H_2O \rightarrow 4H_2CrO_4 + 3(NH_4)_2SO_4 + 6H_2SO_4$$

$$2H_2CrO_4 + 6FeSO_4 + 2H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 8H_2O$$

$$10FeSO_4(NH_4)_2SO_4 + 2KMnO_4 + 8H_2SO_4 \rightarrow 5Fe_2(SO_4)_3 + 10(NH_4)_2SO_4 + K_2SO_4 + 2MnSO_4 + 8H_2O$$

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2.1.9 Determination of Magnesium:
8 – Hydroxy Quinoline [Oxime] Method or Hg Cathode Method:

Principle:

Interfering elements are first separated by using ether and electrolysis method using the mercury electrode to eliminate after H_2S separation the magnesium is precipitated as magnesium 8-hydroxy quinolate and finally determined gravimetrically by weighing the precipitate or volumetrically by bromination with potassium borate [$KBrO_3$] – Potassium Bromide [KBr] mixture

Required Solutions:

1. Ammonium Sulphide Solution: 50ml of dil NH_4OH with 1liter water and saturated with H_2S gas
2. Ammonium Oxalate Solution: A 10% solution of ammonium oxalate is prepared by dissolving 100g of ammonium oxalate in 300ml of water and diluted to 1liter
3. 8-Hydroxy Quinolate Solution: 4% solution f 8-hydroxy Quinoline is prepared by dissolving 40g of a substance in 200ml of CH_3COOH [1:4] and diluted to 1liter with CH_3COOH.
4. $KBrO_3$ - KBr solution [0.05N]: dissolve 1.3917g of $KBrO_3$-KBr in water diluted to 1liter with distilled water in VF
5. Standardization of sodium thiosulphate solution [$Na_2S_2O_3$] [0.05N] : Take 25ml of $KBrO_3$ – KBr mixture in a conical flaks to this add 30ml distilled water and 2g of KI the contents are shaken thoroughly and then add 10ml HCl [1:1] titrate the contents with $Na_2S_2O_3$ solution until color changes to pale yellow then add 2ml of freshly prepared starch indication and continue the titration until it becomes color less this is the end point from the titrant value we can calculate the strength of the sodium thiosulphate
6. Starch Indicator
7. Iron

Procedure:

5g of the sample is taken in a beaker and add 40ml of [1:1] HCl and heat until the reaction is complete then add 15ml of [1:1]HNO_3 to oxidize the iron and evaporate to dryness cool, add 25ml of HCl and digest until salts are dissolved

Transfer the solution into a separating funnel rinsing the beaker with [1:1] HCl and add 200ml of ethyl ether and shake vigorously allow the layers to separate and the acid layer is drawn off. The acid layer is evaporated gently to 5ml to remove the ether 20ml of HNO_3 and 10ml of $HClO_4$ are added to the evaporated solution and evaporation is carried out to white fumes. To this add 50ml of water stirred vigorously. To dissolve the salts the contents are filtered through a coarse texture paper the residue and the paper are washed with hot water about 10-12times the residue is discarded.

Transfer the filtrate to a mercury cathode cell and electrolysis until the bulk of the iron has been removed. Transfer the solution from the cell to a 250ml beaker to this solution add 0.3g of ferrous ammonium sulphate and then ammonium hydroxide until neutral to litmus paper and finally add 10ml in excess pass a rapid stream of H_2S through the solution for 20min and allowed the precipitate to settle filter through a paper into a 400ml beaker and wash with ammonium sulphide discard the precipitate.

Add HCl [1:1] to the filtrate until neutral to litmus and then add an excess and boil the filtrate to reduce the volume and to remove H_2S add 10ml of ammonium oxalate solution and NH_4OH [1:1] until the solution is neutral to litmus. Add an excess of 10ml allow standing for 1-2hours then the precipitate is filtered through a filter paper washed the precipitate with ammonium oxalate solution discard the precipitate.

Make the filtrate just acid to litmus with HCl[1:1] heat to 60-70°C and then add 10ml of 8-hydroxy Quinoline solution add ammonium hydroxide until neutral to litmus and an addition 10ml in excess stir vigorously and stand for 30min to allow the precipitate is settle filtered and dry at 160°C and weigh as magnesium 8-hydroxy quinolate

$$\% \, of \, Mg = \frac{Wt \, of \, Precipitate \, X \, 0.0778 \, X \, 100}{wt \, of \, the \, Sample}$$

$$GF = 0.0778 = \frac{Mg}{Mg - 8Hydroxy \, Quinolate}$$

Volumetric Method:

Dissolve the precipitate in 30ml [1:1] HCl to this add known volume of $KBrO_3$ – KBr mixture sufficiently and In excess the solution is yellow in color add 2g of KI make it dissolved and immediately titrated with standard sodium thiosulphate using starch as indicator

$$\% \, of \, Mg = \frac{[A - B] X \, C \, X 0.00304 \, X \, 100}{Wt \, of \, the \, Sample}$$

A ml of sodium thiosulphate solution required to titrate the blank

B ml of sodium thiosulphate solution required to titrate the sample

C Normality of thiosulphate

2.2 Analysis of Blast Furnace Slag:

The composition of Slag's produce in Blast Furnace is varied but the type of constituents is one and the same.

Blast furnace slag consists of Silicates of calcium and magnesium with small amount of other compounds of Ca, Mg, Mn, Al and Fe.

The chief constituents present in the slag are SiO_2, Al_2O_3, MgO. Cao, MnO, FeO, Fe_2O_3, S, P, Fluoride, B_2O_3

Blast Furnace slag is not soluble by acid solvent so it is fused with the fusion salts.

$$Na_2CO_3 + CaOSiO_2 \rightarrow Na_2SiO_3 + CaO + CO_2$$

$$Na_2CO_3 + MgOAl_2O_3 \rightarrow 2NaAlO_2 + MgO + CO_2$$

This fused mass is extracted with HCl

2.2.1 Determination of SiO_2:

Low silica Slag's: 0.5g of the sample is taken in a pt or porcelain dish and is margin with 5ml water. To this add 25ml of ConHCl is added and heat the solution for digestion of the components by a steam bath at 99-100°C for about ½ hour the contents are evaporated to dryness at low heat

High Silica Slag's and Containing Fluorides: 0.5g of the sample is taken into a pt or porcelain crucible and mixed with 3g of anhydrous sodium carbonate. Heat the crucible for about 30min the contents are extracted with hot water. Few drops of HCl is added to destroy turbidity the crucible is cooled and the contents are transferred to a porcelain crucible with 30ml of HCl[1:1] the contents are evaporated to dryness at low heat 15ml of con HCl and 25ml Hot water are added to the residue and heated until salts are dissolved the solution is filtered over a filter paper.

Then the precipitate is washed with 5% HCl for several times and then with hot water until free from chloride. Then the precipitate along with filter paper is placed in the crucible and dried at 110°C for 20min and then ignited at 1000-1050°C until constant weight is obtained then repeat the same procedure in iron ore analysis for silica.

2.2.2 Determination of Al_2O_3: Same as in Iron ore Analysis

2.2.3 Determination of Fe_2O_3: Same as in Iron ore analysis

2.2.4 Determination of MnO:

The filtrate obtained after the determination of Al_2O_3 and Fe_2O_3 is boiled to about 150ml and 1ml of bromine + liquid ammonia or 5ml of $(NH_4)_2S_2O_8$ and add 20-25ml of NH_4OH is added and the solution is boiled for 10min. Then allow the solution to settle the precipitate, filtered and washed with hot water then dried, ignited in a platinum crucible for about ½ hour at 900°C. The residue is cooled and weighed as Mn_3O_4. Then we calculate the MnO present in the sample by using the formula.

$$\% \, of \, MnO = \frac{Wt \, of \, Mn_3O_4 \, X \, GF \, X \, 100}{Wt \, of \, Sample} \qquad GF = \frac{MnO}{Mn_3O_4}$$

2.2.5 Determination of CaO and MgO:

The constants are determined after the determination of Mn as in Iron ore analysis

2.2.6 Determination of FeO:

Same as in Iron Ore Analysis

2.2.7 Determination of Sulphur:

Same as Steel

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2.3 Analysis of Refractive Materials

2.3.1 Analysis of Fire Clay:

Fire clay is used as refractive material. Fire clay is associated with combined water and other impurities which render these materials unsuitable for the manufacture of Refractories. The impurities usually associated are alkali [Na_2O and K_2O], TiO_2, Iron, Al_2O_3, Mn, CaO, MgO and organic compounds. The alkalis iron, oxides, calcium and magnesium if present even in small quantities, refractoriness of the stand and clay is adversely affected.

2.3.2 Dissolution:

The sample is fused with Na_2O_2 the fused mass is treated with HCl and evaporates to dryness. Dilute with water digest the contents and filtered. The insoluble residue is used for estimation of silicon. The filtrate is used for determination of other contents.

Contents:

1. Determination of Moisture
2. Determination of Loss on Ignition
3. Determination of CO_2 and Combined water
4. Determination of Organic Matter
5. Determination of Silica
6. Determination of Iron
7. Determination of Al_2O_3
8. Determination of TiO_2
9. Determination of Mn
10. Determination of CaO
11. Determination of Alkali [K_2O and Na_2O]

$$K_2O = 0.6309 \times KCl$$

$$Na_2O = 0.5309 \times NaCl$$

Procedure for all contents as in iron ore analysis

Fluor Spar:

It is widely used in metallurgical industries as a neutral flux.

It is used as refractive materials in metallurgical industries.

It is added for increasing the fluidity with out affecting the properties of the slag.

Fluorspar main contents is CaF_2 along with small impurities such as SiO_2, Al_2O_3, Fe_2O_3, P_2O_4, $CaCO_3$, $MgCO_3$ etc.

2.3.2.1 Dissolution: Same as Fire Clay

2.3.2.2 Contents:

1. Determination of Moisture
2. Determination of Loss on Ignition
3. Determination of CO_2 and Combined water
4. Determination of Organic Matter
5. Determination of Silica
6. Determination of Iron
7. Determination of Al_2O_3
8. Determination of P_2O_5
9. Determination of CaF_2
10. Determination of MgF_2
11. Determination of $CaCO_3$ and $MgCO_3$

2.3.2.2.1 Determination of CaF_2:

CaO is estimated and calculated as CaF_2

$$\% \text{ of } CaF_2 = 1.3923 \times \% \text{ of } CaO$$

2.3.2.2.2 Determination of MgF_2:

MgO is estimated and calculated as MgF_2

$$\% \text{ of } MgF_2 = 0.6633 \times \% \text{ of } MgO$$

Analysis of Fluxes

2.3.3 Lime stone, Dolomite and Magnesite:

Lime stone and dolomite are mainly used as fluxes in iron and steel making processes. Burnt dolomite is also used as refractory material

Lime Stone: Lime stone consists of essentially Calcium carbonate and little amount of magnesium carbonate

Dolomite: it is an equimolecular compound of calcium and magnesium carbonates

Magnesite: It is composed mainly magnesium carbonate and has a little amount of calcium carbonate

Dissolution: Same as Fire Clay

Contents to be analyzed:

1. Determination of Moisture
2. Determination of Loss on Ignition
3. Determination of CO_2 and Combined water
4. Determination of SiO_2
5. Determination of Fe_2O_3
6. Determination of Al_2O_3
7. Determination of CaO
8. Determination of MgO